

Novel 2-propenyl cyclopentadienyl lanthanide complexes as single component methyl methacrylate (MMA) polymerization catalysts

Yanlong Qian^{a,*}, Muhammad D. Bala^a, Muhammad Yousaf^a, Hao Zhang^a,
Jiling Huang^a, Junquan Sun^b, Chengfeng Liang^b

^a Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China

^b Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, PR China

Received 11 December 2001; received in revised form 14 April 2002; accepted 23 April 2002

Abstract

A new set of allyl-functionalized cyclopentadienyl (Cp') lanthanocenes were synthesized and characterized by MS, IR and EA. A structure in which the lanthanide metal is a nine-coordinate center solvated by two THF molecules was proposed. No evidence of intramolecular coordination of the alkenyl C=C to the central metal was observed. Single component bulk polymerization of MMA catalyzed by Cp' ytrocene indicated that at the optimum condition of 40 °C and MMA/catalyst molar ratio of 400:1 a predominantly syndiotactic ($rr > 70\%$) polymer with $M_n > 500,000$ and molecular weight distribution (M_w/M_n) < 1.4 is obtained. The effects of variation in temperature, time of polymerization and initiator concentration was also studied. The title catalysts showed moderate activity for MMA/catalyst molar ratio of up to 1200:1. At a molar ratio of 800:1 a polymer $M_n = 1.6 \times 10^6$ was obtained. The electron donating influence of the functional group on catalyst activity was discussed. The effects of co-catalysts on the polymerization were also studied.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanides; 2-Propenylcyclopentadiene; Methyl methacrylate; Single-component catalyst

1. Introduction

Metallocene complexes bearing substituents at the cyclopentadienyl (Cp) rings have been of great importance to organometallic chemistry and catalysis [1]. This interest is due to their capacity to act as coordination polymerization catalysts or catalyst precursors [2]. A variety of functional groups have been studied as side-chain additions to the Cp ring. These includes alkoxyalkyl (ROR') [3]; alkyl (R-) [4]; trialkylsilylene (R₃Si-) [5]; amine (R₂N-) [6]; and ω-alkenyl (CH₂=CHR-) [7,8] based metallocenes.

Reports have shown that the ω-alkenyl (CH₂=CHR-) Cp ligands have been successfully used for the synthesis of organometallic complexes with Co [9]; Ni (II) [10]; Ti [7,11]; Zr [1,8,11] and Hf [1] metals. Qian et al. [12] have found its Ti- based complexes to exhibit high conversion (100%) in the isomerization of 1,5-hexadiene. A very recent review [13] outlined the importance of functionalized-Cp ligands and their application in organometallic synthesis, but to the best of our knowledge there is no report yet on the application of (CH₂=CHR-) functionalized-Cp ligand to form rare-earth metals complexes. The introduction of ω-alkenyl-substitution to ordinary Cp compounds creates two types of situations chemically, both have been reported in the literature [13].

* Corresponding author. Fax: +86-21-6470-2573.
E-mail address: qianling@online.sh.cn (Y. Qian).

On one hand, the side group may coordinate to the central metal in which case a product more stable than the un-substituted Cp metallocene is obtained. On the other hand, no intra-molecular coordination was observed and the metallocene will easily undergo further reactions (e.g. insertion and even substitution) via the C=C double bonds. Both situations will have some impact on the activity of the substituted Cp metallocene in catalysis.

One of the principal targets in catalyst design has been a single-component catalyst with the activities of the commonly employed two-component systems but without the need for co-catalysts. The incorporation of an alkenyl side-chain to a Cp ring attached to a lanthanide metal center is expected to yield self-activating catalysts for the initiation of polymerization of both polar and non-polar monomers. In the light of this, we hereby report on the synthesis of 2-propenyl (CH₂=CHCH₂-)-functionalized-Cp lanthanide complexes and their application as MMA polymerization catalysts.

2. Experimental

2.1. Materials

All operations involving the handling of air sensitive materials were carried out under dry argon using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether, toluene and *n*-hexane were freshly distilled from sodium benzophenone ketyl under argon prior to use. MMA (Shanghai Fei Da Chemical Reagent Factory) was washed with dilute NaOH solution until colorless, dried over anhydrous CaCl₂ for 2 days, CaH₂ for another 2 days, then vacuum distilled into ice-cooled container containing CaH₂.

Anhydrous lanthanide trichlorides were prepared according to literature [14] from the oxides (Shanghai Yue Long non-ferrous metals company). Allyl alcohol (Shanghai Chemical Reagent Factory) was dried over Na₂SO₄ and distilled prior to use collecting the middle fraction. α -Toluenesulfonyl chloride (Ts-Cl, China Songjiang Glue and Chemical Reagent Company) was recrystallized from petroleum ether. NaCp was prepared by the usual method. For example, to prepare 0.5 mol NaCp, a 500 ml three-necked flask was first vacuum dried and flushed several times with

dry argon, then cooled to -30 °C using a combination of dry ice/acetone as coolant. Then, 0.5 mol (33 g) of freshly cracked CpH was slowly dropped on to a slightly excess molar quantity of Na wire (13 g) in 300 ml THF, and stirred until no further sign of activity on the surface of the Na wire.

