

# Polymerization of Polar Monomers Using Cyclopentadienyl Complexes of the Alkaline Earth Metals

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**Summary:** Tetramethylcyclopentadienyl complexes of magnesium, calcium and strontium are efficient catalysts at  $-78^{\circ}\text{C}$  for the solution polymerization of polar monomers such as alkyl methacrylates in the presence of only small amounts of triethylaluminium as cocatalyst. The molecular mass of the resulting polymers is predictable on the monomer/catalyst ratio. The polymerization reaction follows a first order kinetics with respect to the initial catalyst concentration. Block-copolymers are easily available by sequential dosage of the monomer. A living polymerization mechanism is proposed involving activation of the catalyst by alkylation and subsequent insertion of coordinated monomers.

**Keywords:** alkaline earth metal complexes; living polymerization; MMA

## Introduction

Organolanthanide complexes are known as outstanding catalysts for the polymerization of polar monomers such as acrylates, lactones, lactides, isocyanates, and oxiranes.<sup>[1]</sup> Yasuda et al. reported in 1993 for the first time on organolanthanide induced polymerizations of methyl methacrylate (MMA). The resulting polymers are obtained at  $0^{\circ}\text{C}$  after very short reaction time showing a narrow molecular mass distribution.<sup>[2]</sup> Mainly organolanthanide(III) derivatives,<sup>[3]</sup> but also organosamarium(II) complexes,<sup>[4]</sup> have been used successfully. Later on we demonstrated that methacrylates with even highly functionalized side chains could be polymerized in high yields using samarocene derivatives resulting in liquid crystalline homopolymers and block copolymers with low polydispersities.<sup>[5]</sup> Due to the comparability of the electronic situation and the molecular structure of alkaline earth metal complexes and those of divalent lanthanides, we investigated

the catalytical activity of alkaline earth cyclopentadienyl complexes.

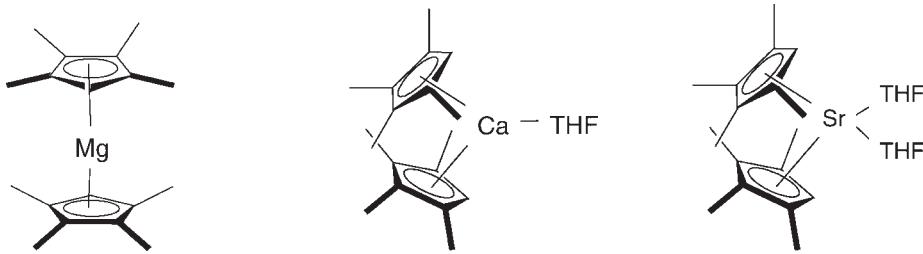
In 1974, Lindsell et al.<sup>[6]</sup> already used bis(cyclopentadienyl) complexes of calcium to polymerize MMA, but they received only yields of about 8% polymeric products. Brittain et al.<sup>[7]</sup> also reported on unsatisfying conversions and broad molecular mass distributions of polymers, using bis (pentamethylcyclopentadienyl) calcium as a catalyst and therefore classified this compound to be very unattractive for this purpose.

Nevertheless, we performed polymerization catalysis with complexes bearing tetramethylcyclopentadienyl ligands ( $(\text{C}_5\text{HMe}_4)_2\text{M}$ , see Scheme 1) which are soluble in common aromatic and polar solvents. Since any remaining decomposition product of the Mg or Ca species would not cause any toxic danger, these catalysts are very promising even for the synthesis of PMMA for medical applications. Furthermore they are easy to prepare<sup>[8]</sup> although their air sensitivity.

## Results and Discussion

The alkaline earth metal complexes  $(\text{C}_5\text{HMe}_4)_2\text{Mg}$ ,  $(\text{C}_5\text{HMe}_4)_2\text{Ca}(\text{THF})$ , and

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**Scheme 1.**

Structure of  $(C_5HMe_4)_2Mg$ ,  $(C_5HMe_4)_2Ca(THF)$ , and  $(C_5HMe_4)_2Sr(THF)_2$ , used as catalysts.

$(C_5HMe_4)_2Sr(THF)_2$  show in the presence of triethylaluminum (TEA) in toluene nearly no catalytic activity for the polymerization of MMA at room temperature. The Mg complex does not produce any polymer, whereas the Ca and the Sr compounds generate 30 and 36% PMMA after a polymerization time of 72 and 50 h, respectively.

