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Synthesis, characterization and application of organolanthanide complexes $(CH_2{=}CHCH_2CH_2C_5H_4)_2Ln{-}Cl\cdot 2THF$ (Ln = Sm, Y, Dy, Er) as methyl methacrylate (MMA) polymerization catalysts

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Abstract

The title complexes $(CH_2{=}CHCH_2CH_2C_5H_4)_2Ln{-}Cl\cdot 2THF$ (Ln = Sm, Y, Dy, Er) were synthesized as air and moisture sensitive free-flowing oils that have been fully characterized by MS, EA and IR. The EA and IR results indicate the presence of coordinated THF molecules. No evidence of intra-molecular coordination of the butenyl side-chain was observed. In association with $Al(i\text{-}Bu)_3$, the complexes have shown high activity for the bulk polymerization of MMA. At a MMA/catalyst (MMA/cat) molar ratio of 2000, temperature of 80 °C and polymerization time of 30 h, the catalyst system produced at a 70% conversion a syndiorich polymer (rr = 62%), $M_\eta = 1.65 \times 10^6$. Effects of temperature, time and molar ratios of MMA/catalyst and catalyst/co-catalyst on the polymerization have been studied. The result showed that higher temperature, longer time and Al/catalyst molar ratio = 10 are conditions suitable for polymerization. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanides; 3-Butenylcyclopentadiene; MMA; Polymerization

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1. Introduction

Metallocene compounds of the rare-earth metals when treated with a Lewis acid cocatalyst such as tri*iso*-butyl aluminum $Al(i\text{-}Bu)_3$ or methylaluminoxane (MAO) generate active catalysts which are isoelectron neutral analogs of the $[Cp_2MR]^+$ d^0 Group 4 catalysts (R = H, alkyl, growing polymer chain). These have been accepted [1] as the active species responsible for the C–C bond formation by insertion of an olefinic substrate $H_2C{=}CHR$ into the metal–carbon bond.

Ligand modification has played a major role in the development of new catalyst systems in which a great level of control over the properties of the resulting polymer is desired. Both the steric and electronic structure of the modified ligand has an impact on the microstructure of the polymer produced, such as the tacticity, degree of conversion and molecular weight.

Metallocene complexes bearing modifications at the cyclopentadienyl (Cp) ring have been of great interest to organometallic chemists, due to their capacity to act as coordination polymerization catalysts or catalyst precursors [2]. A variety of functional groups have been used as side-chain modification to the Cp ring. These among many include alkoxyalkyls (ROR′) [3]; alkyls (R–) [4]; alkylsilyls (R_3Si–) [5]; amines (R_2N–) [6]; and ω-alkenyls ($CH_2{=}CHR$–) [7–9].

Reports have shown that the ω-alkenyl ($CH_2{=}CHR$–) modified Cp ligands have been applied on Co [2], Ni (II) [10], Ti [7,11], Zr [8,9,11,12], Hf [12]. Qian et al. [13] have found its Ti-based complexes to exhibit high conversion (100%) in the isomerization of 1,5-hexadiene. The Zr-based complexes synthesized by Qian and coworkers [9] exhibited a very high activity (10^6–10^7 g PE mol Zr^{-1} h^{-1}) for ethylene polymerization even at low [Al]/[Zr] ratio (100 ~ 500). A very recent review [14] outlined the importance of functionalized-Cp ligands and their application in organometallic synthesis, but to

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the best of our knowledge there is no report yet on the application of ω-alkenyl (CH_2=CHR–) functionalized-Cp ligands on rare-earth metals. In the chemistry of ω-alkenyl-substituted compounds, either the stabilization of reactive species or further reactions (e.g. insertion through coordination) of the double bond are expected. Both situations and the corresponding impact on reactivity have been reported in the literature [14].

In this report we discuss the synthesis of butenyl (CH_2=$CHCH_2CH_2$–) functionalized-Cp lanthanide complexes and their utilization in the activation of syndiotactic polymerization of MMA.

2. Results and discussion

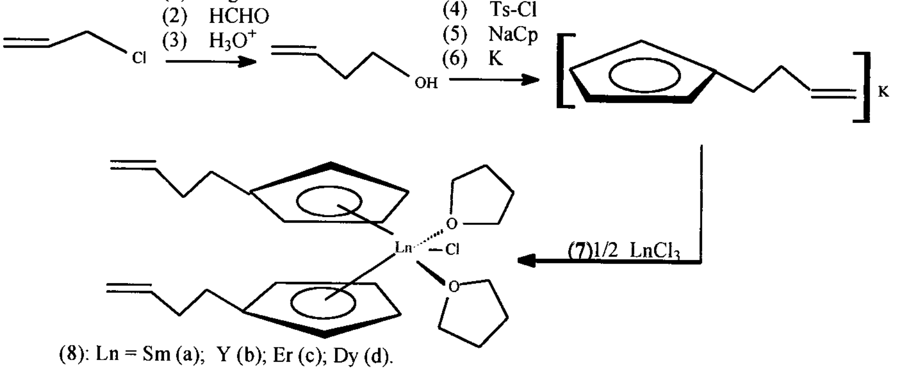
2.1. Synthesis and characterization of catalyst precursors

Synthesis of sandwich and half-sandwich Cp complexes of the transition and rare-earth metals bearing functionalities in the side-chain of the Cp fragment have attracted tremendous attention during the last decade. This is due to the fact that the side chain can be used to modify the chemical and physical properties of the classical Cp complex. The title complexes were easily obtained using commonly employed metathetical procedures as outlined in Scheme 1.

