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# Polymerization of methyl methacrylate with alane complexes of bivalent lanthanidocenes

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## Abstract

Alane complexes of some bivalent ytterbocenes, $L_2YbAlH_3 \cdot NEt_3$ ($L = C_5Me_5$ (**IV**), 1-$SiMe_3$Ind (**V**), 9-$SiMe_3$Flu (**VI**)) were found to provide stereospecific polymerization of methyl methacrylate. The apparent activities of initiators **IV**–**VI** were estimated to be a few times greater than those of their monometallic analogues $L_2Yb \cdot THF$ (**I**–**III**). The polymerization was shown to proceed via the formation of a catalytically active intermediate, $L_2YbAlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2(CO_2Me)]$ which was proposed to exist in various forms. At low temperatures the alane fragment did not disrupt the stereocontrol mechanism originating from the metallocene template. The catalysts **IV**–**VI** produced an atactic pMMA at 0°C. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Bivalent ytterbocenes; Alane complexes; Methyl methacrylate polymerization

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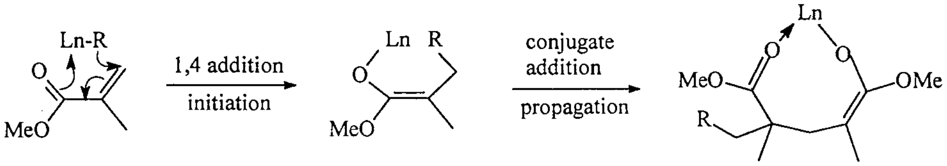
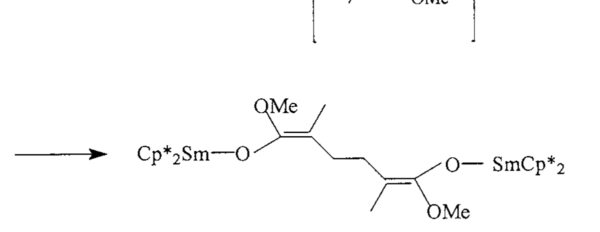
## 1. Introduction

Recently, some achiral trivalent and bivalent lanthanidocenes [1–7] have been shown to catalyze efficiently the highly syndiospecific living polymerization and co-polymerization of methacrylic and acrylic monomers giving high molecular weight polymers with an extremely narrow molecular weight distribution. The microstructures of polymers obtained with monometallic trivalent organolanthanides, $(C_5Me_5)_2LnR$ ($Ln = Sm, Yb, Lu, Y$; $R = H, Me, AlMe_4$) [1,2], were shown to be consistent with chain-end stereochemical control arising from initial 1,4 addition of the M–R functionality to methyl methacrylate (MMA) to generate an enolate which then undergoes rapid Michael conjugate addition sequence:



Examination of the MMA polymerization with monometallic bivalent samarocenes [5,7] has given the basis for a hypothesis that initiation of this process occurs through reductive dimerization of MMA to form a bisinitiator, comprising two lanthanide(III) enolates joined through their double bond termini:



K. Soga and co-workers have reported highly syndiotactic [8] and isotactic [9,10] polymerization of MMA

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Table 1
Polymerization conditions and properties of PMMA obtained with bivalent ytterbocenes[a]

| Run | Catalyst structure | *T*, °C | $M_n^{obs}$ $\times 10^{-3}$ | $M_n^{calc}$ $\times 10^{-3}$ | $M_w/M_n^b$ | rr | mr | mm[c] | IE[d], % | A[e], $\times 10^{-5}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $(C_5Me_5)_2Yb \cdot THF$ | 0 | 205.8 | 100 | 1.20 | 84 | 13 | 3 | 97 | 1.00 |
| 2 | $(C_5Me_5)_2Yb \cdot THF$ | −40 | 220.9 | 100 | 1.51 | 89 | 10 | 1 | 90 | 0.46 |
| 3 | $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ | 0 | 115.5 | 100 | 1.81 | 66 | 23 | 11 | 87 | 11.41 |
| 4 | $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ | −40 | 118.3 | 100 | 1.74 | 93 | 6 | 1 | 84 | 1.22[f] (5.08)[g] |
| 5 | $(C_5Me_5)_2YbAlH_3 \cdot NEt_3^h$ | −40 | 970.4 | 1000 | 1.85 | 92 | 7 | 1 | 97 | |
| 6 | $(SiMe_3Ind)_2Yb \cdot THF$ | −40 | 224.2 | 100 | 1.42 | 17 | 11 | 72 | 89 | 0.42 |
| 7 | $(SiMe_3Ind)_2YbAlH_3 \cdot NEt_3$ | −40 | 137.6 | 100 | 1.72 | 14 | 11 | 75 | 73 | 1.25[f] (2.20)[g] |
| 8 | $(SiMe_3Flu)_2Yb \cdot THF$ | −40 | 244.1 | 100 | 1.62 | 4 | 24 | 72 | 82 | 0.23 |
| 9 | $(SiMe_3Flu)_2YbAlH_3 \cdot NEt_3$ | −40 | 126.9 | 100 | 2.08 | 3 | 18 | 79 | 79 | 0.93[f] (1.39)[g] |
| 10 | A[i] | −40 | 54.3 | 50 | 1.69 | 92 | 7 | 1 | 92 | 5.56 |

[a] [MMA] = 2 ml, solvent–toluene 50 ml, mon/cat = 1000; [b] by GPC related to PS standards; [c] by $^{13}$C-NMR; [d] initiator efficiency ($k \times M_n^{calc}/M_n^{obs}$; $k = 2$ for $L_2Yb \cdot THF$, $k = 1$ for $L_2YbAlH_3 \cdot NEt_3$); [e] catalytic activity ($\%_{conversion} \times (M_{Yb})^{-1} \times min^{-1}$), given as mean value calculated for the points well fitted on the linear sections of the kinetic curves; [f] including a 20 min induction period; [g] substracting a 20 min induction period; [h] mon/cat = 10000; [i] mon/cat = 500.

using achiral and $C_2$-symmetric dialkylzirconocenes, respectively, in combination with stoichiometric amounts of activators such as $CPh_3B(C_6F_5)_4$, in the presence of a large excess of diethylzinc or trialkylaluminium. The non-transition metal compounds have been assumed as activators of MMA not involved in the propagation reaction.