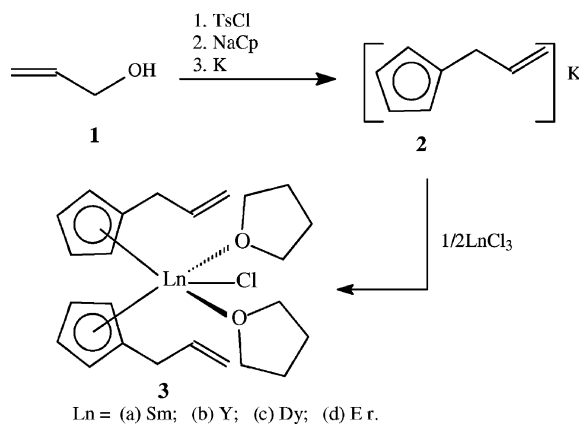
2.2. Characterization

The ¹H NMR spectra were recorded on a Bruker AVANCHE500 500 MHz NMR spectrometer at room temperature in CDCl₃. Inherent viscosity of poly MMA in CHCl₃ was determined at 30 °C with an Ubbelohde-type viscometer. Viscosity average molecular weight was calculated as $[\eta] = 5.5 \times 10^{-3} M_{\eta}^{0.79}$ (cm³/g) (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. Element analyses were performed by the analytical laboratory of Shanghai Institute of Organic Chemistry.

2.3. Preparation of ligand: allyl-cyclopentadienyl potassium

The ligand was synthesized by a slight modification of the method of Erker and Aul [1]. Into a dry 500 ml three-necked flask fitted with an overpressure bubbler and magnetic stirrer was transferred 300 ml of dry ether. Then 0.2 mol (38 g) recrystallized Ts-Cl was added and stirred for 5 min to dissolve. The flask was then chilled in ice to 0–5 °C and 0.2 mol (14 ml) allyl alcohol was added drop wise via syringe. Then 15 g grounded KOH was slowly added to initiate the highly exothermic reaction. Stirring was continued for further 3 h at room temperature. The solution was filtered through a Buckner funnel and the ether removed in vacuum to give 42 g (99%) of a clear liquid.

NaCp (0.2 mol) was transferred to a pre-dried and argon-flushed 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. Then the flask was cooled to -30 °C and the allyl tosylate was slowly dropped



Scheme 1.

from the third arm. Stirring was continued for a further 3 h. Then the white cake-like solution was hydrolyzed with 100 ml of acidified ice water (5% HCl). The aqueous layer was washed with two portions 30 ml ether. The combined organic portion was dried over MgSO_4 and distilled under reduced pressure, giving the product in 42% yield at 27–31 °C, 15 mm Hg. The colorless product was reacted with an excess amount of potassium chips in THF at –20 °C to give the reddish colored ligand 2-propenyl cyclopentadienyl potassium. The general synthetic route is presented in Scheme 1.

2.4. Synthesis of complex: $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Ln}-\text{Cl}\cdot 2\text{THF}$, Ln = Sm; Y; Dy; Er

All four complexes were synthesized via the same route. Typical is the case of the erbium complex: to pre-dried Schlenk tube was transferred 0.95 g (3.43 mmol) of ErCl_3 , followed by 30 ml of THF. After stirring for 5 min, two molar equivalent of the ligand (6.86 mmol) allyl-Cp potassium was syringed in, degassed and sealed. After stirring for 24 h at room temperature, the reaction mixture was centrifuged, and the light yellow solution was concentrated in vacuo. The crude oily product was extracted twice with diethyl ether and twice with *n*-hexane. Removal of volatiles in vacuo gave a clear yellow oily complex in 45% yield. The prepared complexes were analyzed by EA, MS and IR. Analytical data are presented below:

2.4.1. $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Sm}-\text{Cl}\cdot 2\text{THF}$ (3a)

Orange oil, 52% yield. Analytically calculated for $\text{C}_{24}\text{H}_{34}\text{SmO}_2\text{Cl}$: C, 53.43; H, 6.37. Found: C, 53.01; H, 6.11. IR (cm^{-1}) 3420 s, 3080 s, 3000 m, 2950 s, 2920 s, 1980 w, 1820 w, 1715 m, 1660 s, 1637 s, 1600 m, 1530 w, 1490 m, 1430 m, 1410 m, 1360 m, 1300 m, 1250 m, 1200 m, 1165 m, 1045 m, 995 m, 905 s, 850 m, 820 m, 770 s, 570 s. MS data: m/z [fragment, relative intensity (%)] = 397[M – 2THF, 1], 362[M – 2THF – Cl, 100], 257[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4\text{Sm}$, 21], 106[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_6$, 66], 72[THF, 6], 66[CpH, 19].