The methodology is the same for all the four complexes. The complexes prepared are all free-flowing clear oils exhibiting the characteristic color of the central metal. All the new complexes are soluble in hydrocarbon solvents such as toluene and *n*-hexane, although they are still very sensitive to air and moisture. This has made purification a rather difficult task. By washing the crude product several times with hexane until no sticky substance precipitates out followed each time by rotary centrifugation, the clear analytically pure (by EA) oils were obtained in moderate (ca. 55%) yields. The resulting oils were characterized by MS, EA and IR. ^{1}H-NMR spectroscopy was not attempted due to the paramagnetic nature of the lanthanide metals. Spence and Piers [8] prepared the corresponding Zr complexes and reported obtaining oils and gummy solids that defied purification and isolation by normal means. However, their complexes were found to be 95% pure by ^{1}H-NMR spectroscopy.

By careful study of the MS dissociation peaks and the IR spectra in addition to the C and H content from the EA we proposed the empirical formula and structure shown in Scheme 1 (**8a**–**d**), in which the metal is a nine-coordinate center solvated by two THF molecules. Only complexes of relatively smaller radii lanthanide metals were isolated. Attempts to isolate the corresponding La and Nd complexes failed. This was anticipated as Schumann et al. [15] noted, large ionic radii lanthanides mostly failed to give isolatable compounds for simple bis(cyclopentadienyl) Ln–Cl complexes, possibly due to steric unsaturation.

The MS spectra of all the complexes show a similar cleavage pattern. The highest M^+ corresponds to the $[(CH_2{=}CHCH_2CH_2C_5H_4)_2Ln{\cdot}Cl]^+$ fragment, this indicates that the two THF molecules are cleaved easily. However, the elemental analysis clearly accounts for their presence. The IR spectra show the presence of ordinary uncoordinated C=C bonds of the 3-butenyl substituents (1637 cm^{-1}), and absorption bands at 1045 and 890 cm^{-1} verify the presence of the coordinated THF molecule [16]. These facts coupled to the concept of hard and soft acids and bases (HSAB) [17], which classifies the rare-earth metals as hard Lewis acids supports the structure of the complexes as containing inter-molecular coordination to solvent molecules rather than the intra-molecular coordination of the C=C bonds of the 3-butenyl substituents. The discussion on the intra-molecular coordination of ω-alkenyl (CH_2=CHR–) side chains in general is still unresolved [14]. Based on these results we conclude that



Scheme 1. Synthetic route to title complexes.

Table 1
Polymerization of MMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2$-Ln–Cl·2THF complexes

Run	Ln	Conversion (%)	M_η ($\times 10^{-3}$)
B22	Y	21.6	714.3
B4	Sm	44.6	1462.5
B23	Dy	16.6	745.1
B24	Er	15.3	1037.8

Polymerization condition: MMA/cat = 2000 (molar ratio); Al/cat = 10; 60 °C; 15 h.

Table 2
Effect of cocatalysts on the polymerization of MMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2$Sm–Cl·2THF

Run	Cocatalyst	Al/cat (molar ratio)	Conversion (%)	M_η ($\times 10^{-3}$)
B9	MAO	10	1.2	248.8
B10	$AlEt_3$	10	10.3	4.0
B5	Al(*i*-Bu)$_3$	2	2.6	1651.5
B6	Al(*i*-Bu)$_3$	5	2.9	1583.2
B4	Al(*i*-Bu)$_3$	10	44.6	1462.5
B7	Al(*i*-Bu)$_3$	15	25.6	1233.0
B8	Al(*i*-Bu)$_3$	20	17.9	218.9
B27	None		Trace (~0.27)	

Polymerization condition: MMA/cat = 2000; 60 °C; 15 h; bulk.

the functional groups of the side-chains remain free and uncoordinated. It is noteworthy that Okuda and Zimmerman [18] succeeded under severe conditions (Na/Hg) in inducing the intramolecular coordination of the C=C double bond to the Co central metal yielding a relatively stable chelate complex.

2.2. Polymerization of MMA

Polymerization of MMA using the title complexes as catalysts was carried out using different cocatalysts. The efficiency of the various catalyst/cocatalyst systems is presented in Tables 1 and 2. To establish the role played by the lanthanide metal Ln in $(CH_2{=}CHCH_2CH_2C_5H_4)_2$Ln–Cl·2THF, Ln = Sm, Y, Dy, Er), polymerization was carried out with the four different complexes each having one of the lanthanide metals as the central atom.