Recently, we have reported [11] the synthesis and characterization of some heterometallic adducts $Cp'_2YbAlH_3 \cdot L$ ($Cp' = C_5Me_5$, *tert*-$Bu_2C_5H_3$; $L = Et_2O$, $C_4H_8O$, $NEt_3$) and have shown them to catalyze atactic polymerization of styrene. The mechanism of this polymerization was shown to be associated with the bimetallic structure of the catalysts. These results raise the intriguing question of whether acrylate polymerization might also arise via bimetallic mechanism.

We communicate here the results of MMA polymerizations with mono- and heterometallic bivalent ytterbocenes as well as the preparation of two novel organolanthanides.

## 2. Results and discussion

The well known $(C_5Me_5)_2Yb$ THF (**I**) [12] was chosen for this study. We also prepared two novel bivalent organolanthanides—bis(1-trimethylsilylindenyl)ytterbium, $(SiMe_3Ind)_2Yb \cdot THF$ (**II**), and bis(9-trimethylsilylfluorenyl)ytterbium, $(SiMe_3Flu)_2Yb \cdot THF$ (**III**). The complexes **I**–**III** were thoroughly purified by repeated recrystallization. The bimetallic adducts of the complexes **I**–**III** with alanes were synthesized in accord with the procedure described previously [11]. Thus, we studied catalytic activities of three bimetallic adducts, $L_2YbAlH_3 \cdot NEt_3$ ($L = C_5Me_5$ (**IV**), 1-$SiMe_3$Ind (**V**), and 9-$SiMe_3$Flu (**VI**)), in MMA polymerization comparing them with those of the monometallic analogues, $L_2Yb \cdot THF$ (**I**–**III**). The polymerizations were performed in toluene. The reaction conditions, polymer properties and catalyst activities are summarized in Table 1. Fig. 1 shows the MMA conversion versus reaction time plots for the polymerizations initiated with the catalysts containing $C_5Me_5$ ligands.

The polymerizations generally were rapid giving syndiotactic (runs 1–5) or isotactic rich (runs 6–9) poly(methylmethacrylates) with high molecular weights and unimodal GPC traces. One can note some differences between the results obtained for monometallic (runs 1, 2, 6, 8) and heterometallic catalysts (runs 3–5, 7, 9). The apparent activities of initiators **IV**–**VI** are greater than those of their monometallic analogues **I**–**III**. Furthermore, a 20 min induction period was observed for all polymerizations performed with catalysts **IV**–**VI** at low temperatures (Fig. 1, Table 1 runs 4, 5, 7, 9). At 0°C, however, the induction period was less than 1 min.

The resultant PMMAs prepared from catalysts **I**–**III** have molecular weights ($M_n^{obs}$) twice that predicted from the monomer to initiator ratio ($M_n^{calc}$). The molecular weights of the polymers prepared from the bimetallic initiators are close to that predicted from the monomer to initiator ratio. At low temperatures the complexes $L_2YbAlH_3 \cdot NEt_3$ produced more stereoregular polymers than that of the catalyst $L_2Yb \cdot THF$ (run pairs 2–4, 6–7, 8–9). However, no stereoselectivity was observed with the initiator $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ at 0°C (run 3) [13]. Since the polymerization with monometallic bivalent organolanthanides has been shown to proceed in a living fashion [2,5], the fact that the values of $M_w$ (weight average molecular weight)/$M_n$ (number average molecular weight) obtained here are far from 1.0 may be explained by partial chain termination caused by deactivation of the catalyst with a trace amount of impurities included in the system. Nevertheless, the values of $M_w/M_n$ of the polymers prepared with bimetallic catalysts are always somewhat larger

