### Synthesis and Characterization of Chiral Poly(alkyl isocyanates) by Coordination Polymerization Using a Chiral Half-Titanocene Complex

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**ABSTRACT:** A new chiral half-titanocene complex,  $[CpTiCl_2(O-(S)-2-Bu)]$ , is synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. This complex is employed for the coordination polymerization of *n*-butyl and *n*-hexyl- isocyanate leading to chiral polymers, as revealed by their CD spectra. Only the left-handed helix is produced, due to the chiral (S)–2-butoxy group, which is bound to the polymer chain end. The polymerization of 3-(triethoxysilyl)propyl isocyanate produces less soluble polymers. On the other hand, phenyl isocyanate reacts slowly with the complex leading quantitatively and selectively to triphenyl isocyanate is slowly and selectively cyclotrimerized in the presence of the

**INTRODUCTION** Half-titanocene alkoxides are known to be efficient initiators for the polymerization of isocyanates.<sup>1</sup> These complexes have been employed for the synthesis of more complex macromolecular architectures containing poly-isocyanate blocks, such as diblock copolymers, triblock terpolymers, graft copolymers, and miktoarm star copolymers.<sup>2</sup> Poly(hexyl isocyanate) has also been grafted from carbon nanotubes by an anchored half-titanocene complex.<sup>3</sup>

It is widely known that polyisocyanates possess a dynamic helical conformation both in solution and in the solid state. Due to the resonance delocalization of the nitrogen and carbonyl electrons and the steric hindrance induced by the steric hindrance of the monomer's side group, polyisocyanates adopt an extended 8/3 helical conformation instead of a restricted coplanar conformation.<sup>4</sup> In the absence of a chiral component, an equal mixture of right- and left-handed helical segments is synthesized. So, the racemic polymer does not exhibit any optical properties.

The synthesis of chiral polymers is of paramount importance, due to their special applications. There are four general ways to obtain optically active polyisocyanates, that is either the pure left-handed or the right-handed helical conformahalf-titanocene complex. However, a statistical copolymer of 2ethylhexyl isocyanate and hexyl isocyanate is produced. The reaction of benzyl isocyanate with the complex leads to a mixture of low molecular weight polymer and cyclotrimer. The polymers are characterized using SEC, NMR, and CD spectroscopy and their thermal properties are investigated by TGA/DSC analysis. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 2141–2151

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tion or an excess of one of these conformations: (a) copolymerization of an optically inactive monomer with an isocyanate enantiomer, (b) termination of the polymerization with a chiral molecule, (c) polymerization employing a chiral initiator, and (d) dissolution of an optically inactive polyisocyanate in an optically active solvent.<sup>4</sup> As far as halftitanocenes are concerned, optically active oligomers<sup>1</sup> and chiral poly(hexyl isocyanate)<sup>5</sup> have been synthesized by chiral half-titanocene initiators.

Poly(isocyanates) are chemically unstable polymers and undergo degradation under several reaction conditions, both in solution and in the solid state. It is believed that degradation begins at the -NH end of the polymer chain. In order to prevent decomposition, termination of the polymerization reaction with other means than HCl/methanol are used.<sup>6</sup> It is also known that polyisocyanates are thermally unstable. The thermal degradation of poly(alkyl isocyanates), the decomposition products and the reaction mechanism have been investigated. The principal decomposition product is the cyclic trimer (trialkyl isocyanurate) in all cases. Intramolecular cyclization is proposed as the mechanism of decomposition dominant of these polymers.7

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In this study, we report the successful synthesis of welldefined, chiral poly(alkyl isocyanates) using a novel halftitanocene complex. The mechanism of the polymerization reaction was investigated by kinetic experiments. The polymers were characterized by size exclusion chromatography (SEC), <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The thermal properties of the materials were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The optical properties were measured by circular dichroism (CD) spectroscopy. The effect of the monomer structure on the performance of the initiator was investigated.