Three different aluminum-based cocatalysts were used: methyl aluminoxane (MAO), $AlEt_3$ and Al(*i*-Bu)$_3$. The best catalytic efficiency of 45% with respect to the conversion of monomer to PMMA and the molecular weight of polymer was obtained with Al(*i*-Bu)$_3$ cocatalyst. Very low conversion of 1.2 and 10.3% was observed for MAO and $AlEt_3$, respectively, under similar conditions. For the Al(*i*-Bu)$_3$ cocatalyst the efficiency increases as the Al/catalyst (Al/cat) molar ratio increases up to a value of 10 and then declines with a further increase in the Al ratio probably due to over alkylation or decomposition of the catalyst. Therefore, we realized that the Al/cat molar ratio of 10 utilizing Al(*i*-Bu)$_3$ as the cocatalyst is the optimum requirement for polymerization. The higher efficiency of Al(*i*-Bu)$_3$ as a cocatalyst in this system may be attributed to steric factors, since the cocatalysts are electronically similar. The large *iso*-butyl ligand may be responsible for imparting the desired orientation and stability to active species required for the initiation and propagation of polymerization. A similar observation was reported for a Ziegler–Natta three-component catalyst system [19]. As the result in Table 3 (blank test) indicates, aluminum enolates from the cocatalyst are

Table 3
Polymerization characterization of MMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2$Sm–Cl·2THF

Run	MMA/cat (molar ratio)	Temperature (°C)	Time (h)	Conversion (%)	M_η ($\times 10^{-3}$)
B1	500	60	15	63.3	22.9
B2	1000	60	15	57.4	240.7
B3	1500	60	15	46.4	937.9
B4	2000	60	15	44.6	1462.5
B26	3000	60	15	14.2	1257.4
B15	2000	0	15	1.7	13.8
B16	2000	20	15	1.9	34.5
B17	2000	40	15	5.6	862.1
B4	2000	60	15	44.6	1462.5
B18	2000	80	15	58.3	1599.3
B19	2000	60	5	2.1	99.7
B25	2000	60	10	10.3	1102.7
B4	2000	60	15	44.6	1462.5
B20	2000	60	20	55.7	1571.3
B21	2000	60	30	70.1	1653.2
Blank [a]	Al(*i*-Bu)$_3$	60	20	33.14	14.0

Polymerization condition: Al(*i*-Bu)$_3$/cat = 10.

[a] Blank (no catalyst added).

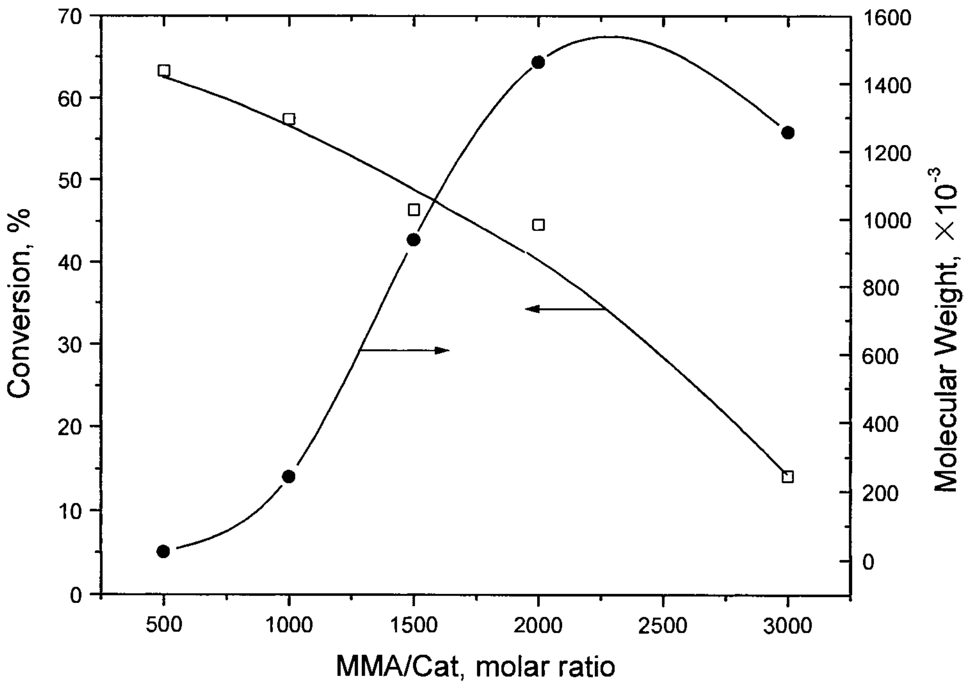


Fig. 1. Effect of MMA/catalyst molar ratio on the polymerization of MMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm–Cl·2THF$.

involved as propagating species. However, the enhanced efficiency and syndiospecificity of the polyMMA obtained accounts for the role of the Ln complexes. We believe that the propagation stage involves the Al enolate generated and coordinated by the Ln complex.

Having established the most appropriate catalyst/cocatalyst system for the polymerization, the effects of varying the different experimental conditions was studied.

The efficiency of each system is derived from the percentage of monomer converted to PMMA and the M_η of the polymer obtained. The observed order of activity $Sm > Y > Dy > Er$ is in line with the order of ionic radii, as it has been noted that larger lanthanide metals exhibit better catalytic properties [20]. On this basis, we selected the samarium complex for further studies.

Keeping the Al–Sm ratio constant, at 10:1, the MMA/catalyst (MMA/cat) molar ratio was varied from 500 to 3000, the polymerization temperature was also varied from 0 to 80 °C and the time of polymerization was varied from 5 to 30 h. The general result is presented in Table 3.

The effect of variation in MMA/cat molar ratio is presented in Fig. 1 (runs B1, B2, B3, B4 and B26). The clear trend from the plot is that as the amount of monomer increases (i.e. decrease in initiator concentration) the molecular weight of the polymer obtained also increase accordingly while the percentage of monomer conversion decreases. A similar relationship has been recorded for living polymerizations using other rare-earth catalyst systems [21,22].

