

# Zwitterionic titanoxanes $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$ and $\{(\eta^5\text{-}^i\text{PrC}_5\text{H}_4)[\eta^5\text{-}1,3\text{-}^i\text{PrC}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$ as catalysts for cationic ring-opening polymerization

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## Abstract

Zwitterionic titanoxanes  $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$  (**I**) and  $\{(\eta^5\text{-}^i\text{PrC}_5\text{H}_4)[\eta^5\text{-}1,3\text{-}^i\text{PrC}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$  (**II**), which contain two positively charged Ti(IV) centres in the molecule, are able to catalyse the ring-opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) in toluene solution and in bulk. The process proceeds with a noticeable rate even at room temperature and accelerates strongly on raising the temperature to 60 °C. The best results have been obtained on carrying out the reaction in bulk. Under these conditions, the use of **I** as a catalyst ( $\epsilon$ -CL:**I** = 1000:1) gives at 60 °C close to quantitative yield of poly- $\epsilon$ -CL with the molecular mass of 197 000. An increase in the  $\epsilon$ -CL:**I** ratio to 6000:1 increases the molecular mass of poly- $\epsilon$ -CL to 530 000. Tetrahydrofuran (THF) is also polymerized under the action of **I** albeit with a lesser rate. However, the molecular mass of the resulting poly-THF can reach rather big values under optimal conditions (up to 217 000 at 20 °C and the THF:**I** ratio of 770:1). A rise in the reaction temperature from 20 to 60 °C results here to a decrease in the efficiency of the process. Titanoxane **II** is close to **I** in its catalytic activity in the  $\epsilon$ -CL polymerization but it is much less active in the polymerization of THF. Propylene oxide (PO), in contrast to  $\epsilon$ -CL and THF, gives with **I** only liquid oligomers in wide temperature and PO:**I** molar ratio ranges (–30 to +20 °C, PO:**I** = 500–2000:1).  $\gamma$ -Butyrolactone and 1-methyl-2-pyrrolidone are not polymerized under the action of **I** at room temperature. The reactions found are the first examples of catalysis of the cationic ring-opening polymerization by zwitterionic metallocenes of the group IVB metals.

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## 1. Introduction

During the past decade, there has been a growing interest in the chemistry of the group IVB zwitter-

ionic metallocenes representing a novel class of organometallics prospective for catalysis (see e.g. [1–12]). The main efforts in this important area have been focused on the study of the synthesis and reactivity of the zwitterionic metallocenes in which the metal atom is in the +4 oxidation state and contains at least one  $\sigma$ -bonded organic group. It is expected that such highly electrophilic metallocenes could be applicable

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as single-component catalysts for Ziegler-type olefin polymerization, and the presently available data support these expectations (see e.g. [13–17]).

Recently, we have reported on the synthesis and structure of the first group IVB zwitterionic metallocenes which do not contain any  $\sigma$ -bonded organic radicals at the metal atom [7,8,12]. Such metallocenes should be inactive in Ziegler-type olefin polymerization but a high electrophilicity of the positively charged metallic centre in their molecules suggests that they could be useful as catalysts for cationic olefin and ring-opening polymerization as well as other processes catalysed or promoted by conventional Lewis acids.

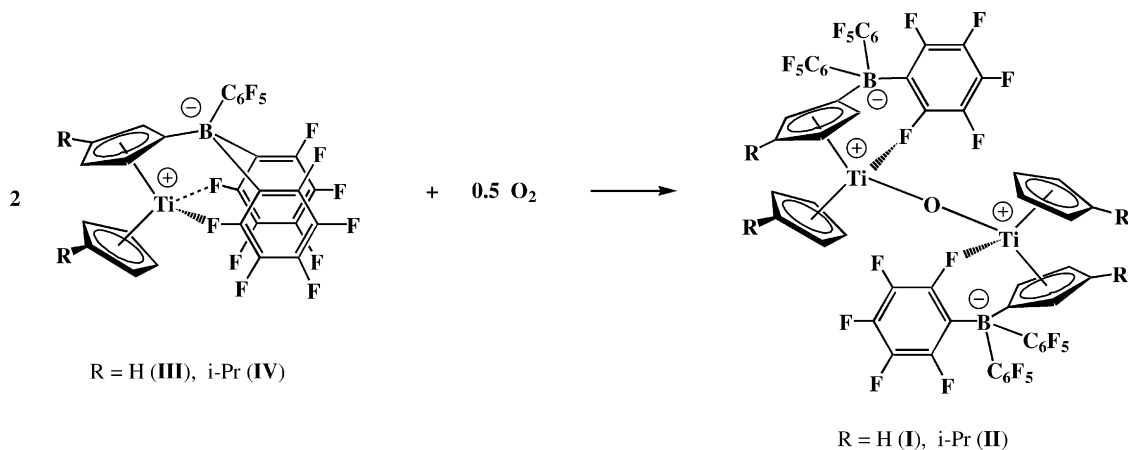
In the present paper, data on the catalytic activity of the previously described [12] zwitterionic titanocene complexes  $\{\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$  (**I**) and  $\{(\eta^5\text{-}^i\text{PrC}_5\text{H}_4)[\eta^5\text{-}1,3\text{-}^i\text{PrC}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}\}_2\text{O}$  (**II**) in cationic ring-opening polymerization of tetrahydrofuran (THF),  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and propylene oxide (PO) are reported. Both complexes are Ti(IV) derivatives and are readily obtained in the interaction of the corresponding Ti(III) zwitterions  $\text{Cp}[\eta^5\text{-C}_5\text{H}_4\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$  (**III**) [7] and  $\{(\eta^5\text{-}^i\text{PrC}_5\text{H}_4)[\eta^5\text{-}1,3\text{-}^i\text{PrC}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{Ti}$  (**IV**) [12] with molecular oxygen from air (Scheme 1).