#### EXPERIMENTAL

#### Materials

CpTiCl<sub>3</sub> (Aldrich, 97%), methanol, hexane, tetrahydrofuran and (S)-2-butanol (Aldrich, 99%) were used as received. Phenyl isocyanate, PhIC, (Aldrich, 98%) was dried over  $P_2O_5$  overnight and distilled under reduced pressure. All other monomers (Aldrich) were dried over CaH<sub>2</sub> overnight and distilled under reduced pressure. Toluene was dried over Na and distilled.

#### Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired by a Varian Unity Plus 300 NMR spectrometer in chloroform-d at 25°C. DSC experiments were performed with a 2910 modulated DSC instrument from TA Instruments. The samples were heated or cooled at a rate of 10°C/min. The samples were annealed at 120°C for 10 min and the measurements were obtained at the second heating run. TGA were performed using a TA Instruments TGA Q50 model under nitrogen at a heating rate of 10°C/min. SEC experiments were conducted at 40°C with a modular instrument consisting of a Waters model 510 pump, a Waters model U6K sample injector, a Waters model 410 differential refractometer, a Waters model 486 UV spectrophotometer and a set of four  $\mu$ -Styragel columns with a continuous porosity range from  $10^6$  to  $10^3$  Å. The columns were housed in an oven thermostatted at 40°C. Tetrahydrofuran was the carrier solvent at a flow rate of 1 mL/ min. The system was calibrated with seven polystyrene (PS) standards with molecular weights in the range of 4000-1,000,000. CD spectra were measured in hexane or tetrahydrofuran solutions using a Jasco J-815 CD spectrometer.

All synthetic procedures were carried out using standard high-vacuum, Schlenk or glovebox techniques, unless stated differently.

#### Synthesis of [CpTiCl<sub>2</sub>(O-(S)-2-Bu)]

In a 50-mL Schlenk flask, CpTiCl<sub>3</sub> (0.2193 g, 0.100 mmol) was added and dissolved in toluene (7.50 mL). In another flask, (S)-2-butanol (92.3  $\mu$ L, 0.100 mmol) and triethylamine (139.4  $\mu$ L, 0.100 mmol) were dissolved in toluene (3.50 mL). The solution of (S)-2-butanol was added dropwise via a pressure equalizing addition funnel to the solution of the metal complex under vigorous stirring. A white precipitate of Et<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup> was formed. After the addition was completed

(about 20 min), the solution was stirred for 3 h and was then filtered through a dry Por.4 sintered glass funnel in an inert atmosphere. The filtrate was collected in a 50-mL Schlenk flask and the solvent was removed in vacuo. The yellow product was dried under vacuum and stored in a drybox. Yield: 0.2400 g (93.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.01 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>(t,3H); 1.38 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> (*d*, 3H); 1.52–1.80 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> (*m*, 2H); 4.76 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub> (*m*, 1H); 6.72 C<sub>5</sub>H<sub>5</sub> (*s*, 5H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$ ): 10.07 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>; 22.72 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>; 32.06 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>; 93.11 CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>3</sub>; 118.82 C<sub>5</sub>H<sub>5</sub>.

#### **Typical Procedure for Polymer Synthesis**

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). To the yellow solution, the monomer (2.0 mL) was added. After the appropriate reaction time, dichloromethane (2 mL) was added and the viscous solution was cooled to 0°C. Subsequently, methanol/aq.HCl (2 mL) was added. The solution became faint yellow immediately and methanol (20 mL) was added. The mixture was concentrated under vacuum (2-3 mL) in order to remove most of the dichloromethane. The polymer was precipitated in methanol (140 mL). After 24 h at -20°C, the liquid was decanted and the purification process was repeated twice. The white polymer was dried under vacuum for 24 h and the yield was determined gravimetrically.