The high molecular weight polymer obtained ($M_\eta > 10^6$) even at low to moderate monomer conversion may be attributed to the autoacceleration which has been established to occur for bulk polymerization of MMA arising from the high viscosity towards the end of the polymerization [23].

Fig. 2 (runs B15, B16, B17, B4 and B18) presents the effect of variation in polymerization temperature. Catalyst efficiency increases directly with an increase in temperature. As the temperature increases both the percentage monomer conversion and the polymer molecular weight increases. This indicates that even for long hours, the high-temperature environment does not hinder the catalyst efficiency. This is in contrast to our observation on the polymerization of MMA activated by pendant allyl–Cp lanthanide complexes [24]. This observation is also rather different from the characteristics of most rare-earth coordination polymerization, where the activity and syndiospecificity of the catalyst fall, as the temperature is raised [25]. In the allyl system, we observed a sharp decrease in molecular weight as the temperature rises, which may be due to the deactivation of the (single component) catalyst, arising from thermally activated side reactions. These side reactions may be the intra-molecular coordination of the allyl-functional groups to the central metal or dimerization of the catalyst via the functional group or both, leading to the inhibition of catalyst efficiency. Neither seems to be happening in the present (dual component) system. It is, therefore, clear that the cocatalyst plays a stabilizing and important role of maintaining the integrity of the catalyst and availability of active species even under unfavorably drastic conditions.

The result of the investigation into the effect of variation in time on the polymerization is presented in Fig. 3 (runs B19, B25, B4, B20 and B21). Within the 30 h range used for the polymerization, the catalyst efficiency increases with an increase in time. The slope of the curve for percentage monomer conversion is much lower than that for polymer molecular weight, which exhibits a steep initial slope, later normalizing after about 15 h. This shows a slow initiation rate system accompanied by a long lifetime growing end and slow termination rate.

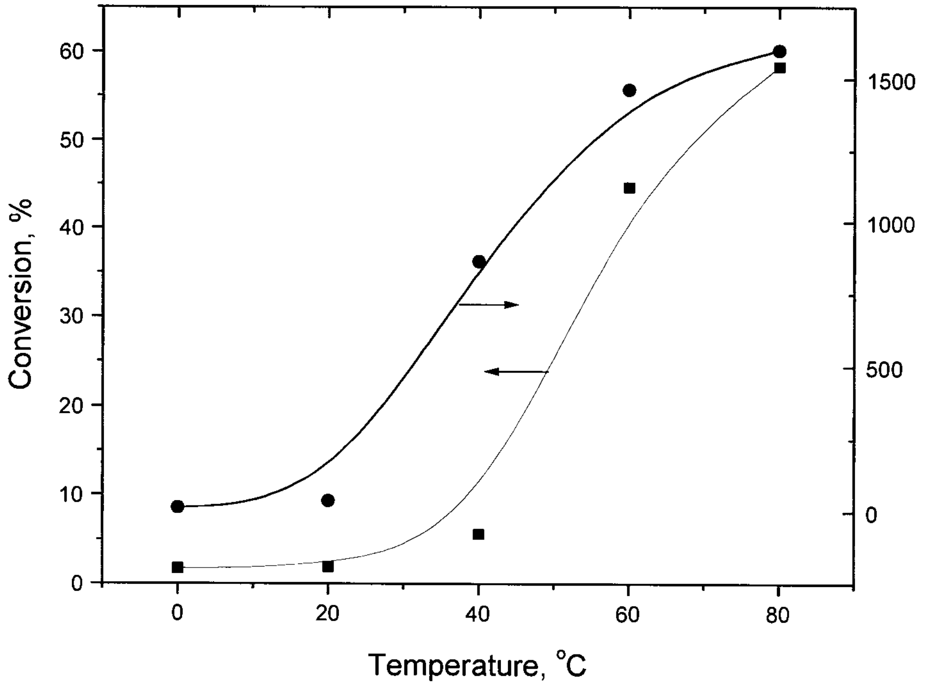


Fig. 2. Effect of temperature on the polymerization of MMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$.