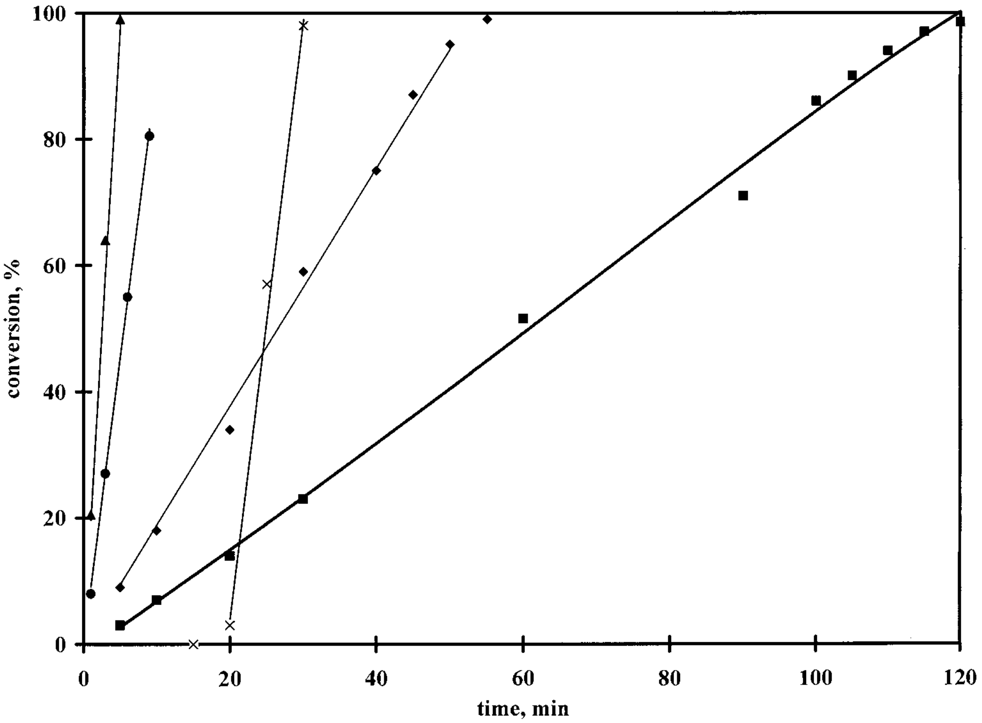

Fig. 1. MMA conversion versus reaction time for the polymerizations initiated with the catalysts containing $C_5Me_5$ ligands: ■-$(C_5Me_5)_2YbTHF$, −40°C; ◆-$(C_5Me_5)_2YbTHF$, 0°C; × -$(C_5Me_5)_2YbAlH_3 \cdot NEt_3$, −40°C; ▲-$(C_5Me_5)_2YbAlH_3 \cdot NEt_3$, 0°C; ●-$(C_5Me_5)_2YbAlH_3 \cdot OEt_2$, −40°C.

than those for the polymerizations initiated with catalysts containing no aluminium. All the results described above imply that MMA polymerizations initiated with mono- and heterometallic complexes proceed in different fashions.

To elucidate this point, we determined the oxidation state of Yb included in the propagation species. The MMA addition to solutions of monometallic complexes **I**–**III** caused an immediate change of color from the original (**I** purple, **II** brick-red, **III** green–yellow) to pale orange which usually corresponds to trivalent ytterbocenes with Yb–O bonds. The EPR spectrum of a mixture of MMA and $(C_5Me_5)_2Yb \cdot THF$ (10:1, $10^{-2}$ M solution in toluene) prepared at 0°C and recorded at −196°C contains a broad singlet ($g = 6.7$) corresponding to an unshared electron of Yb(**III**). The $^1$H-NMR spectrum of this system displays a number of broad unresolvable resonances that are common for compounds containing the paramagnetic Yb(**III**) atom. The unimodality of GPC curves along with narrow molecular weight distribution and high initiator efficiency (Table 1) are indicative of almost complete conversion of metallocene molecules to the propagation species and their uniformity in this system. These observations along with the results of molecular weight studies of the polymers obtained with monometallic initiators (runs 1, 2, 6, 8) support the recent hypothesis [5,7] that the initiation with bivalent lanthanidocenes occurs through reductive dimerization of MMA to form a bisinitiator containing trivalent lanthanidocene moiety.

In contrast, the EPR spectrum of a mixture of MMA and $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ (10:1, $10^{-2}$ M solution in toluene) prepared at 0°C and recorded at −196°C contains no resonances. This system exhibits a clean $^1$H-NMR spectra (see below). This fact may be unequivocally attributed to no change in the oxidation state of ytterbium(+2) during the polymerization. Again, the unimodality of GPC curves along with narrow molecular weight distribution and high initiator efficiency are indicative of almost complete conversion of metallocene molecules to the propagation species and their uniformity in these systems.

To provide a closer insight to the catalytic behavior of the heterometallic initiators studied here, we performed a reaction of the complex $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ with two equivalents of MMA in toluene at 0°C. The solution was held for 1 h at 0°C and then cooled to −95°C resulting in precipitation of a purple X-ray amorphous solid (A) whose elemental analysis corresponded to the composition $(C_5Me_5)_2YbAlH_3[(MMA)_2]$. Among the complete slow hydrolysis products of A analyzed by GC/MS only a mixture of $C_5Me_5H$ and $MeCO_2CH(Me)CH_2CMe_2CO_2Me$ was found in ratio ca. 2:1. Complex A dissociated in pentane to afford a purple solution of $(C_5Me_5)_2Yb$ and a pyrophoric white sediment (B) characterized as $AlH_2[MMA]_2$ by slow alcoholysis (ratio H/Al is ca. 2:1) and elemental analysis. Complete hydrolysis of B gave