### Synthesis of 2-Ethylhexyl Isocyanurate

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). To the yellow solution, 2-ethylhexyl isocyanate, EHIC, (2.0 mL, 11.20 mmol) was added. The solution was stirred for 10 days. A sample from the reaction mixture was taken for NMR measurement. Yield (by NMR):  $\sim$ 18%.

#### Synthesis of Triphenyl Isocyanurate

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). To the yellow solution, PhIC (2.0 mL, 18.40 mmol) was added leading to the formation of an orange solution. After 2 h, the solution became red. After 46 h, the solution darkened and a solid was visible. Seven days later all liquids were evaporated in vacuo and dichloromethane was added under stirring, until the solid was dissolved. After 24 h at  $-20^{\circ}$ C, a white solid precipitated from the dichloromethane solution and filtered through a Por.4 sintered glass funnel. It was washed with cold dichloromethane. Yield: 2.0819 g (95%).

# Synthesis of Poly(benzyl isocyanate), PBzIC, and Tribenzyl Isocyanurate

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). Benzyl isocyanate, BzIC, (2.0 mL, 19.05 mmol) was added to the yellow solution. After 3 h, a sample for <sup>1</sup>H NMR analysis was taken to determine the quantity of the polymer and the cyclotrimer. Dichloromethane (2 mL) was then added and the viscous solution was cooled to 0°C, followed by the addition of methanol/aq.HCl (2 mL). The solution became faint yellow at once and more methanol (20 mL) was added. The mixture was evaporated under vacuum (2–3 mL) in order to remove most of the dichloromethane. The content of the Schlenk flask was then transferred to a 400-mL beaker containing methanol (140 mL). The purification process was conducted as stated previously. Yield (by NMR):  $\sim$ 40% polymer,  $\sim$ 9% cyclotrimer.

### Synthesis of 3-(Triethoxysilyl)propyl isocyanate, PTEOSiPIC

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(0-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). 3-(Triethoxysilyl)propyl isocyanate, TEOSiPIC, (2.0 mL, 8.07 mmol) was added to the yellow solution. After 7 h, a sample for <sup>1</sup>H NMR analysis was taken. Dichloromethane (2 mL) was added and the viscous solution was cooled to 0°C, followed by the addition of methanol/aq.HCl (2 mL). The solution became faint yellow immediately and an extra quantity of methanol (20 mL) was added. The mixture was evaporated under vacuum (2-3 mL) in order to remove most of the dichloromethane. The content of the Schlenk flask was transferred to a 400-mL beaker containing methanol (140 mL). The white solid was filtered through a Por.4 sintered glass funnel. The white polymer was dried under vacuum for 24 h. The polymer was partially soluble in toluene, tetrahydrofuran, chloroform. Yield (by NMR):  $\sim$ 75%.

## Synthesis of Poly(2-ethylhexyl isocyanate-co-hexyl isocyanate), PEHIC-co-PHIC

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(0-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). EHIC (2.0 mL, 11.43 mmol) was subsequently added. After 21 h, the solution viscosity and color remained unchanged and hexyl isocyanate, HIC, (2.0 mL, 13.81 mmol) was added. After 5 h, the solution became more viscous and the color was orange. After 24 h, the stirring stopped, dichloromethane (2 mL) was added and the viscous solution was cooled to 0°C, followed by the addition of methanol/aq.HCl (2 mL). The solution became faint yellow and methanol (20 mL) was added. The mixture was evaporated under vacuum (2-3 mL) in order to remove most of the dichloromethane. The content of the Schlenk flask was then transferred to a 400-mL beaker containing methanol (140 mL). After 24 h at  $-20^{\circ}$ C, the liquid was decanted and the purification process was repeated twice. The white polymer was dried under vacuum for 24 h. Yield: 1.150 g (35%).