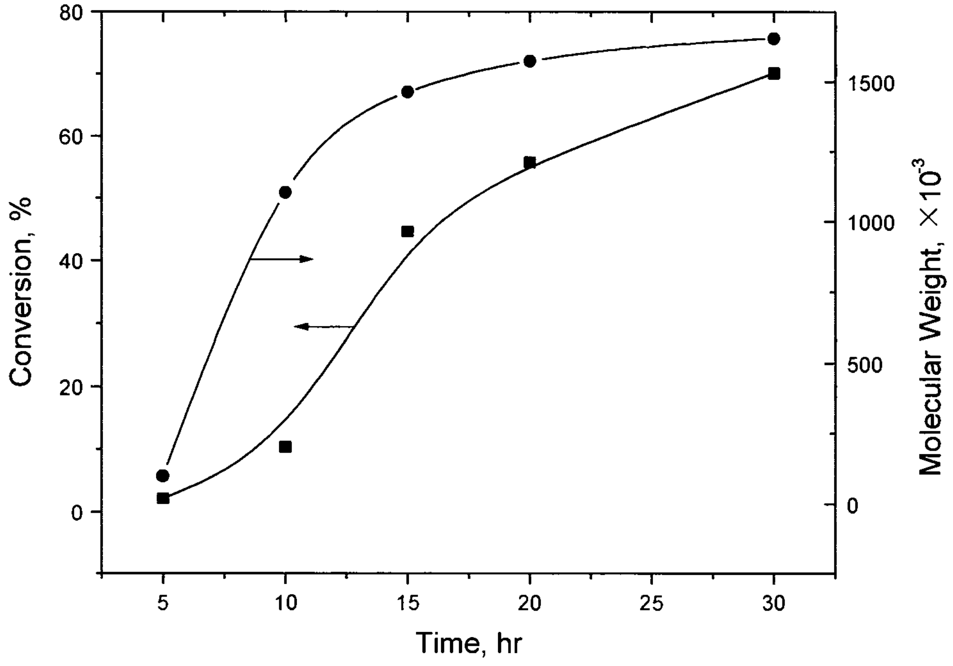


Fig. 3. Effect of polymerization time on PMMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$.

Table 4
Effect of solvent on polymerization catalyzed by (CH_2=$CHCH_2CH_2$-$C_5H_4)_2$Sm–Cl·2THF

Run	Solvent	Conversion (%)	M_η ($\times 10^{-3}$)
B11	Toluene	6.4	1154.4
B12	Petroleum ether	2.9	824.4
B14	CH_2Cl_2	6.0	671.0
B13	THF	4.3	786.6

Polymerization condition: MMA/catalyst = 2000; Al(*i*-Bu)/cat = 10; 60 °C; 15 h; solvent–MMA = 1:1 (volume).

The effect of different solvents on the polymerization was studied and the result is presented in Table 4.

Generally a very low percentage of monomer was converted, although high molecular weight polymers were obtained. The possibility that the solvents employed introduced traces of impurities that served as transfer agents cannot be ruled out. These will negatively affect the efficiency of the catalyst. Coordination of solvent molecules to the central metal may also contribute to the observed differences in activity.

The molecular weight distribution M_w/M_n, of polymers produced under different polymerization conditions was recorded and the GPC plots are presented in Figs. 4 and 5. Fig. 4 representing polymerization at 80 °C is unimodal in nature indicating the presence of only a single active propagation site in the system, while Fig. 5 for polymerization at 60 °C is bimodal indicating the production of heterogeneous products, with the first peak comprising high molecular weight fraction and the second peak comprising basically low molecular weight fractions. The molecular weight distribution (ca. 3.0) is much better than what has been reported for similar multi-component lanthanide metal coordinated MMA polymerization [19]. It is also clear from Fig. 5 and from an earlier discussion, that polymerization at much lower temperatures will yield polymers with improved molecular weight distribution although this will give predominantly low molecular weight fractions.

The tacticity of PMMA produced under different reaction conditions have been determined by the ^{1}H-NMR spectroscopy of the polymers in $CDCl_3$. The result is presented in Fig. 6(a)–(c) and summarized in Table 5.

In line with the established procedure, the tacticity of PMMA prepared under different conditions was estimated from these 500 MHz ^{1}H-NMR spectra (Me

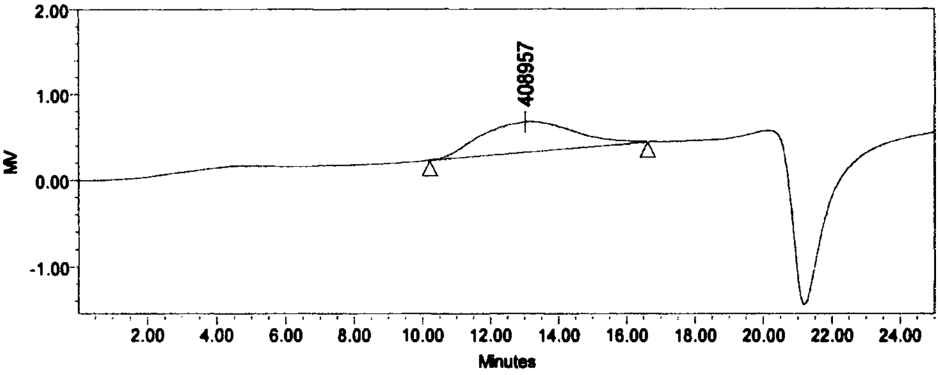


Fig. 4. GPC plot for the polymerization of MMA catalyzed by (CH_2=$CHCH_2CH_2C_5H_4)_2$Sm–Cl·2THF. M_n = 119 652; M_w = 336 147; M_p = 229 016; M_z = 670 537; M_z + 1 = 994 794; M_w/M_n = 2.81. Polymerization condition: MMA/cat = 2000; Al(*i*-Bu)$_3$/cat = 10; 80 °C; 15 h.