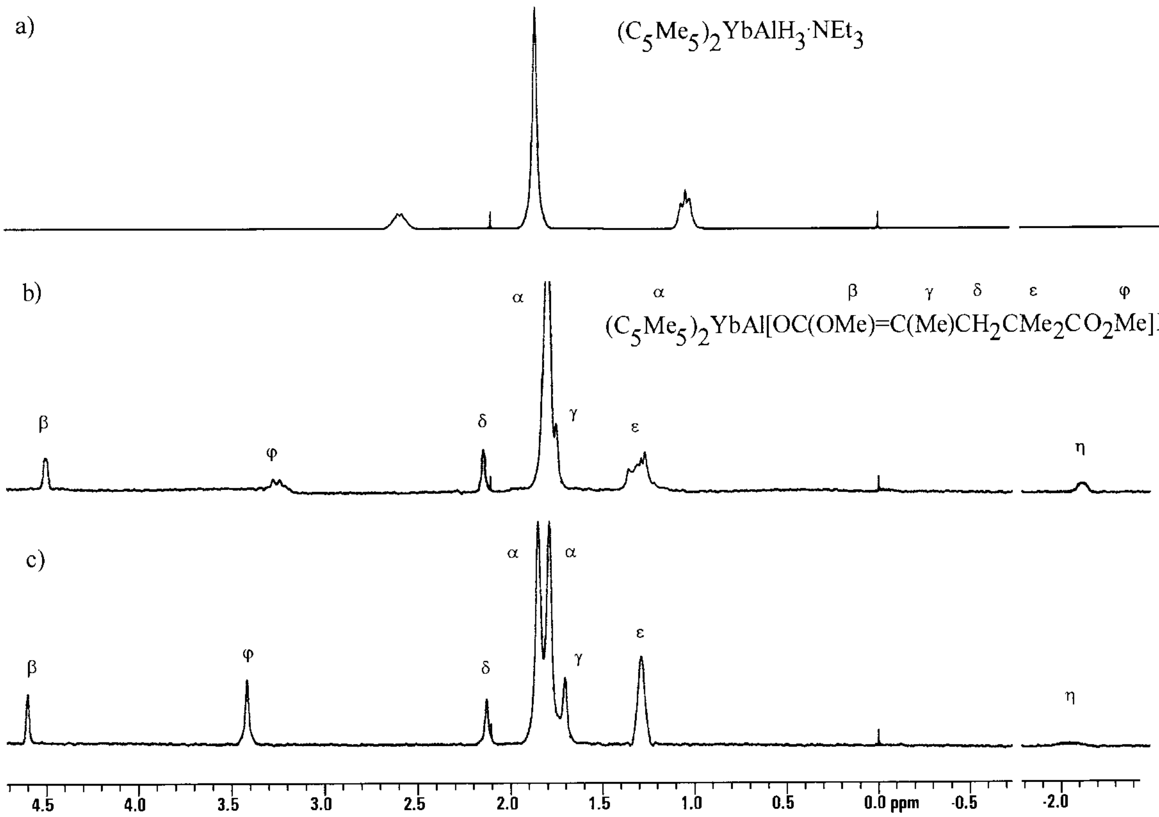

Fig. 2. $^1$H-NMR spectra of $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$, toluene 25°C (**a**), $(C_5Me_5)_2YbAlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$, toluene 0°C (**b**), $(C_5Me_5)_2YbAlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$, toluene $-55$°C (**c**).

$MeCO_2CH(Me)CH_2CMe_2CO_2Me$ analyzed by $^1$H-NMR and GC/MS. These results indicate the formation of a $(C_5Me_5)_2Yb$ adduct with $AlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ which could arise from the 1,4 addition of methyl methacrylate to an Al–H bond followed by Michael conjugate addition of the second monomer molecule. Although the dissociation of A to the very electrophilic unsaturated ytterbocene seems to be strange, this fact is not unprecedented. Lanthanidocenes solvated with THF or other ligands containing O or N are known to lose the Lewis base molecule in aliphatic solvents. The latter also favor the dissociation of lanthanidocene alane complexes to metallocene and alane components [14]. The dissociation of the bimetallic adduct A may also be prompted by the insolubility of the aluminium fragment in pentane.

Fig. 2 shows the $^1$H-NMR spectra of A recorded in toluene-$d_8$ at $-55$ (**c**) and 0°C (**b**) [15] compared with the spectrum of $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ (**a**, toluene 25°C). At $-55$°C, the resonances of the $[-OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ moiety appear as singlets indicative of no equilibrium in the system at this temperature. A slight broadness of all the signals may be related to the higher sample viscosity at low temperatures. The $C_5Me_5$ ligands display, however, two resonances of equal intensity. This phenomenon may be tentatively attributed to the fact that two $C_5Me_5$ ligands in the 'frozen' structure of A have different spatial environments. At 0°C the resonances of both the $\varphi$ and $\varepsilon$ methyl groups are multiplets but the $C_5Me_5$ ligands display one broad intense singlet. Such behavior seems to be associated with the co-existence of various species in the system at elevated temperatures. The resonance of hydride atoms in complex **IV** could not be observed even at 80°C owing to the quadrupole moment of aluminum atom. In the spectra of A, however, the hydride resonance (broad signal centered at $\delta$ $-2.11$) can be observed even at 0°C (Fig. 2, **b**). At low temperatures the broadness of this signal increases as expected (Fig. 2, **c**).

Collecting all the results described above, we can tentatively ascribe to complex A a number of possible structures (Fig. 3) in which $(C_5Me_5)_2Yb$ may be bonded with $AlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ through O or/and H bridges. A simulation of these structures in terms of the semiempirical method [16] predicts the form '**a**' to be more stable while forms '**b**', '**c**' and '**d**' have almost an equal probability of existing. Indeed, the structure '**a**' is in good agreement with the NMR spectrum recorded at $-55$°C. Taking into account that the carbonyl and

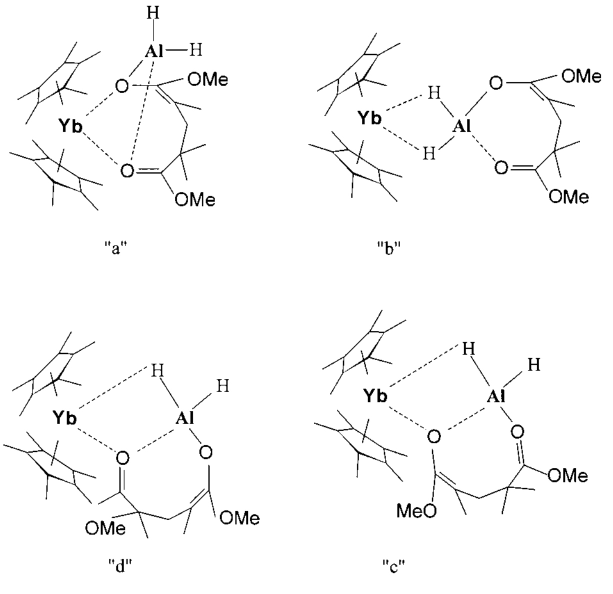

Fig. 3. Proposed structures of $(C_5Me_5)_2YbAlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ (A).