#### Synthesis of a Copolymer of BzIC and HIC

In a 50-mL Schlenk flask, [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] (0.0600 g, 0.233 mmol) was dissolved in toluene (0.5 mL). BzIC (2.0 mL, 19.05 mmol) was then added to the yellow solution. After 21 h, HIC (2.0 mL, 13.81 mmol) was added. After 24 h, the solution became very viscous; dichloromethane (2 mL) was added and the viscous solution was cooled to  $0^{\circ}$ C, followed by the addition of methanol/aq.HCl (2 mL). The solution became faint yellow and methanol (20 mL) was added. The mixture was evaporated under vacuum (2–3 mL) in order to remove most of the dichloromethane. The content



SCHEME 1 Synthesis of [CpTiCl<sub>2</sub>(O-(S)-2-Bu)].

of the Schlenk flask was then poured in a 400-mL beaker containing methanol (140 mL). After 24 h at  $-20^{\circ}$ C, the liquid was decanted and the purification process was repeated twice. The white polymer was dried under vacuum for 24 h. Yield: 0.8160 g (21%).

#### Kinetic Study of the Polymerization of HIC

Four vials containing a magnet, a 0.525 M solution of [CpTi-Cl<sub>2</sub>(O-(S)-2-Bu)] in toluene (0.30 mL) and HIC (1.50 mL) were stirred at 20°C for specific time intervals. Samples were taken to monitor the reaction progress by <sup>1</sup>H NMR and SEC experiments.

#### **RESULTS AND DISCUSSION**

#### Synthesis and Characterization of [CpTiCl<sub>2</sub>(0-(S)-2-Bu)]

The goal of this study was the synthesis of chiral polyisocyanates. In order to achieve this, a chiral alkoxo half-titanocene complex was employed.

The complex [CpTiCl<sub>2</sub>(O-(S)-2-Bu)] was synthesized by modifying already known procedures for similar compounds.<sup>1</sup> The chirality of the complex derives from the alkoxy ligand (Scheme 1). The stereogenic carbon atom should be as close as possible to the oxygen atom, to maximize chiral induction to the polymer chain. There should also be as limited stereochemical hindrance as possible so as to achieve the maximum initiation rate. For these reasons, (S)-2-butanol was employed.

The complex was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. All peaks were assigned as expected in both <sup>1</sup>H and <sup>13</sup>C NMR spectra, except for those of the cyclopentadienyl ring. Only one peak appears both in <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, although more were expected (Fig. 1). This phenomenon is common in (half) titanocene complexes and is attributed to lability processes of the substituents that render all the ring atoms equivalent.<sup>8,9</sup> The complex is moisture sensitive and (S)-2-butanol is observed in the <sup>13</sup>C NMR spectrum (-**C**H-OH, 64.35 ppm).

#### **Polymerization of Isocyanates**

It should be emphasized that the (S)-2-butoxy ligand is covalently bound to the end of the polymer chain. Thus, after the second monomer unit is incorporated in the polymer chain, this chiral alkoxy group is already far from the metal atom and does not contribute to the chirality of the metal centre anymore. Nevertheless, this does not imply that the polymerization does not proceed in a chiral manner. On the contrary,





**FIGURE 1** <sup>1</sup>H (a) and <sup>13</sup>C (b) NMR spectra of  $[CpTiCl_2(O-(S)-2-Bu)]$  (\*(S)-2-butanol).

the end of the growing polymer chain, which is bound to the metal, is chiral due to the developing single-handed helix from the other chain end. Therefore, the whole polymerization procedure evolves in a chiral manner. In other words, the (S)-2-butoxy chain end induces a left-handed helical polymer chain, which induces the chirality to the metal centre (Scheme 2). This detail is emphasized in order to discriminate this complex and the polymerization process from others, where the chiral substituent is bound (or supposed to be bound) to the metal centre during the entire polymerization process and is not incorporated into the polymer chain.