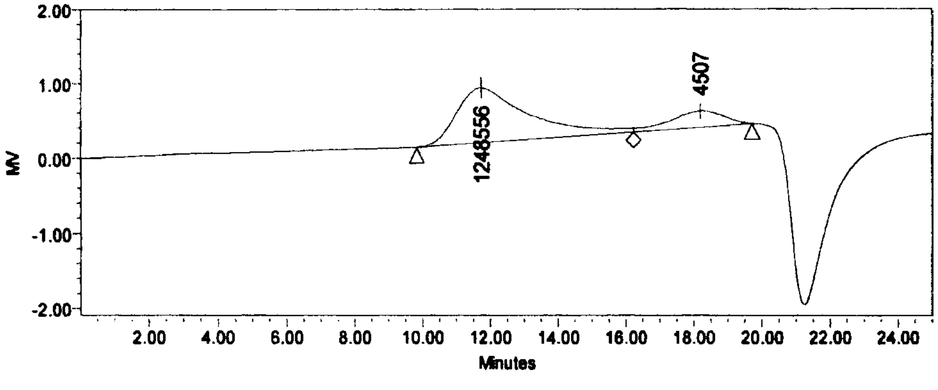


Fig. 5. GPC plot for polymerization of MMA catalyzed by (CH_2=$CHCH_2CH_2C_5H_4)_2$Sm–Cl·2THF. First peak: M_n = 188 543; M_w = 586 828; M_p = 699 191; M_z = 970 089; M_z + 1 = 1 290 058; M_w/M_n = 3.11. Second peak: M_n = 2523; M_w = 3765; M_p = 2524; M_z = 5703; M_z + 1 = 7852; M_w/M_n = 1.45. Polymerization condition: MMA/cat = 2000; Al(*i*-Bu)$_3$/cat = 10; 60 °C; 15 h.

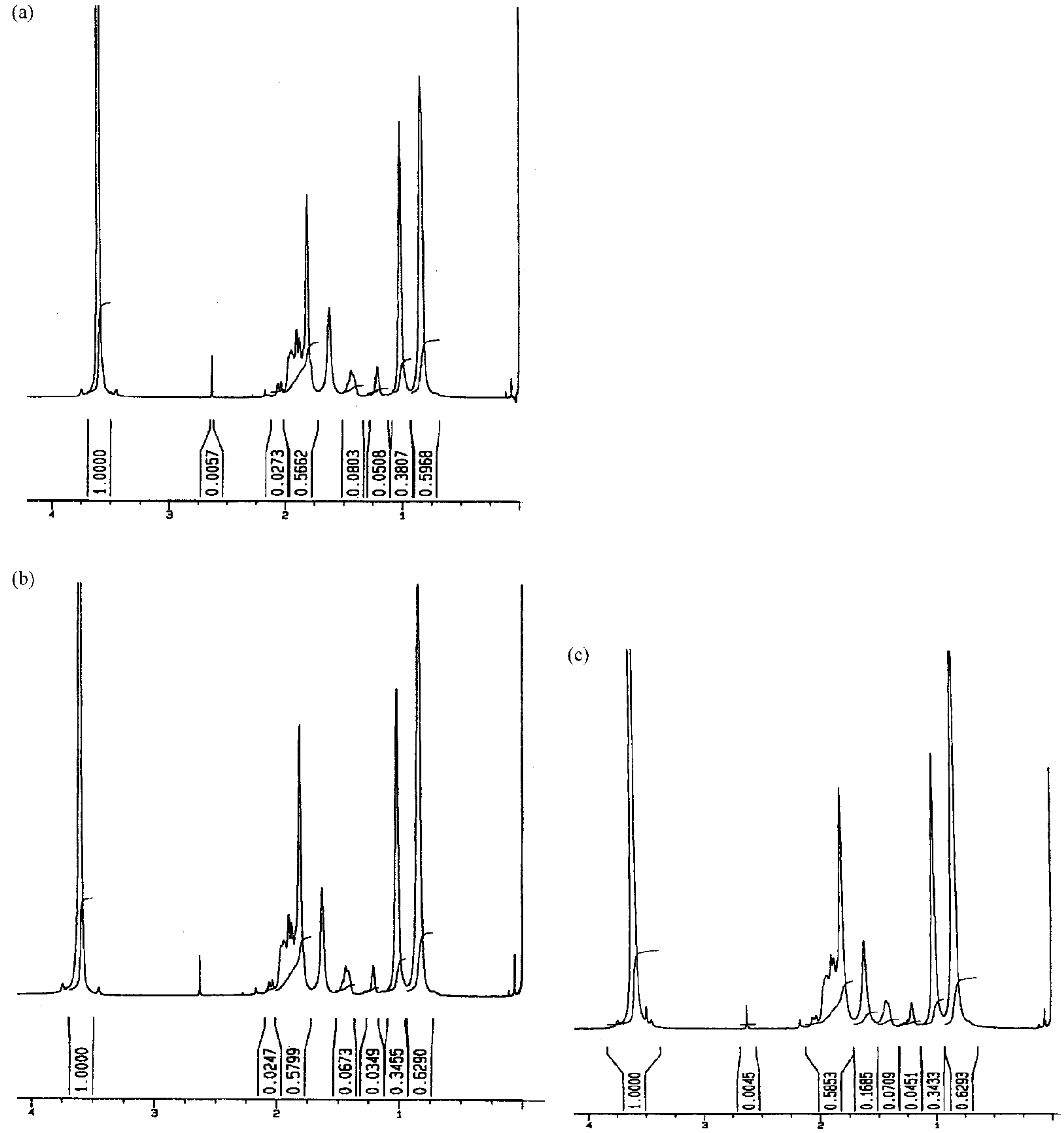


Fig. 6. (a) ^{1}H-NMR plot for PMMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$, run B18. (b) ^{1}H-NMR plot for PMMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$, run B21. (c) ^{1}H-NMR plot for PMMA catalyzed by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$, run B4.