enolate ligands occupy frontal positions in the bisectral plane of a metallocene sandwich [17], one of the $C_5Me_5$ ligands should be closer to the $AlH_2$ moiety than the other one. The simulation mentioned above reveals that the distance between an Me group of the cyclopentadienyl ligand and a hydride atom may be as short as 1.8 Å (2.4–2.5 Å for '**b**', '**c**' and '**d**'), that implies the possibility of electronic effects induced by $AlH_2$ through space. Taking into account the intramolecular rotation of $C_5Me_5$ ligands around their bond axis to the metal, the downfield shift of the resonance of one ligand becomes understandable. The multitude of species observed in the spectrum recorded at 0°C may be associated with the co-existence of some or all the forms '**a**'–'**d**'. These species may result from the intramolecular rotation of the aluminum component at increased temperatures or from Equilibrium 1.

$$A' \leftrightarrow (C_5Me_5)_2Yb + B \leftrightarrow A'' \qquad (1)$$

where A′ and A″ are the species '**a**'–'**d**'.

The same behavior of the partially hydrolyzed alane fragment was observed for the complex $Cp_2Ti(\mu_2\text{-}H)_2AlH(OCH_2CH_2NMe_2)$ [18]. This supposition is also supported by the fact that $(\mathit{tert}\text{-}Bu_2C_5H_3)_2Yb\cdot(THF)_2$ in toluene solution exists as a bisolvate only at low temperatures and reversibly loses one THF molecule at room temperature [19], i.e. at low temperature a bivalent lanthanidocene may coordinate two oxygen ligands while monocoordination is preferred with increasing temperature.

The results of MMA polymerizations support the supposition about the predominance of the form '**a**' at low temperatures and the co-existence of the forms '**a**'–'**d**' at elevated temperatures. Indeed, a high stereocontrol (Table 1, runs 4, 5, 7, 9) may only be expected for structure '**a**' in which the chain growth occurs in the coordination sphere of the lanthanide atom. As one can see from the similarity of $^{13}C$-NMR spectra profiles in the CO region for the polymers obtained at −40°C with mono- and heterometallic initiators containing the same ligands (Table 2), the alane fragment does not disrupt the stereoregulatory operation originating from the metallocene architecture [13]. Dramatic loss of stereospecifity at 0°C (run 3) can be rationalized taking into account the possibility of propagation on the structures '**b**'–'**d**' in which the fragment $[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ comes out from the coordination sphere of the lanthanide atom. Thus, conjugation sequences occur out of the Yb coordination sphere giving atactic segments in the resultant polymer. Wider molecular weight distribution observed for the polymers prepared with heterometallic initiators also supports a combined operation of various catalytically active species.

The isolated complex A was tested as an initiator of MMA polymerization at −40°C (run 10). No induction period was observed in this case. A comparison of

Table 2
Pentad structure of PMMA[a]

| Run | Pentad fraction[b], (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mrrm | rrrm | rrrr | mmrm | mrmr | mmrr | rmrr | mmmm | mmmr | rmmr |
| 1 | 0 | 21.4 | 67.0 | 0 | 0 | 8.7 | 8.7 | 0 | 2.9 | 2.9 |
| 2 | 0 | 19.8 | 73.3 | 0 | 0 | 6.4 | 6.4 | 0 | 0.5 | 0.5 |
| 3 | 2.3 | 21.5 | 46.2 | 5.0 | 5.0 | 14.9 | 14.9 | 3.5 | 6.6 | 6.6 |
| 4 | 0 | 12.6 | 83.7 | 0 | 0 | 2.1 | 2.1 | 0 | 1.6 | 1.6 |
| 6 | 2.7 | 5.4 | 8.5 | 0 | 0 | 6.6 | 5.3 | 66.0 | 5.5 | 0 |
| 7 | 2.4 | 5.0 | 6.1 | 0 | 1.0 | 6.7 | 4.9 | 68.8 | 5.1 | 0 |
| 8 | 2.1 | 2.0 | 1.0 | 14.8 | 14.8 | 2.7 | 2.7 | 61.4 | 16.0 | 0 |
| 9 | 1.8 | 1.7 | 1.0 | 13.6 | 13.6 | 2.5 | 2.5 | 70.3 | 9.1 | 0 |

[a] Polymerization conditions: refer to Table 1.

[b] Observed in $^{13}C$-NMR spectra of carbonyl resonances.

complex A activity with that of complex **IV** (runs 4, 5) suggests that the 20 min induction period observed in the polymerizations performed with the catalysts **IV**–**VI** at low temperature (runs 4, 5, 7, 9) may be associated with the incipient competing recoordination of aluminium by MMA and the loss of a triethylamine. When polymerization was initiated with $(C_5Me_5)_2YbAlH_3 \cdot OEt_2$ prepared in situ [11], no induction period was observed even at low temperatures (Fig. 1). This correlates with the decreasing donor power of Lewis bases from $NEt_3$ ($DN = 30.7$) to $Et_2O$ ($DN = 19.2$) [20]. Induction has been previously observed for styrene polymerizations initiated with alane complexes of bivalent ytterbocenes [11] and has been shown to be associated with incipient recoordination of aluminium by styrene.