2.4.2. $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Y}-\text{Cl}\cdot 2\text{THF}$ (3b)

Pale yellow oil, 55% yield. Analytically calculated for $\text{C}_{24}\text{H}_{34}\text{YO}_2\text{Cl}$: C, 60.30; H, 7.18. Found: C, 59.44; H, 6.80. IR (cm^{-1}) 3400 s, 3080 s, 3000 m, 2950 s, 2920 s, 1980 w, 1820 w, 1715 m, 1660 s, 1637 s, 1600 s, 1530 w, 1490 w, 1430 m, 1410 w, 1360 m, 1300 w, 1260 w, 1200 w, 1165 w, 1045 w, 995 m, 905 m, 850 w, 820 w, 770 m, 680 m. MS data: m/z [fragment, relative intensity (%)] = 334[M – 2THF, 4], 299[M – 2THF – Cl, 8], 194[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4\text{Y}$, 1], 106[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_6$, 77], 72[THF, 3], 66[CpH, 15].

2.4.3. $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Er}-\text{Cl}\cdot 2\text{THF}$ (3c)

Yellow oil, 45% yield. Analytically calculated for $\text{C}_{24}\text{H}_{34}\text{ErO}_2\text{Cl}$: C, 51.81; H, 6.17. Found: C, 51.80; H, 5.78. IR (cm^{-1}) 3500 s, 3080 s, 3000 m, 2950 s, 2920 s, 2880 s, 2740 w, 1980 w, 1820 w, 1715 m, 1637 s, 1600 s, 1530 w, 1490 w, 1460 m, 1430 s, 1360 m, 1300 w, 1260 w, 1200 w, 1050 w, 1045 m, 995 m, 905 s, 830 m, 780 s, 680 s. MS data: m/z [fragment, relative intensity (%)] = 411[M – 2THF, 13], 376[M – 2THF – Cl, 93], 271[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4\text{Er}$, 6], 106[$\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_6$, 27], 74[THF + 2, 2], 66[CpH, 2].

2.4.4. $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Dy}-\text{Cl}\cdot 2\text{THF}$ (3d)

Yellow oil, 42% yield. Analytically calculated for $\text{C}_{24}\text{H}_{34}\text{DyO}_2\text{Cl}$: C, 52.26; H, 6.23. Found: C, 52.16; H, 5.50. IR (cm^{-1}) 3400 s, 3080 s, 3000 s, 2950 s, 2920 s, 1980 w, 2200 w, 1820 w, 1730 m, 1660 m, 1637 s, 1430 w, 1410 w, 1380 w, 1350 w, 1290 w, 1260 w, 1200 w, 1090 w, 1060 w, 1045 w, 995 m, 905 m, 850 w, 820 w, 680 m, 640 m. MS data: m/z [fragment, relative intensity (%)] = 409[M – 2THF,

5], 374[M – 2THF, 35], 269[CH₂=CHCH₂C₅H₄Dy, 1], 106[CH₂=CHCH₂C₅H₆, 99], 74[THF + 2, 3], 66[CpH, 5].

2.5. Polymerization of MMA

Polymerization was carried out in a sealed ampoule tube with a rubber stopper. The required amounts of reagents were introduced into the ampoule by a syringe under a dry argon atmosphere. After introducing the catalyst (solvent and co-catalyst when required), the monomer MMA is charged. Polymerization was carried out at a constant temperature in a water bath for a selected period of time. After the polymerization, the ampoule was opened and ethanol containing 5% HCl was introduced to terminate the reaction and precipitate out the polymer.

3. Results and discussions

3.1. Synthesis and characterization

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 [13]. 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 complexes were easily obtained using commonly employed metathetical procedures as outlined in Scheme 1.

The methodology is basically the same for all the four complexes. The prepared complexes are all free-flowing clear oils exhibiting the pale colors that are characteristic to lanthanide metal complexes. All the new complexes are soluble in hydrocarbon solvents such as toluene and *n*-hexane, though they are still sensitive to air and moisture. Purification was achieved by washing the crude product several times with ether then with *n*-hexane until no sticky substance precipitates out, followed by rotary centrifugation after each washing. The clear analytically pure (by EA) oils were obtained in moderate (50% ca.) yields. The resulting oils were characterized by MS, EA and IR. Spence and Piers [8] prepared the corresponding Zr complexes and reported obtaining oils and gummy solids which defied purification and

isolation by normal means. However, their complexes were found to be 95% pure by ¹H NMR spectroscopy.

By 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 as shown in Scheme 1 (3a–d), in which the metal is a nine-coordinate center solvated by two THF molecules. Only complexes of relatively smaller ionic radii lanthanide metals were isolated. Attempts to isolate the corresponding La and Nd complexes failed. This was not surprising as it is well-known [15] that large ionic radii lanthanide metals mostly failed to give isolable compounds for simple bis(Cp)Ln–Cl complexes, possibly due to steric unsaturation.

The MS spectra of all the complexes show similar cleavage pattern. The highest M⁺ corresponds to the [bis(allyl-Cp)Ln–Cl] fragment; this indicates that the 2THF molecules are easily cleaved. But the elemental analysis indicated their presence. The IR spectra shows the presence of ordinary uncoordinated C=C bonds of the allyl substituents (1637 cm⁻¹), and absorption bands at 1045 and 890 cm⁻¹ verify the presence of coordinated THF molecule [16]. In addition to these facts the concept of hard and soft acids and bases (HSAB) [17] classifies the rare-earth metals as hard Lewis acids, therefore, it is chemically more likely to have the structure of the complexes as containing inter-molecular coordination of the rare-earth metal to THF molecules rather than intra-molecular coordination of the C=C bonds of the allyl substituents. Based on these results we conclude that the functional groups of the side-chains remain free and uncoordinated. The characterized complexes when used as polymerization catalysts especially for polar monomers like MMA, it is expected [18] that the small electron-donating allyl substituents will improve catalytic activity by virtue of electronic effects while imposing little steric hindrance.