Table 5
Tacticity of MMA polymerized by $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm{-}Cl{\cdot}2THF$

Run	Fig. 6	Temperature (°C)	Time (h)	Conversion (%)	M_η ($\times 10^{-3}$)	Tacticity (%)		
						rr	mr	mm
B18	a	80	15	58.3	1599.3	58	37	5
B21	b	60	30	70.1	1653.2	62	34	4
B4	c	60	15	63.3	22.9	62	34	4

Polymerization conditions: MMA/catalyst (molar ratio) = 2000; $Al(i\text{-}Bu)_3$/cat = 10.

peak; mm 1.17, mr 0.98, rr 0.78 ppm) [26–28]. The results indicate that the present catalyst system gives predominantly syndiotactic polymers.

The fact that syndiotacticity is not much affected by temperature or time changes is noteworthy. Even at 80 °C after about 15 h of polymerization, the syndiotacticity is still 58%. Improvement in syndioselectivity of the catalyst at lower temperature is in line with the observed trend for lanthanide-catalyzed polymerization of MMA [29].

3. Experimental

All operations involving the handling of air sensitive materials were carried out under dry Ar using standard Schlenk techniques. Tetrahydrofuran (THF), Et_2O, toluene and *n*-hexane were freshly distilled from sodium benzophenone ketyl under Ar prior to use. MMA was washed with dilute NaOH solution until colorless, dried over anhydrous $CaCl_2$, and vacuum distilled into ice-cooled container containing CaH_2.

Anhydrous lanthanide trichlorides were prepared according to the procedure outlined in the literature [30]. Allyl chloride was dried over $CaSO_4$ and distilled prior to use collecting the middle fraction. α-Toluene sulfonyl chloride(Ts–Cl, $C_6H_5CH_2SO_2Cl$) was recrystallized from petroleum ether. Magnesium powder was washed with ether to remove surface oxide coating and baked in vacuo. Paraformaldehyde was dried over P_2O_5 in a dessicator for 2 days in vacuo. NaCp was prepared by the usual method. Into a dry ice–acetone cooled three-necked flask, freshly cracked CpH was slowly dropped on to a slightly excess molar quantity of Na wire in THF, and stirred until no further sign of activity on the surface of the Na.

3.1. Characterization

The ^{1}H-NMR spectra were recorded in a Bruker AVANCHE500 500 MHz NMR spectrometer at room temperature (r.t.) in $CDCl_3$. Inherent viscosity of PMMA in $CHCl_3$ was determined at 30 °C with an Ubbelohde-type viscometer. Viscosity average molecular weight was calculated as $[\eta] = 5.5 \times 10^{-3}\ M_\eta^{0.79}$ ($cm^3\ g^{-1}$) (where M_η = viscosity average molecular weight). Molecular weight distribution (M_w/M_n) values were obtained from Waters-208 LC/GPC chromatograms employing polystyrene standards for calibration. Mass spectra were obtained on a HP5989A mass spectrometer with EI (70 eV). Infrared spectra were recorded on a Nicolet Magna-IR 550 spectrometer as KBr pellets or Nujol mulls. Element analysis was performed by the analytical laboratory at the Shanghai Institute of Organic Chemistry.

3.2. Preparation of ligand: butenyl-cyclopentadienyl potassium

The starting material 3-but-1-enol was first synthesized via the Grignard process according to the literature procedure [31] (Scheme 1, steps 1–3). Into a dry 500 ml three-necked flask was transferred 300 ml of ether, followed by 0.5 mol (95 g) of Ts–Cl and 0.5 mol (28 g) 3-buten-1-ol in succession (step 4). The mixture was stirred for 5 min giving a solution. An ice bath was placed beneath the flask and 15 g of powdered KOH were added slowly, and stirred continuously at r.t. for another 3 h. The 3-butenyl tosylate was separated by Buckner filtration as the filtrate in a 99% yield after removing all the volatiles in vacuo.

NaCp (0.5 mol) was transferred to a pre-dried and Ar-full 500 ml three-necked flask with one arm of the flask fitted with an overpressure oil bubbler. On the middle arm of the flask was a mechanical stirrer set at a moderate speed. The flask was cooled using dry ice–acetone at −30 °C and the allyl tosylate was slowly dropped from the third arm. Stirring was continued for additional 3 h. The white cake-like solution was hydrolyzed with 100 ml of ice cold water containing 5% HCl. The aqueous layer was washed with two portions of 30 ml ether. The combined organic portion was dried over $MgSO_4$ and distilled under reduced pressure, giving the product in 42% yield at 37–42 °C, 10 mmHg (step 5). The colorless product was reacted with an excess amount of potassium chips in THF at −20 °C to give the reddish colored ligand 3-butenylcyclopentadienyl potassium (step 6). The general synthetic route is presented in Scheme 1.

3.3. Synthesis of complex: $(CH_2{=}CHCH_2CH_2\text{-}C_5H_4)_2Ln\text{–}Cl\cdot 2THF$. Ln = Sm, Y, Dy, Er

All the four complexes were synthesized via the same route. Typical is the samarium complex. To pre-dried 100 ml Schlenk tube 0.95g (3.7 mmol) of $SmCl_3$ was transferred, followed by 30 ml of THF. After stirring for 5 min, two molar equivalent of the ligand (7.4 mmol) 3-butenylcyclopentadienyl potassium in THF was transferred by hypodermic syringe, degassed and sealed. After stirring overnight at r.t., the reaction mixture was centrifuged. The whitish KCl precipitate was washed with THF and the combined orange solution was concentrated in vacuo. The crude oily product was extracted once with Et_2O and twice with *n*-hexane. Removal of volatiles in vacuo gave clear mobile orange oil in 57% yield. The complexes prepared were analyzed by EA, MS and IR. Analytical data are presented below.