We also tested the monometallic enolate B as an initiator. Only poor oligomerization activity ($M_n \leq 10000$) and no stereoselectivity were observed in the temperature range −40– +25°C. Hence, the catalytic activity and stereocontrol of alane complexes of bivalent ytterbocenes in the polymerization of MMA are provided by the formation and unique function of a bimetallic adduct comprising the chelate $AlH_2[OC(OMe)=C(Me)CH_2C(Me)_2CO_2Me]$ coordinated to the metal sandwich.

## 3. Conclusions

Alane complexes of bivalent organolanthanides can efficiently catalyze stereoregular polymerization of MMA at low temperatures producing high molecular weight polymers. The polymerization proceeds via the formation of an incipient adduct of metallocene with $AlH_2[OC(OMe)=C(Me)CH_2C(Me)_2CO_2Me]$. At low temperatures the stereochemistry is controlled by the metallocene architecture. The mechanism of stereoregulation is disrupted at higher temperatures.

## 4. Experimental section

### *4.1. General considerations*

All operations were performed under argon by using standard Schlenk techniques. MMA was washed twice with 5% aqueous solution of KOH, five times with water, then was dried over $Na_2SO_4$, $CaH_2$ for 4 days and activated molecular sieves 3A for a week and finally was distilled with $AlEt_3$ before use. Toluene, benzene, pentane and hexane were all washed with $H_2SO_4$, five times with water, were then dried over $CaCl_2$ and further refluxed over $LiAlH_4$ for 3 h. Benzene and alkanes were distilled before use. Toluene was distilled from $LiAlH_4$, the distillate was refluxed over the Na/K alloy for 3 h, and afterwards distilled before use. THF was refluxed over KOH for 2 h, the distillate was refluxed with sodium benzophenone ketyl until the solution becomes violet, the distillate was refluxed over the Na/K alloy and was distilled before use. Diethyl ether and $NEt_3$ were distilled over $LiAlH_4$ before use. Deuterated solvents were distilled over LiD before use. $AlCl_3$ was twice sublimed in a sealed tube. Alanes were prepared by the Schlesinger reaction [21] and were used as solutions in benzene ($AlH_3 \cdot NEt_3$) or in ether ($AlH_3 \cdot Et_2O$). NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz). Gel permeation chromatographic analyses were run on a Hewlett Packard 1050 using $10^5$A, $10^4$A and 10A Styragel columns in THF. The molecular weights of polymers were determined using polystyrene standards. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400. The samples for elemental analysis were sealed in a tin foil in a glove box. Analysis for ytterbium was done using standard techniques [22]. Analysis for aluminium was done using an Atomic Absorption Spectrometer Varian SpectrAA-250plus. X-band EPR spectra were recorded at 77 K with a Varian E-3 radiospectrometer of 3 cm range with a B4-modulation frequency of 100 KHz and Mn(+2) as a reference. GC/MS analyses were run on a Hewlett Packard 5890 chromatograph (capillary columns Ultra 2 (0.2 mm × 25 m), the initial temperature—50°C for 3 min, rate of heating—20°C $min^{-1}$, final temperature—320°C, injector temperature—300°C, carrier-helium, flow—5 psi, total flow—50 ml $min^{-1}$) and a Hewlett Packard 5971 Mass spectrometer as detector (scan, 2–600 a.m.u., initial time 90 s).

### *4.2. Synthesis of $(1\text{-}SiMe_3Ind)_2Yb \cdot THF$ (**II**) (mixture of syn- and anti-forms)*

To a THF solution (100 ml) of 1-trimethylsilylindene (6.5 mmol, obtained from indenyl lithium and $SiMe_3Cl$ in diethyl ether) NaH powder (13 mmol) was added. The mixture was stirred overnight and then was slowly added to a grey–green solution of $YbI_2$ (3.1 mmol; obtained from Yb powder (3.4 mmol) and $I_2$ (6.2 mmol)) in THF (200 ml) with vigorous magnetic stirring. The mixture became red–brown immediately. The solution was stirred overnight. The THF was removed under vacuum, the residue was extracted with benzene (200 ml) and the extract was filtered. Evaporation of the solvent gave a brown–gold foamed mass. It was crystallized from hexanes at −30°C affording a brick-red solid which was dried in vacuum at 50°C for 5 h yielding 1.81 g (94%) of **II**. Two repeated crystallizations from hexane–THF (20:1) at −30°C followed by drying in vacuum at 50°C for 5 h afforded 1.55 g (80.5%) of red-brick polycrystals. Found, %: C, 54.43; H, 6.25; Yb, 28.0; calc. for $C_{28}H_{38}Si_2OYb$, %: C, 54.25; H, 6.18; Yb, 27.9.

$^1$H-NMR ($C_6D_6$, 70°C, $\delta$ ppm): 7.71 br.d. (1H, $J_{H-H} = 2.5$ Hz), 7.52 br.d. (1H, $J_{H-H} = 2.5$ Hz), 6.95 m. (2H) ABCD system; 6.33 br.s. (2H) Cp; 3.20 br.s. (4H), 1.46 br.s. (4H) THF; 0.63 s. (9H) $SiMe_3$.