3.2. Polymerization of MMA

Single component polymerization of MMA was conducted using the title complexes. All the complexes showed some activity to the monomer. An initial study was made to establish the conditions for optimum catalyst efficiency in terms of conversion of monomer to PMMA and polymer molecular weight. To establish the role played by the lanthanide

Table 1
Polymerization of MMA catalyzed by allyl-Cp lanthanide complexes

Run	Ln	Conversion (%)	M_n ($\times 10^{-3}$)
13	Y	42.7	141.0
33	Sm	15.1	93.2
34	Dy	25.3	48.8
35	Er	1.4	164.6

Polymerization condition: MMA/catalyst = 400 (molar ratio), 40 °C, 24 h, bulk.

metal Ln in $(\text{CH}_2=\text{CHCH}_2\text{C}_5\text{H}_4)_2\text{Ln}-\text{Cl}\cdot 2\text{THF}$, Ln = Sm; Y; Dy; Er), polymerization was carried out with the four different complexes each having one of the lanthanide metals as central atom. The results are presented as shown in Tables 1 and 2.

At a mild condition of 40 °C, MMA/catalyst molar ratio = 400 and bulk polymerization for 24 h, it was observed that the yttrium complex produced the best overall result. A conversion of 42.7% and $M_n = 141,000$ was obtained with the yttrium complex while the erbium complex produced a conversion of only 1.4%, but recording the highest $M_n = 164,600$. Other metals gave results somewhat in between. These results indicate that the role of the f-orbital to the polymerization is minimal as Y ($3\text{S}^2 3\text{P}^6 3\text{D}^{10} 4\text{S}^2 4\text{P}^6 4\text{D}^1 5\text{S}^2$) has no f-orbital configuration. Similar observation on the role of the f-orbital was made by Yasuda et al. [19]. Based on these initial

observations, we conducted a more detailed study on the yttrium complex. The effect of such factors as temperature, time of polymerization and variation in catalyst concentration was studied. The dependence of the polymer molecular weight and monomer conversion on initiator concentration is presented in Fig. 1.

The molecular weight increases with a decrease of initiator concentration and recorded a maximum of $M_n = 1.66 \times 10^6$ at a conversion of 26.8%. The inverse dependence of molecular weight on initiator concentration for living polymerization of MMA has been well established for example see Yasuda et al. [20]. At a MMA/catalyst = 200 (mol/mol) ratio the rate of polymerization was instantaneous, achieving a 100% conversion within seconds. As the ratio increases to 400 (mol/mol), conversion decreased by half as well. This behavior may be attributed to transfer reactions within the system. As it has been pointed out [20] that the conventional drying of MMA over CaH_2 is not sufficient, if the goal is to realize an ideal living polymerization. Normally the monomer and solvents still contain 30 ppm ca. water. This and/or oxygen within the system is enough to drastically affect the conversion as amount of monomer increases, especially as the catalyst is highly oxophilic and hydrophilic. Because at a MMA/catalyst molar ratio of 200 the reaction is too rapid to be further studied, and at a molar ratio of 800 the conversion is time dependent. We conclude

Table 2
Polymerization characterization of MMA catalyzed by allyl-yltrocene

Run	MMA/catalyst (molar ratio)	Temperature (°C)	Time (h)	Conversion (%)	M_n ($\times 10^{-3}$)
6	200	40	24	100	72.7
7	400	40	24	42.7	141.0
8	800	40	24	26.8	1661.2
10	1200	40	24	13.7	1316.5
11	400	0	24	13.9	48.7
12	400	20	24	19.8	828.9
7	400	40	24	42.7	141.0
14	400	60	24	58.4	31.3
42	400	80	24	65.7	28.3
15	400	40	4	14.9	15.5
16	400	40	8	28.8	52.2
18	400	40	16	31.5	58.6
7	400	40	24	42.7	141.0
17	400	40	30	54.4	191.7
19	400	40	40	67.5	261.3