A remarkable feature of **I** and **II** is the presence of two zwitterionic units in their molecules. In each of these units, the positively charged Ti (IV) centre forms a coordinative bond with the *ortho*-fluorine atom of one of the  $\text{C}_6\text{F}_5$  substituents.

## 2. Results and discussion

The first indications on the ability of the above-mentioned zwitterions **I** and **II** to catalyse cationic ring-opening polymerization have been obtained during attempts to grow crystals of **I** suitable for an X-ray diffraction study. Both zwitterions are practically insoluble in aliphatic and aromatic hydrocarbons but they are good soluble in THF, acetone and other donor solvents. Therefore, attempts have been made to recrystallize **I** from the solvents of this type, and THF was chosen in the first experiments for this purpose. However, it turned out unexpectedly that on keeping a THF solution of **I** at room temperature under Ar it gradually thickens and after two days turns into a transparent rubber-like material. A study of this material has shown that it is poly-THF. Under similar conditions, the Ti(III) zwitterion **III** did not catalyse the THF polymerization because of apparently a considerably lower Lewis acidity of the Ti(III) centre in **III** as compared to that of Ti(IV) in **I**.

In Table 1, data on the influence of the reaction time and the THF:**I** molar ratio upon the efficiency of the ring-opening polymerization of THF at room temperature are presented. One can see that although the rate of the polymerization is not high, the molecular masses of poly-THF can reach rather big values under optimal conditions. The best results have been obtained when the reaction was carried out at the THF:**I** molar ratio of 770:1. In this case, the yield of poly-THF after 30 days amounts to 24% and its molecular mass



Scheme 1.

Table 1  
Ring-opening polymerization of THF under the action of **I** (20 °C)

[ <b>I</b> ] <sub>0</sub> (mol l <sup>-1</sup> )	THF: <b>I</b> (mol/mol)	Reaction time (days)	Polymer yield (%)	Molecular mass
0.016	770:1	8	7	211 000
0.016	770:1	30	24	217 000
0.013	950:1	34	14	121 000
0.011	1120:1	34	6	108 000

attains 217 000. A decrease in the reaction time to 8 days results in a decrease in the polymer yield but its molecular mass remains practically the same under these conditions. An increase in the THF:**I** molar ratio from 770:1 to 950:1 and then to 1120:1 diminishes both the yield of poly-THF and its molecular mass. A rise of the reaction temperature to 60 °C leads also to a lowering in the efficiency of the THF polymerization. Zwitterionic titanoxane **II** is much less active than **I** in this process.

Considerably higher polymerization rates and polymer yields can be achieved if ε-CL is used as a monomer. The reactions with ε-CL were performed in a toluene solution and in bulk. In both cases, a rapid dissolution of the catalysts in the presence of ε-CL occurred and thus the process of the polymerization proceeded under homogeneous conditions. In all experiments carried out in toluene, the initial concentration of ε-CL was kept constant (2 mol l<sup>-1</sup>) while the catalyst concentration was varied.

The results obtained are given in Table 2 from which it is seen that ε-CL differs strongly from THF in its behavior in the polymerization under the action of **I** and **II**. In the case of ε-CL, the process also proceeds at room temperature but the yield of the resulting polymer is here much greater than that on using THF. An-

other essential difference in the behavior of ε-CL and THF is a sharp increase in the efficiency of the ε-CL polymerization on raising the temperature from 20 to 60 °C, in contrast to its considerable decrease in the case of THF (see earlier). Finally, in the polymerization of ε-CL zwitterions **I** and **II** exhibit close activity while in the THF polymerization zwitterion **II**, as mentioned above, is much less active than **I**.