### 4.3. *Synthesis of (9-SiMe$_3$Flu)$_2$Yb · THF (**III**)*

To a THF solution (100 ml) of 9-trimethylsilylfluorene (6.5 mmol, obtained from fluorenyl lithium and $SiMe_3Cl$ in diethyl ether) NaH powder (13 mmol) was added. The mixture was held with vigorous stirring overnight and then slowly added to the grey–green solution of $YbI_2$ (3.1 mmol; obtained from Yb powder (3.4 mmol) and $I_2$ (6.2 mmol)) in THF (200 ml) with vigorous magnetic stirring. After 2 h the mixture became green. The solution was stirred overnight and the THF was removed under vacuum. The residue was extracted with benzene (200 ml) and solids were removed by filtration. Evaporation of the filtrate gave a green solid. It was crystallized from toluene–THF (20:1) at − 30°C to give 2.04 g (91%) of green–yellow crystals of **II** which were dried in vacuum at 40°C for 2 h. Two repeated crystallizations from toluene–THF (20:1) at − 30°C followed by drying in vacuum at 50°C for 5 h afforded 2.01 g (89.7%) of green–yellow polycrystalline needles. Found, %: C, 60.17; H, 6.03; Yb, 24.0; calc. for $C_{36}H_{42}Si_2OYb$, %: C, 60.06; H, 5.88; Yb-24.0.

$^1$H-NMR ($C_6D_6$, 70°C, $\delta$ ppm): 7.89 d. (1H, $J_{H-H} = 2.5$ Hz), 7.77 d. (1H, $J_{H-H} = 2.5$ Hz), 7.08 tr. (1H, $J_{H-H} = 2.5$ Hz), 6.82 tr. (1H, $J_{H-H} = 2.5$ Hz) ABCD system; 2.68 m. (4H), 1.07m. (4H) THF; 0.63 s. (9H) $SiMe_3$.

Alane complexes of ytterbocenes were prepared as described [11] and were used as solution in toluene.

### 4.4. *Polymerization of MMA initiated by ytterbocenes complexes*

A typical example is given below. The toluene solution of one of the initiators was added at once to a toluene solution of MMA (2 ml) with vigorous magnetic stirring at the requisite temperature (the total volume of toluene was 50 ml). In measured time intervals, aliquots (5 ml) were withdrawn by disposable syringe and quenched with acidified methanol. The resulting polymers were twice precipitated from $CH_2Cl_2$ into methanol and dried at 65°C in vacuum. Polymer microstructure was characterized by $^{13}$C-NMR using standard analyses [23].

### 4.5. *Isolation of (C$_5$Me$_5$)$_2$YbAlH$_2$[OC(OMe)=C(Me)CH$_2$C(Me)$_2$CO$_2$Me] (A)*

A toluene solution (50 ml) of MMA (0.400 g, 4 mmol) was slowly added to a toluene solution (25 ml) of $(C_5Me_5)_2YbAlH_3 \cdot NEt_3$ (1.15 g, 2 mmol) at 0°C with vigorous magnetic stirring. The solution was stirred for 1 h and then cooled to − 95°C resulting in precipitation of a highly air sensitive purple amorphous solid. The solution was removed from the solid with a filter-transfer needle to another Schlenk flask. Then, without disconnecting the set, the same toluene was condensed through the needle to the flask containing the solid at − 196°C. The mixture was heated to 0°C for a short period of time and cooled to − 95°C. The solution was removed again from the solid with a filter-transfer needle. Resulting solid was dried in vacuum at 15°C for 20 h, yield 0.961 g (71%). Decomposition temperature was 83°C.

Found, %: C, 53.37; H, 7.30; Yb, 25.8; Al, 4.2; calc. for $C_{30}H_{49}O_4YbAl$, %: C, 53.48; H, 7.33; Yb, 25.7; Al, 4.0.

A total of 150 ml of wet degassed diethyl ether were slowly added with vigorous stirring to a solution of A (0.324 g) in diethyl ether (20 ml). The mixture was stirred overnight and filtered. The solution was dried with $Na_2SO_4$ and ether was removed under reduced pressure. In accordance with GC/MS the resulting oil was found to consist of $C_5Me_5H$ and $MeCO_2CH(Me)CH_2CMe_2CO_2Me$ in mol ratio 2:1. The response times were quantified by adding measured amounts of $MeCO_2CH(Me)CH_2CMe_2CO_2Me$ (obtained from the hydrolysis of B) and $C_5Me_5H$ to the analyzed mixture.

$C_5Me_5H$ (5.60 min), $m/z^+$: 136 ($M^+$), 135 (100%, $M^+$–H), 119, 107, 105, 91; $MeCO_2CH(Me)CH_2CMe_2CO_2Me$ (7.62 min), $m/z^+$: 171 ($M^+$–OMe), 146, 143 (171-CO), 126, 115 ($MeOOCC(Me)_2CH_2$), 111 (171-HCOOMe), 102, (143-$CMe_2$), 87 (MeOOCCHMe), 83 (100%, 111-$C_2H_4$), 69, 59 (COOMe), 55, 41.

### 4.6. *Isolation of AlH$_2$[OC(OMe)=C(Me)CH$_2$C(Me)$_2$CO$_2$Me] (B)*

Complex A (0.53 g, 0.787 mmol) was dissolved in pentane (50 ml). Stirring the solution for 1 h afforded a purple solution (see below) and a highly air sensitive white sediment. The mixture was filtered and the precipitate was twice washed with 20 ml of pentane and dried in vacuum for 2 h. Yield: 0.16 g (88%). Decomposition temperature was 101°C.

Found, %: C, 52.20; H, 9.22; Al, 11.7; calc. for $C_{10}H_{19}AlO_4$, %: C, 52.17; H, 9.19; Al, 11.7.

A 0.1% solution of ethanol in toluene was slowly added with vigorous stirring to a suspension of B (0.16 g, 0.696 mmol) in toluene at 22°C. A total of 14.7 ml of hydrogen was released. H/Al ratio is 1.89:1.