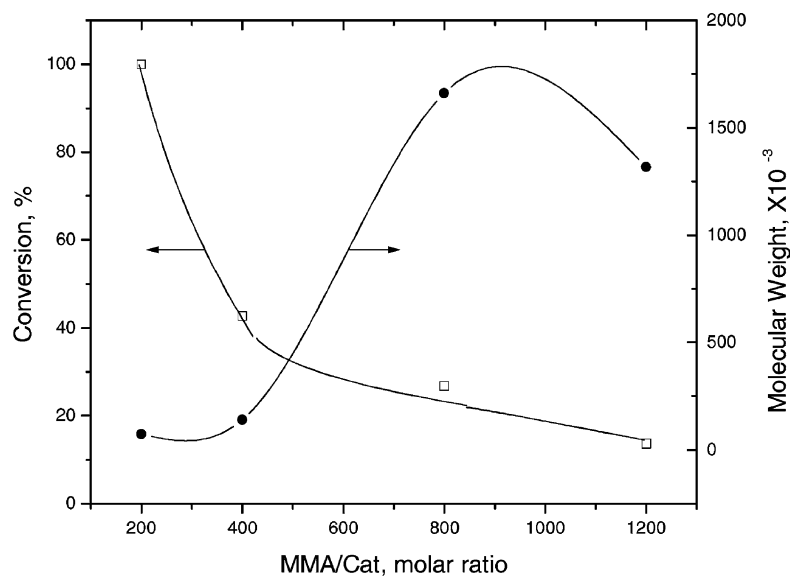


Fig. 1. Effect of initiator concentration on PMMA catalyzed by allyl-tytrocene.

that MMA/catalyst (mol/mol) ratio = 400 is the optimum initiator concentration for further studies.

The effect of variation in polymerization temperature on MMA conversion and M_n is presented in Fig. 2. Polymerization temperature was varied from

0 to 80 °C. MMA conversion increases with a rise in temperature, while the molecular weight initially increased, peaked at 20 °C (room temperature) and then declined as temperature increases. We attributed the sudden decrease in M_n as temperature rises to

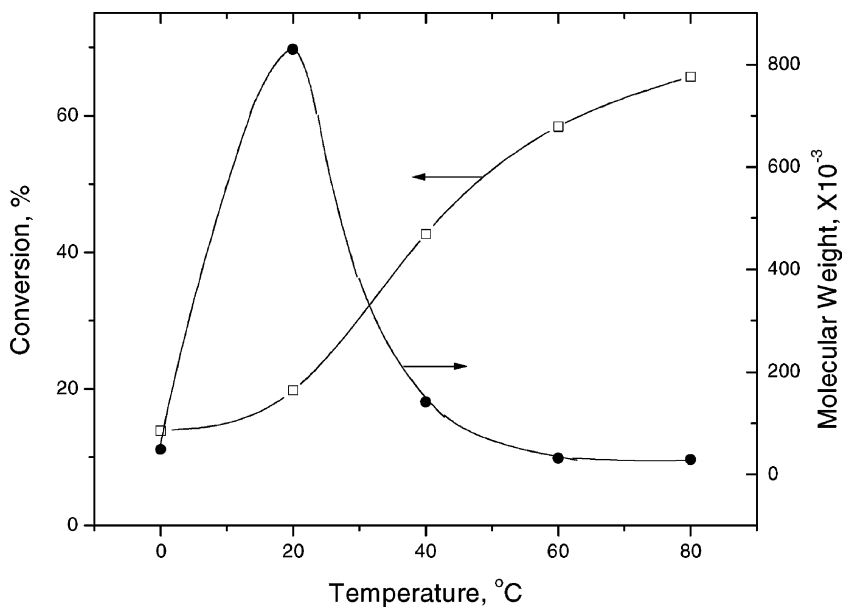


Fig. 2. Effect of temperature on PMMA catalyzed by allyl-tytrocene.

the structure of the catalyst. Under normal conditions, as evidenced by analysis of the catalyst, the allyl functional group attached to the Cp is free and uncoordinated to the central metal atom. But it is inherently unstable and this instability is promoted by heat. Therefore, as the temperature rises, the side reactions of dimerization of the active species and coordination of C=C of the allyl group to the central metal are in active competition with the propagation of the polymer, resulting in drastic decrease in catalyst efficiency.

The increase in conversion with a rise in temperature may in part be due to temperature aided polymerization of pure uninhibited MMA to low molecular weight polymers and oligomers. Here, polymer obtained is of very low M_n (28,300 at 80 °C, against 828,900 at 20 °C). The fact that catalyst activity generally decreased with rise in temperature is consistent with observations for lanthanide mediated MMA polymerizations [20,21].

Fig. 3 presents the result of the influence of time of polymerization on M_n and percentage MMA conversion. Both indicators increase directly with time. Therefore, it can be concluded that at the optimum conditions, the polymerization of MMA using the title complexes is time dependent.

Table 3

Effect of co-catalyst on polymerization of MMA catalyzed by allyl-yltrocene

Run	Co-catalyst	Al/catalyst (molar ratio)	Conversion (%)	M_n ($\times 10^{-3}$)
	MAO	10	1.1	
21	AlEt ₃	10	95.3	110.8
24	Al(<i>i</i> -Bu) ₃	10	49.0	18.6
25	Al(<i>i</i> -Bu) ₃	15	61.4	13.4
26	Al(<i>i</i> -Bu) ₃	20	75.6	9.7
7	None		42.7	141.0

Polymerization condition: MMA/catalyst = 400 (molar ratio), 40 °C, 24 h, bulk.

To gain further insight into the process of polymerization initiation by the title complexes a study of the influence of co-catalysts was investigated. The result is presented in Table 3.