In contrast, at low temperatures the solution polymerization of MMA in toluene catalyzed by each of the three examined alkaline earth metal complexes results in narrow distributed PMMA in the presence of TEA and at least the double amount of catalyst. The yields depend strongly on the polymerization temperature. At  $-78^\circ C$ , MMA can be nearly completely converted into the polymer using the calcium as well as the strontium complex. The measured number average molecular mass  $M_n$  corresponds to the estimated molecular mass calculated as the product of the molecular mass of the repeat unit, the initial ratio of monomer and catalyst concentration  $[M]_0/[cat]_0$ , the yield, and a factor corresponding to the catalyst recovery as shown in Figure 1 for the polymers obtained using  $(C_5HMe_4)_2Sr(THF)_2$  as a catalyst.

The catalyst  $(C_5HMe_4)_2Mg$  produces PMMA at temperatures down to  $-78^\circ C$  only in yields up to 50%. The yield increases with decreasing monomer concentration. Using  $(C_5HMe_4)_2Ca(THF)$  as a catalyst at temperatures above  $-50^\circ C$ , the polymerization stops before complete conversion is achieved accompanied by broader distributions ( $M_w/M_n$  up to 2). In both cases deactivation processes of the

catalyst via partial decomposition of the magnesium as well as the calcium complex should be responsible for this decreasing activity.

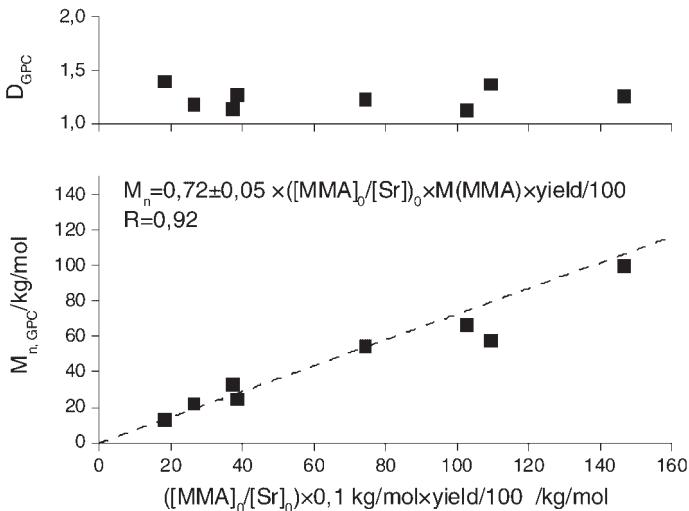
$^1H$  NMR spectroscopic investigations showed the formation of mainly syndiotactic polymers. In both cases of  $(C_5HMe_4)_2Ca(THF)$  and  $(C_5HMe_4)_2Sr(THF)_2$  used as catalyst, the syndiotacticity increases with decreasing polymerization temperature (Table 1).

### Mechanism

We suggest that in the first step the alkaline earth metal complex is alkylated by TEA creating an electronically unsaturated very active species. A monomer molecule coordinates the positive polarized metal center via the carbonyl group resulting in an activation of the double bond to which the alkyl ligand can be transferred to form an intermediate alkoxide. The repeated coordination of monomers and their insertion into the metal-oxygen bond generates the polymer.

### Kinetic Studies

The polymerization reaction is very fast even at low temperatures and low catalyst concentrations. Due to the fast reaction it was not possible to investigate the reaction kinetics *in situ* via spectroscopic methods. For this reason we decided to determine the kinetic parameters by following the development of the average molecular mass. Therefore, the yield is indicated by the linear relationship between the molecular mass of the polymer and the initial ratio

**Figure 1.**

Linear relationship between  $M_n$  and the initial ratio of MMA and  $(C_5HMe_4)_2Sr(THF)_2$  used as catalyst at a polymerization temperature of  $-78^\circ\text{C}$ , 2–3 h polymerization time,  $[TEA]/[\text{cat}] = 7–20$ . The polydispersity  $D$  remains constant.

$[\text{MMA}]/[\text{catalyst}]$  shown in Figure 1 for  $(C_5HMe_4)_2Sr(THF)_2$  as the catalyst. Independent on any polymerization temperature below  $0^\circ\text{C}$ , the molecular mass increases with increasing polymerization time to nearly similar values of a final molecular mass  $M_{n,\text{final}}$  predetermined by the ratio of monomer and catalyst as shown in Figure 2.

The propagation constant  $k_p$  can be calculated from the slope of a semilogarithmic plot of the difference of the momentary molecular mass and the final molecular mass  $M_{n,\text{final}} - M_{n,t}$  (as a measure of the momentary conversion) against the reaction

time  $t$ . The resulting Arrhenius plot indicates an activation energy of 20 KJ/mol (Figure 3), which corresponds to the value for radical polymerizations.<sup>[9]</sup>