On carrying out the polymerization of ε-CL in a toluene solution in the presence of **I**, the best results are obtained at the ε-CL:**I** molar ratio of 2500:1. The use of such a ratio gives after 10 days at 60 °C close to quantitative yield of poly-ε-CL with the molecular mass of 265 000. Both an increase and a decrease in the ε-CL:**I** ratio diminish the molecular mass of the polymer. The effect of the ε-CL:**I** ratio on the yield of poly-ε-CL is of different character. Here, a gradual fall in the polymer yield (from 99 to 61%) is observed when the ε-CL:catalyst ratio is increased from 1000:1 to 6000:1.

The efficiency of the ε-CL polymerization under the action of **I** can be further increased if the process is carried out in bulk. The use of such a polymerization procedure noticeably enhances both the reaction rate and the polymer yield. As seen from Table 2, when the polymerization of ε-CL is conducted in bulk

Table 2  
Ring-opening polymerization of ε-CL under the action of complexes **I** and **II** as catalysts<sup>a</sup>

Catalyst	Solvent	ε-CL:catalyst (mol/mol)	<i>t</i> (°C)	Reaction time (days)	Polymer yield (%)	Molecular mass
<b>I</b>	Toluene	1000:1	60	10	99	161 000
	Toluene	2500:1	60	10	96	265 000
	Toluene	4000:1	60	10	80	226 000
	Toluene	6000:1	60	10	61	161 000
	–	1000:1	20	27	95	83 000
	–	1000:1	60	8	97	197 000
	–	4000:1	60	8	88	365 000
	–	6000:1	60	8	69	538 000
<b>II</b>	–	1000:1	60	8	97	216 000

<sup>a</sup> In all experiments carried out in toluene, the initial concentration of ε-CL is 2 mol l<sup>-1</sup>.

at the  $\epsilon$ -CL:I ratio of 1000:1 a full conversion of the monomer into the polymer at 60 °C is reached in 8 days and the molecular mass of the resulting poly- $\epsilon$ -CL attains 197 000 which is markedly greater than that in the case of the polymerization in a toluene solution. An increase in the  $\epsilon$ -CL:I ratio from 1000:1 to 6000:1 decreases the polymer yield (to 69%) but the molecular mass of poly- $\epsilon$ -CL is still further enhanced (to 530 000) under such conditions.

Experiments on the ring-opening polymerization of PO have shown that this monomer exhibits an extremely high reactivity towards zwitterion **I**. Thus, on the addition of even very small amounts of **I** to PO at room temperature, a violent reaction starts to proceed after several minutes, resulting in an explosion (!!!). At lower temperatures (<0 °C), the process occurs more smoothly but leads to the formation of only liquid oligomers in wide temperature and PO:I molar ratio ranges (–30 to +20 °C, PO:I = 500–2000 : 1).  $\gamma$ -Butyrolactone and 1-methyl-2-pyrrolidone, in contrast to  $\epsilon$ -CL and THF, are not polymerized under the action of **I** at 20 °C.

The reactions found are the first examples of catalysis of the cationic ring-opening polymerization by zwitterionic metallocenes of the group IVB metals.

### 3. Experimental

All experiments on polymerization were performed in an Ar atmosphere with careful exclusion of air and moisture using standard Schlenk techniques. The starting **I** and **II** were prepared according to published procedures [12]. Toluene and THF were purified in the usual manner and freshly distilled prior to use over sodium (toluene) or from sodium/benzophenone (THF) under Ar. Commercial  $\epsilon$ -CL, PO,  $\gamma$ -butyrolactone and 1-methyl-2-pyrrolidone were dried over molecular sieves and distilled before use under Ar. The IR spectra of poly- $\epsilon$ -CL and poly-THF were recorded (as films) on a IFS-25 Bruker instrument. The NMR spectra were registered on a Bruker ARX 400 spectrometer at 20 °C in  $C_6D_6$ . The molecular masses of poly- $\epsilon$ -CL were measured by the GPC method on a Hewlett Packard liquid chromatograph 1090 HP (SDV column  $10^4 \text{ \AA} + 10^3 \text{ \AA} + 100 \text{ \AA}$  (Polymer Standard Service), eluent THF) and were corrected by the universal calibration relative to

polystyrene standards. The molecular masses of poly-THF were calculated from viscosimetry measurements in ethyl acetate at 30 °C using the equation  $[\eta] = 4.22 \times 10^{-4} M^{0.65}$ .