Out of the three co-catalysts used only aluminum triethyl (AlEt₃) showed any positive influence on polymerization. Conversion improved from 43 to 95% compared to the system not employing any co-catalyst, but the polymer molecular weight is still comparatively lower. Obviously no polymer was obtained with MAO, due to mainly the high oxophilicity of the catalyst. With aluminum tri-isobutyl (Al(*i*-Bu)₃), only

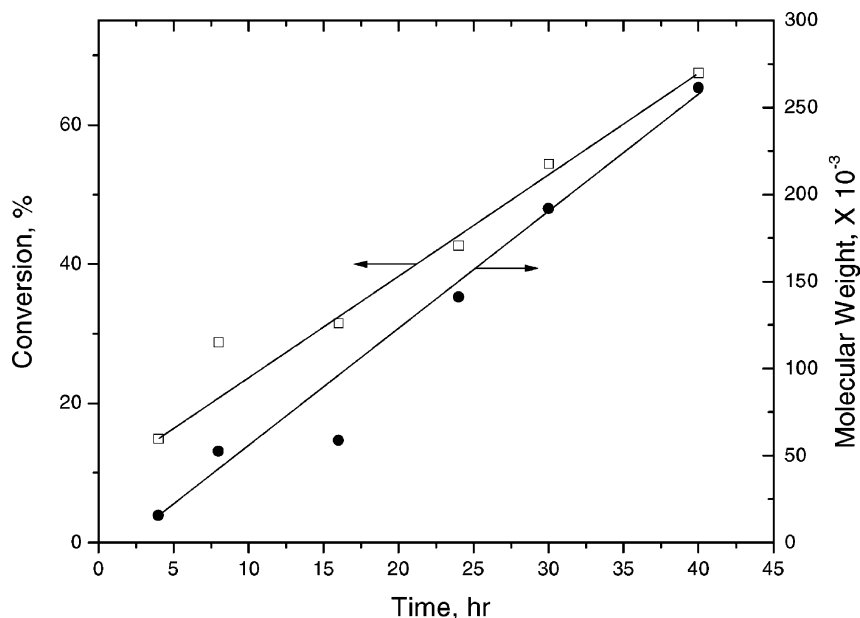


Fig. 3. Effect of reaction time on PMMA catalyzed by allyl-yltrocene.

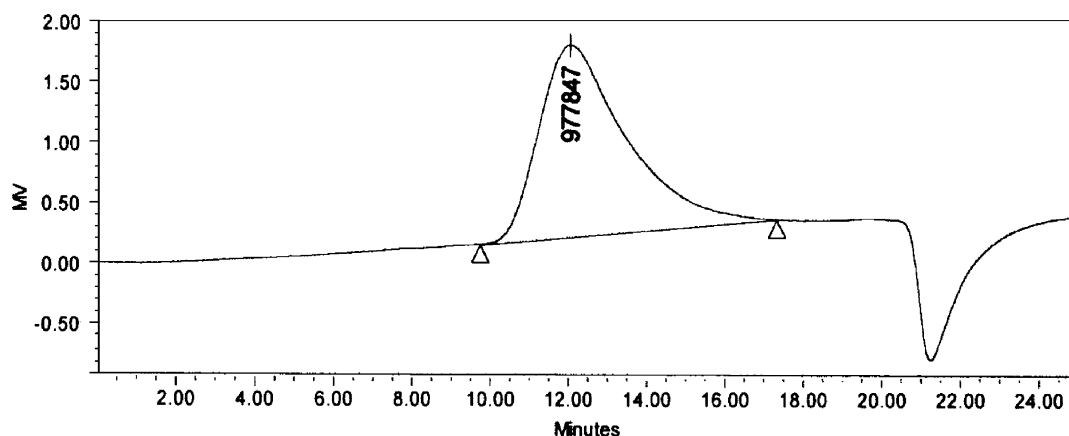


Fig. 4. GPC curve for polymerization of MMA at: MMA/catalyst = 1200; 10°C; 24 h; $M_n = 156,136$; $M_w = 491,616$; $M_w/M_n = 3.15$.

a slight improvement in catalyst efficiency was observed, this is due to steric limitations while alkylating the catalyst as the bulk size of the isobutyl ligand will nullify any electronic benefits from the co-catalyst.

Molecular weight distribution (M_w/M_n) of PMMA obtained under different polymerization conditions was studied by GPC and the result are presented in Figs. 4 and 5. Fig. 4 is a unimodal curve, a contrast to the bimodal Fig. 5. The difference in the nature of the two curves explains the general influence the reaction conditions have on the polymerization of MMA using the present system.

The GPC curves shows that a heterogeneous set of products are obtained when polymerization was con-

ducted at a higher temperature (Fig. 5). This behavior is not usual for homogeneous, single-site catalysts, and could be due to the side reactions that are induced by heat and the presence of traces of impurity in the form of bimolecular chain transfer agents that induce premature chain termination. At a lower temperature (10°C) these side reactions are suppressed and the general coordination of the catalyst is maintained, hence a homogeneous unimodal GPC curve was obtained.

The molecular weight distribution is highly influenced by polymerization conditions. Polymerization at a lower temperature (below 20°C results in low molecular weight polymer of wide distribution ($M_w/M_n > 3$).