### Copolymerization

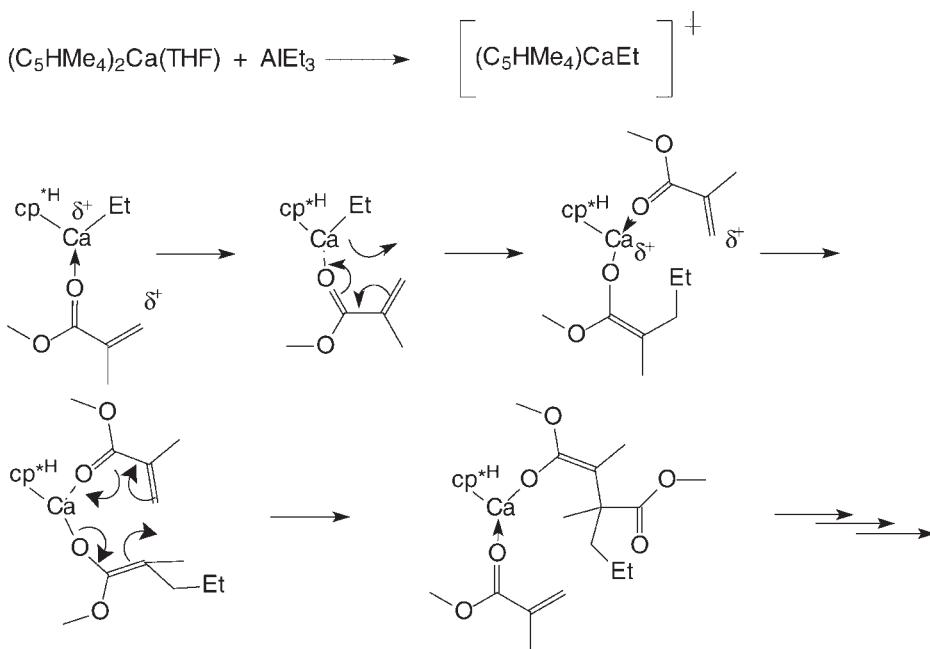
In order to demonstrate the living character of the polymerization process and to get an information about the lifespan of the active species we performed copolymerization reactions using  $(C_5HMe_4)_2Sr(THF)_2$  as catalyst by sequential dosage of the monomer. In general the polymerization stops after the complete monomer consumption and can be immediately restarted by the subsequent addition of monomers. Is the added amount of monomer similar to the initial one, the polymerization proceeds with the same kinetic parameters until the double of the molecular mass is reached (Figure 4). Obviously no deactivation process appears, because the narrow distribution remains unchanged over the whole polymerization time.

In the same manner block-copolymers of PMMA-co-poly(butyl methacrylate) and PMMA-co-poly(ethyl methacrylate) can be

**Table 1.**

Tacticity of PMMA as a function of polymerization temperature and catalyst used, signal of the methyl group due to the syndiotactic triad/%.

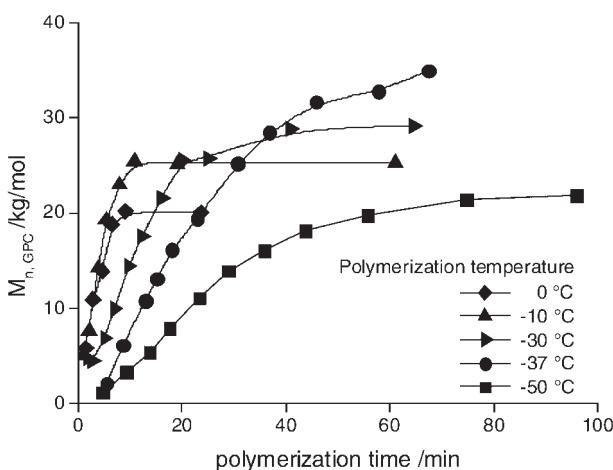
T/°C	Catalyst used	
	$(C_5HMe_4)_2Ca(THF)$	$(C_5HMe_4)_2Sr(THF)_2$
0	18	32
-10	20	41
-30	28	46
-37	30	52
-50	56	60

**Scheme 2.**

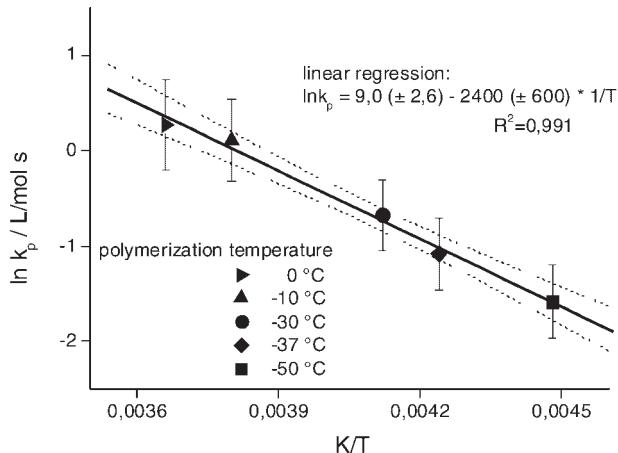
Possible insertion mechanisms of the MMA polymerization reaction catalyzed by  $(C_5HMe_4)_2Ca(THF)$ , involving coordination of the monomer and transfer of a leaving alkyl group on the activated double bond ( $cp^*H = C_5HMe_4$ ).

prepared. The polymerization of the first PMMA block is achieved after 20 min. When the comonomer is added only after 150 min, the polymerization results in a

blend of copolymer and the homo PMMA indicating that 30% of the active species keep their ability to initiate polymerization up to 2,5 h generating.