A total of 80 ml of a degassed mixture THF–$H_2O$ (10:1) was slowly added with vigorous stirring to a solution of B (0.15 g, 0.652 mmol) in THF (50 ml). The mixture was stirred overnight, afterwards the solvent was removed under reduced pressure. The residue was dissolved in 50 ml of ether and filtered. The solids were twice washed with ether (40 ml), the combined solution was dried with $Na_2SO_4$ and ether was removed under reduced pressure affording 0.11 g of $MeCO_2CH(Me)CH_2CMe_2CO_2Me$ (83%).

GC/MS (7.64 min) $m/z^+$: 171, 146, 143, 126, 115, 111, 102, 87, 83, 69, 59, 55, 41.

$^1$H-NMR ($CDCl_3$, 20°C, $\delta$ ppm,): 3.64 s. (3H), 3.63 s. (3H), 2.37 m. (1H), 1.65 d, 1.91 d. ($J_{H-H} = 7.3$ Hz, 2H), 1.17 s. (3H), 1.13 d. ($J_{H-H} = 7.5$ Hz, 3H), 1.11 s. (3H).

### 4.7. $(C_5Me_5)_2Yb$

Cooling the purple pentane solution (obtained in the previous part) at −78°C afforded a purple amorphous solid which was filtered, washed twice with 10 ml of cold pentane (−78°C) and dried in vacuum for 2 h. Yield: 0.18 g (51%), $T_m = 93$°C.

Found, %: C, 54.78; H, 7.11; Yb, 38.8; Al, <0.01; calc. for $C_{20}H_{30}Yb$, %: C, 54.16; H, 6.82; Yb, 39.0. $^1$H-NMR ($C_6D_6$, 20°C, $\delta$ ppm,): 1.92 br.s.

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## References

[1] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908.

[2] H. Yasuda, H. Yamamoto, M. Yamashita, et al., Macromolecules 26 (1993) 7134.

[3] E. Ihara, M. Morimoto, H. Yasuda, Macromolecules 28 (1995) 7886.

[4] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115.

[5] B.M. Novak, L.S. Boffa, Papers presented at the ACS Meeting, San Francisco Ca., 38, no.1, 1997, p. 442.

[6] H. Yasuda, E. Ihara, M. Morimoto, T. Kakeji, Papers presented at the ACS Meeting, San Francisco Ca., 38, no.1, 1997, p.444.

[7] L.S. Boffa, B.M. Novak, Macromolecules 27 (1994) 6993.

[8] H. Deng, T. Shiono, K. Soga, Macromol. Chem. Phys. 196 (1995) 1971.

[9] H. Deng, T. Shiono, K. Soga, Macromolecules 28 (1995) 3067.

[10] H. Deng, K. Soga, Macromolecules 29 (1996) 1847.

[11] S. Ya Knjazhanski, E.S. Kalyuzhnaya, L.E. Elizalde Herrera, B.M. Bulychev, A.V. Khvostov, A.I. Sizov, J. Organomet. Chem. 531 (1997) 19.

[12] T.D. Tilley, R.A. Andersen, B. Spenser, H. Ruben, A. Zalkin, D.H. Tempeleton, Inorg. Chem. 19 (1980) 2999.

[13] The stereoregulatory operation of complexes **II**, **III**, **V** and **VI** at 0°C will be described in a separate paper.

[14] (a) S.Ya. Knjazhanski, E.B. Lobkovski, B.M. Bulychev, V.K. Belsky, G.L. Soloveichik, J. Organomet. Chem. 419 (1991) 311. (b) G.L. Soloveichik, B.M. Bulychev, S.Ya. Knjazhanski, V.K. Belsky, Metalloorg. Chim. 5 N 1 (1992) 135 (Russ).

[15] Complete D-NMR study of this system will be reported soon.

[16] (a) Spartan, version 5.03, Wave Function Inc. (1998) Wave Function Ed. (b) W.J. Hehre, L.D. Burke, A.J. Shusterman, W.J. Pietro, Experiment in Computation Organic Chemistry (1995) Wave Function Ed. (c) W.J. Hehre, Practical Strategies for Electronic Structure Calculations (1995) Wave Function De. (d) since Spartan does not handle most of lanthanides the simulations were performed for $(C_5Me_5)_2Gd^{II}AlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$, $\{(C_5Me_5)_2Gd^{III}AlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]\}^+$ (both with PM3(tm) method), and $(C_5Me_5)_2CaAlH_2[OC(OMe){=}C(Me)CH_2C(Me)_2CO_2Me]$ (PM3 method), in none-solvent mode, indicating the greater stability of the form '**a**' in every case.

[17] (a) J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729. (b) J.V. Ortiz, R. Hoffmann, Inorg. Chem. 24 (1985) 2095.

[18] Unpublished data from our laboratory.

[19] S.Ya. Knjazhanski, B.M. Bulychev, A.V. Khvostov, A.I. Sizov, Izv. Ross. Akad. Nauk 7 (1996) 1833.

[20] R.W. Taft, R.J. Pienta, M.J. Kalmet, E.M. Arnett, J. Org. Chem. 46 (1981) 661.

[21] A.E. Finholt, A.C. Bond, H.I. Schlesinger, J. Am. Chem. Soc. 74 (1951) 4585.

[22] E.V. Voloshina, Metody analiza materialov dlya elektronnoi tekhniki, M., NIITEKhIM (1983) 77.

[23] (a) R. Chujo, K. Hatada, R. Kitamura, T. Kitayama, H. Sato, Y. Tanaka, Polym. J. 19 (1987) 413. (b) R. Subramanian, R.D. Allen, J.R. McGrath, T.C. Ward, Polym. Prep. Am. Chem. Soc. Div. Polym. Chem. 26 (1985) 238. (c) G. Moad, D.H. Solomon, T.H. Spurling, S.R. Johns, R.I. Willing, Aust. J. Chem. 39 (1986) 43.