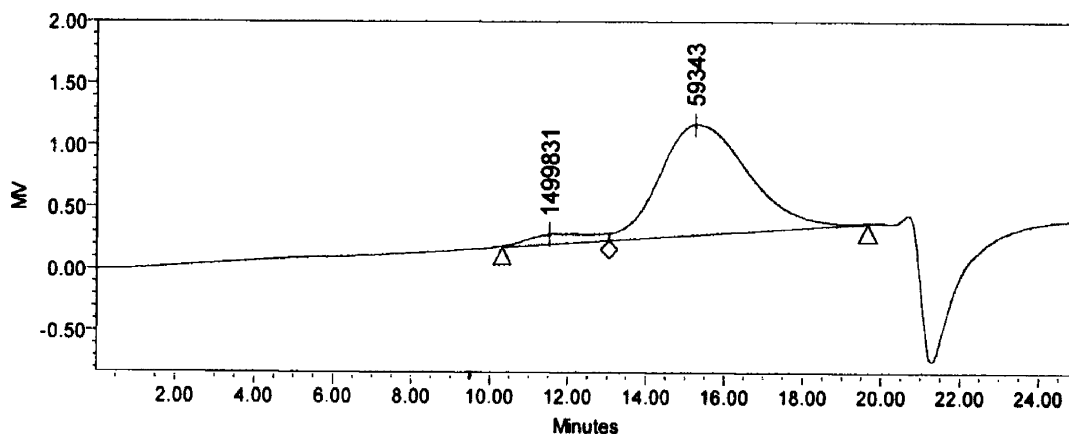


Fig. 5. GPC curve for polymerization of MMA at: MMA/catalyst = 400; 40°C; 24 h; first peak $M_n = 537,102$, $M_w = 766,427$, $M_w/M_n = 1.39$; second peak $M_n = 15,280$, $M_w = 35,920$, $M_w/M_n = 2.35$.

At higher temperatures, the molecular weight distribution is generally narrower (<1.5) for the high molecular weight fraction of the heterogeneous set of products, and still around 2.3 for the low molecular weight fraction. By extrapolation, therefore, we conclude that by choice of conditions, PMMA of varying molecular weight, distribution of molecular weight and, hence, varying chemical and physical properties may be produced.

In line with established procedure the tacticity of PMMA prepared under different conditions was estimated from the 500 MHz ^1H NMR spectra of the polymers in CDCl_3 (Me peak; 1.17 ppm; *mr*, 0.98; *rr*, 0.78 ppm) [22]. The results are presented in Figs. 6–8.

As established by Bovey and Tiers [23] and Bovey [24], the distinctive pattern for tacticity occurs in the $-\text{CH}_2-$ region (1.5–2.5 ppm) of the spectra from which it is apparent that the PMMA produced is predominantly syndiotactic although some isotactic patterns are detectable. It is important to note that the syndiospecificity of the catalyst is negligibly affected by polymerization conditions. Even at 40 °C for 24 h a syndiotacticity 70% ca. was maintained. This is similar to results reported for single component lanthanide mediated MMA polymerizations [20,25].

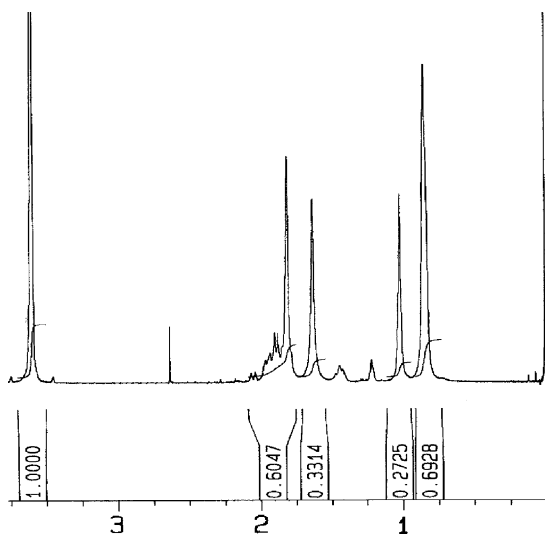


Fig. 6. ^1H NMR spectrum of PMMA catalyzed by allyl-yltrocene, *rr* = 72%, *mr* = 28%. Polymerization condition: MMA/catalyst = 200 (mol/mol), 40 °C, 24 h; 100% conversion; $M_n = 72,700$.

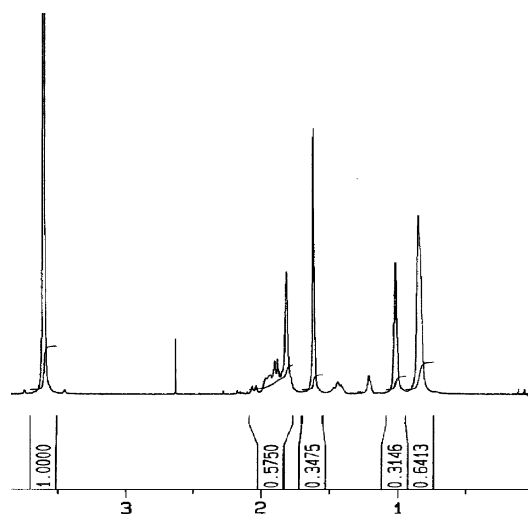


Fig. 7. ^1H NMR spectrum of PMMA catalyzed by allyl-yltrocene, *rr* = 67%, *mr* = 33%. Polymerization condition: MMA/catalyst = 400 (mol/mol), 20 °C, 24 h; 19.8% conversion; $M_n = 828,000$.