3.3.1. $(CH_2{=}CHCH_2CH_2C_5H_4)_2Sm\text{–}Cl\cdot 2THF$ (**3a**)

Orange oil. Yield: 57%. Anal. Calc. for $C_{26}H_{38}SmO_2Cl$: C, 54.93; H, 6.75. Found: C, 54.77; H, 6.23%.

IR (cm^{-1}): 3920w, 3420s, 3080s, 2950s, 2920s, 2850s, 1980w, 1820w, 1730m, 1660s, 1637s, 1600s, 1500m, 1430m, 1410m, 1370m, 1320m, 1300m, 1250m, 1200m, 1165m, 1150m, 1130m, 1060m, 1045m, 1030m, 1000s, 950m, 905s, 850m, 820m, 770s, 710m, 570s. MS; m/z (fragment, relative intensity): 425 [M − 2THF, 1], 390 [M − 2THF − Cl, 16], 306 [$CH_2{=}CHCH_2CH_2C_5H_4SmCl$, 6], 120 [$CH_2{=}CHCH_2CH_2C_5H_5$, 31], 71 [THF − 1, 1], 65 [Cp −, 6].

*3.3.2. $(CH_2{=}CHCH_2CH_2C_5H_4)_2Y{-}Cl \cdot 2THF$ (**3b**)*

Light brown oil. Yield: 58%. Anal. Calc. For $C_{26}H_{38}YO_2Cl$: C, 61.59; H, 7.57. Found: C, 61.70; H, 7.30%. IR (cm^{-1}): 3920w, 3420s, 3080s, 2920s, 2850s, 2750w, 1820w, 1715m, 1660s, 1637s, 1600s, 1500w, 1440m, 1460m, 1410m, 1360m, 1330w 1300w, 1260m, 1200w, 1165w, 1060s, 1045s, 1000s, 905s, 850m, 770s, 680s, 520m. MS; m/z (fragment, relative intensity): 366 [M − 2THF + 4, 2], 243 [$CH_2{=}CHCH_2CH_2C_5H_4YCl$, 2], 120 [$CH_2{=}CHCH_2CH_2C_5H_5$, 22], 71 [THF − 1, 7], 65 [Cp −, 18].

*3.3.3. $(CH_2{=}CHCH_2CH_2C_5H_4)_2Er{-}Cl \cdot 2THF$ (**3c**)*

Pink oil. Yield: 53%. Anal. Calc. for $C_{26}H_{38}ErO_2Cl$: C, 53.35; H, 6.56. Found: C, 53.60; H, 6.33%. IR (cm^{-1}): 3920w, 3480s, 3080s, 2950s, 2920s, 2850s, 2740w, 2450w, 2280w, 1980w, 1820w, 1705m, 1637s, 1600s, 1560m, 1540m, 1490m, 1460s, 1360s, 1340m, 1300m, 1260m, 1190m, 1050s, 1045s, 1000s, 905s, 830s, 780s, 680s, 560m. MS; m/z: (fragment, relative intensity): 439 [M − 2THF, 9], 404 [M − 2THF − Cl, 100], 320 [$CH_2{=}CHCH_2CH_2C_5H_4ErCl$, 76], 120 [$CH_2{=}CHCH_2CH_2C_5H_5$, 10], 65 [Cp −, 4].

*3.3.4. $(CH_2{=}CHCH_2CH_2C_5H_4)_2Dy{-}Cl \cdot 2THF$ (**3d**)*

Dark red oil. Yield: 57%. Anal. Calc. for $C_{26}H_{38}DyO_2Cl$: C, 53.78; H, 6.61. Found: C, 53.40; H, 6.22%. IR (cm^{-1}): 3920w, 3500s, 3080s, 2950s, 2920s, 2850s, 1980w, 1820w, 1730m, 1660s, 1600s, 1490m, 1440m, 1410m, 1360m, 1330m, 1300m, 1260m, 1200m, 1150m, 1100m, 1060s, 1045s, 1000s, 905s, 850m, 820s, 780s, 720m, 680m, 640m. MS; m/z (fragment, relative intensity): 437 [M − 2THF, 7], 402 [M − 2THF − Cl, 35], 318 [$CH_2{=}CHCH_2CH_2C_5H_4DyCl$, 60], 120 [$CH_2{=}CHCH_2CH_2C_5H_5$, 11], 71 [THF − 1, 1], 65[Cp −, 3].

3.4. Polymerization of MMA

Polymerization was carried out in a dry and sealed ampoule tube with a rubber stopper. The required amounts of reagents were introduced into the ampoule by a syringe under a dry Ar atmosphere. After introducing the catalyst (and solvent when required), the monomer MMA, usually 1 ml, is charged. The cocatalyst was then introduced to initiate the reaction. Polymerization was carried out at a constant temperature in a water bath with occasional shaking for a certain period. After polymerization, the ampoule was opened and EtOH containing 5% HCl was introduced to terminate the reaction and precipitate the polymer.

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