**Figure 2.**

Time dependent development of the molecular mass (in accordance to GPC) of PMMA catalyzed by  $(C_5HMe_4)_2Sr(THF)_2$ ; reaction conditions: 0,13 mmol  $(C_5HMe_4)_2Sr(THF)_2$ , 1 mmol TGA, 47 mmol MMA, 50 mL toluene, temperature between  $-50$  and  $0$  °C.

**Figure 3.**

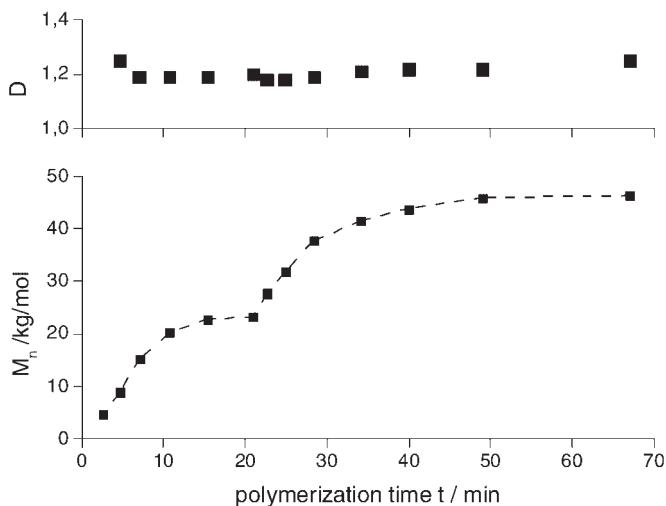
Arrhenius Plot for the polymerization of MMA in toluene catalyzed by  $(C_5HMe_4)_2Sr(THF)_2$ .

## Experimental Section

All polymerization experiments were conducted under rigorous exclusion of air and moisture under an atmosphere of nitrogen in a schlenck line or in a glove box. All solvents were freshly distilled over sodium and benzophenone before use. MMA was dried over  $CaH_2$  and distilled under

reduced pressure. The catalysts  $(C_5HMe_4)_2Mg$ ,  $(C_5HMe_4)_2Ca(THF)$ , and  $(C_5HMe_4)_2Sr(THF)_2$  were synthesized as described elsewhere.<sup>[8]</sup>

In a typical polymerization procedure, 3 mL of a solution of the metal complex (90  $\mu$ mol) in toluene were added via a syringe to 15 mL of a thermostated mixture of the monomer (28 mmol) and TEA

**Figure 4.**

Restart of the polymerization after complete monomer conversion at 20 min, reaction conditions: 0,13 mmol  $(C_5HMe_4)_2Sr(THF)_2$ , 1 mmol TEA, 2  $\times$  47 mmol MMA, 50 mL toluene,  $T = -30^\circ C$ .

(0.4 mmol). The colorless solution turned instantly into dark yellow and the viscosity increased visibly. After 2 h the polymerization was quenched by pouring the solution into 250 mL of MeOH to precipitate the polymer. It was dried at room temperature at  $10^{-2}$  mbar. The polymer tacticity was determined dissolved in  $\text{CDCl}_3$  by  $^1\text{H}$ -NMR spectroscopy on a Bruker ARX 200, the glass transition temperature was measured via DSC on a Perkin Elmer DSC-7. The molecular mass distribution was determined by size exclusion chromatography on a WATERS GPC 150C equipped with a PLgel Mixed-C column and a RI detector (Wyatt Optilab) using THF as eluent with a flow rate of 1 mL/min at room temperature. The column was calibrated with narrow distributed PMMA standards (Polymer Laboratories).

## Conclusion

Bis(tetramethylcyclopentadienyl) complexes of Mg, Ca, and Sr polymerize MMA and other polar monomers at low temperature in the presence of only small excess of  $\text{AlEt}_3$  with high conversions. Narrow molecular mass distributions and predictable molar masses of the resulting

PMMA as well as the possibility to prepare block-copolymers prove them to be very attractive catalysts. The temperature sensitivity of the catalysts regarding deactivation decreases with the size of the central atom; the Sr compound results in fairly good conversions even at  $0^\circ\text{C}$ , while  $(\text{C}_5\text{HMe}_4)_2\text{Mg}$  is inactive at this temperature.

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