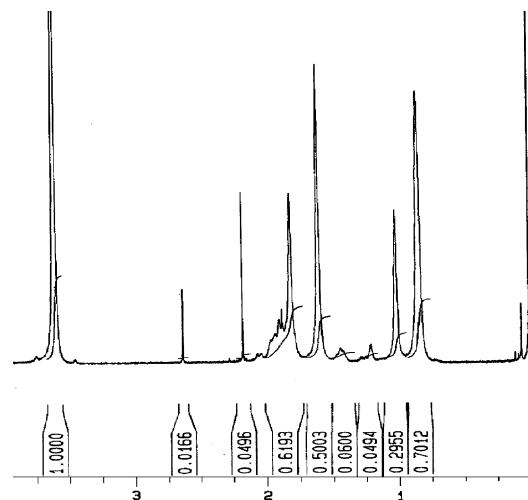


Fig. 8. ^1H NMR spectrum of PMMA catalyzed by allyl-yltrocene, *rr* = 67%, *mr* = 28%, *mm* = 5%. Polymerization condition: MMA/catalyst = 400 (mol/mol), 40 °C, 40 h; 67.5% conversion; $M_n = 261,300$.

4. Conclusions

Allyl functionalized-Cp lanthanide complexes of the late lanthanide metals have been synthesized as

free-flowing oily products, which were successfully characterized and found to be of high purity.

Used as single component catalysts for the polymerization of a polar monomer (MMA), the title complexes were found to exhibit high activity and syndiospecificity yielding very high molecular weight polymers. Polymerization temperature was observed to be the one main factor that greatly affects catalyst efficiency. By careful choice of optimum reaction conditions (20–40 °C, MMA/catalyst (mol/mol) = 400–800) a predominantly syndiotactic (rr = 70%), moderately disperse ($M_w/M_n < 2.0$) polymer of high molecular weight ($M_n > 500,000$) results.

Acknowledgements

This project was supported by special funds for Major State Basic Research Projects (Grant no. G1999064801), National Natural Science Foundation of China (Grants no. 20072004 and 29871010).

References

- [1] G. Erker, R. Aul, Chem. Ber. 124 (1991) 1301.
- [2] H. Yasuda, Prog. Polym. Sci. 25 (2000) 573.
- [3] C. Qian, D. Zhu, D.J. Li, J. Organomet. Chem. 430 (1992) 175.
- [4] Yu.K. Gunko, B.M. Bulychev, G.L. Soloveichik, J. Organomet. Chem. 419 (1991) 299.
- [5] M.F. Lappert, A. Singh, Inorg. Syn. 27 (1990) 168.
- [6] W.A. Herrmann, R. Anwander, F. Munck, W. Scherer, Chem. Ber. 126 (1993) 331.
- [7] J. Okuda, K.E. Du Plooy, P.J. Foscano, J. Organomet. Chem. 495 (1995) 195.
- [8] R.E.v.H. Spence, W.E. Piers, Organometallics 14 (1995) 4617.
- [9] J. Okuda, K.H. Zimmermann, Chem. Ber. 122 (1989) 1645.
- [10] H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, P. Betz, Chem. Ber. 124 (1991) 441.
- [11] K.A. Butakoff, D.A. Lemenovskii, P. Mountford, L.G. Kuz'mina, A.V. Churakov, Polyhedron 15 (1996) 489.
- [12] Y. Qian, G. Li, Y. He, W. Chen, B. Li, S. Chen, J. Mol. Catal. 60 (1990) 19.
- [13] C. Müller, D. Vos, P. Jutzi, J. Organomet. Chem. 600 (2000) 127.
- [14] M.D. Taylor, C.P. Carter, J. Inorg. Nucl. Chem. 24 (1962) 387.
- [15] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
- [16] R.J.H. Clark, J. Lewis, D.J. Machin, R.S. Nyholm, J. Chem. Soc. (1963) 379.
- [17] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
- [18] A. Kucht, H. Kucht, S. Barry, J.C.W. Chien, M.D. Rausch, Organometallics 12 (1993) 3075.
- [19] H. Yasuda, M. Furo, M. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115.
- [20] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, Macromolecules 26 (1993) 7134.
- [21] J. Sun, G. Wang, Z. Shen, Chin. J. Appl. Chem. 10 (1993) 1.
- [22] R.C. Ferguson, D.W. Ovenall, Polym. Prep. 26 (1985) 182.
- [23] F.A. Bovey, G.V.D. Tiers, J. Polym. Sci. 44 (1960) 173.
- [24] F.A. Bovey, J. Polym. Sci. 46 (1960) 59.
- [25] J. Sun, Z. Pan, Y. Zhong, W. Hu, S. Yang, Eur. Polym. J. 36 (2000) 2375.