#### 3.1. Polymerization of THF

To 0.0101 g (0.0075 mmol) of complex **I**·0.5PhCH<sub>3</sub> was added 0.47 ml (0.418 g, 5.8 mmol) of THF in an Ar atmosphere and the resulting solution was allowed to stand without stirring at room temperature under Ar. Within 24 h, the solution began to thicken and after 48 h it turned into a transparent dark red rubber-like material. After 34 days, the product was dissolved in 4 ml of CHCl<sub>3</sub> and the resulting solution was treated with 20 ml of ethanol under stirring. The precipitated white solid polymer was filtered off, washed with a small amount of ethanol and dried at 70 °C in vacuum. The yield of poly-THF is 0.10 g (24%),  $M = 217\,000$ . IR (solid film,  $cm^{-1}$ ): 1113 (s, C–O–C), 2852 (s, CH<sub>2</sub>), 2948 (s, CH<sub>2</sub>), 3422 (br, OH).

#### 3.2. Polymerization of $\epsilon$ -CL in bulk

To 0.0175 g (0.0129 mmol) of complex **I**·0.5 PhCH<sub>3</sub> was added 5.5 ml (5.86 g, 51.3 mmol) of  $\epsilon$ -CL and the resulting yellow–brown solution was heated at 60 °C under Ar. During the course of heating, the reaction mixture gradually became viscous and after 3 days it was transformed into a light yellow rubber-like material. After 8 days, the resulting light yellow glassy product was dissolved in 60 ml of toluene and the obtained solution was poured into an excess of methanol. The precipitated white solid poly- $\epsilon$ -CL was separated by decanting, washed with methanol and dried for 6–8 h in vacuum. The yield of poly- $\epsilon$ -CL is 5.16 g (88%),  $M_w = 365\,000$ . IR (solid film,  $cm^{-1}$ ): 1732 (s, COO), 2866 (s, CH<sub>2</sub>), 2944 (s, CH<sub>2</sub>), 3438 (m, OH). <sup>1</sup>H-NMR ( $C_6D_6$ ,  $\delta$ , ppm): 2.10 (t, 2H,  $\alpha$ -CH<sub>2</sub>), 1.50 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.17 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.40 (m, 2H,  $\delta$ -CH<sub>2</sub>), 3.96 (t, 2H,  $\epsilon$ -CH<sub>2</sub>). <sup>13</sup>C-NMR ( $C_6D_6$ ,  $\delta$ , ppm): 34.11 ( $\alpha$ -CH<sub>2</sub>), 28.68 ( $\beta$ -CH<sub>2</sub>), 24.83 ( $\gamma$ -CH<sub>2</sub>), 25.74 ( $\delta$ -CH<sub>2</sub>), 64.05 ( $\epsilon$ -CH<sub>2</sub>), 172.75 (C=O).

#### 3.3. Polymerization of $\epsilon$ -CL in toluene

To 0.0106 g (0.0078 mmol) of complex **I**·0.5 PhCH<sub>3</sub> was added under Ar 2.09 ml (2.235 g, 19.6 mmol)

of  $\epsilon$ -CL and 7.78 ml of toluene and the resulting yellow–brown solution was heated without stirring at 60 °C in an Ar atmosphere. Within 24 h, the solution has become oily and after 6 days it turned into a light yellow rubber-like product. After 10 days, an excess of methanol was added to the reaction mixture and the precipitated light yellow solid poly- $\epsilon$ -CL was separated by decanting, washed with methanol and dried for 6–8 h in vacuum. The yield of poly- $\epsilon$ -CL is 2.16 g (96%),  $M_w = 265\,000$ . The IR and NMR spectra of the isolated polymer were very similar to those of the poly- $\epsilon$ -CL obtained by the  $\epsilon$ -CL polymerization in bulk (see earlier).

### 3.4. The reaction of PO with complex I

To 0.0152 g (0.0112 mmol) of complex I-0.5 PhCH<sub>3</sub> in a Schlenk tube cooled with liquid dinitrogen was added 0.75 ml (0.62 g, 10.7 mmol) of PO in vacuum. Next, temperature of the mixture was raised to –15 °C and the resulting solution was allowed to stand at the same temperature under Ar. Within 10–15 min, the solution has become oily but then the process of the thickening of the mixture stopped. After 30 days, the viscous liquid product was dissolved in 4 ml of CHCl<sub>3</sub>. Subsequent treatment of the obtained solution with an excess of ethanol did not lead to the precipitation of solid polymer.

Safety note: it is not recommended to mix complex I with PO at room temperature because it can result in an explosion.

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