#### Hexyl Isocyanate

The organotitanium mediated polymerization of isocyanates is fully reversible, that is, there is equilibrium between polymerization and depolymerization.<sup>1</sup> Therefore, in order to suppress the depolymerization reaction and achieve high yields the polymerization has to be conducted at high con-



**SCHEME 2** The metal centre becomes chiral due to the developing left-handed helix during propagation.



FIGURE 2 <sup>1</sup>H NMR spectrum of PHIC bearing (S)–2-butoxy end group.

centrations. During the propagation process, the solution becomes very viscous and the polymerization is terminated with methanol/aq.HCl before completion. If the reaction is not terminated at the appropriate time (yield), the product has a broad molecular weight distribution, due to the inhomogeneity of the reaction mixture. The termination reaction must be carried out at  $0^{\circ}$ C, due to the reaction of methanol with the remaining monomer to give a carbamate product.<sup>10</sup> This alcohololysis reaction is greatly exothermic and is, probably, catalyzed by the titanium complex or HCl. A sudden rise in the temperature results in polymer degradation and formation of the undesired cyclotrimer, trihexyl isocyanurate. The incorporation of the alkoxy group at the end of the polymer chain is easily demonstrated in the <sup>1</sup>H NMR spectrum by the assignment of the multiplet peak at 3.25 ppm to the -CH- proton (h) (Fig. 2). The molecular weight of the polymer can be determined by this peak (3.25 ppm) and the peak of the polymer chain at 3.70 ppm (- $CH_2$ - (f)).

The chirality of the polymer chain is verified by the CD spectrum. The polymer exhibits a Cotton effect at 255 nm, due to the n- $\pi$ \* transitions of the amide chromophore, which is negative. This leads to the conclusion that the helix is lefthanded (M). At shorter wavelengths (205 nm) an exciton couplet is shown, due to the arrangement of the chiral amide linkages along the main chain [Fig. 3(a)]. The stability of the helical structure in solution in relation with the temperature was also studied. The structure changes progressively (from rigid rod to coil) upon increasing temperature in agreement with the literature.<sup>11</sup> This behavior is reversible in heating and cooling cycles. This phenomenon is not readily observed [Fig. 3(b)] in a low molecular weight polymer ( $M_w = 7000$ ), meaning that the helical structure remains intact at least up to 55°C (Fig. 3).

The thermal behavior of the solid polymer upon heating was studied by DSC and TGA. Two samples with (a)  $M_{w,a} = 9900$  and (b)  $M_{w,b} = 8500$  were measured (Table 1). Weak transitions were observed for each sample (Fig. 4). The first transition ( $T_{1,a} = -106.1^{\circ}$ C,  $T_{1,b} = -96.0^{\circ}$ C) is attributed to the mobility of the *n*-hexyl side groups of the polymer. It has



**FIGURE 3** CD spectra of PHIC  $M_w = 7000$ . (a) 20°C and (b) 20, 35, 45, and 55°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

been proposed that the alkyl chains, which form a sheath around the stiff main chain, become less rigid and this sheath softens.<sup>12a</sup> The second transition ( $T_{\rm g,a} = -41.4^{\circ}$ C,  $T_{\rm g,b} = -40.8^{\circ}$ C) is referred to as the glass transition temperature. There is a variety of reported  $T_{\rm g}$  values in the literature, from -15 to  $-50^{\circ}$ C.<sup>2,12a</sup> As expected, the polymer with lower molecular weight has lower transition temperature. Conformational changes in the polymer backbone, which have been reported<sup>2,12a</sup> in the 40–75°C range were not observed in our samples. This indicates that the helical structure remains intact up to 75°C. Another indication that supports this conclusion is the weakness of the transitions, which is attributed to the rigidity of the polymer due to its chemical structure and its low molecular weight. It is well

**TABLE 1** Thermal Transitions of PHICs of Different  $M_{\rm w}$  by DSC

| Sample | <b>M</b> w <sup>a</sup> | I ( <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> ) <sup>a</sup> | <i>T</i> <sub>1</sub> (°C) | <b>7</b> g (°C) |
|--------|-------------------------|--|----------------------------|-----------------|
| 1      | 9900                    | 1.17   | -106.1                     | -41.4           |
| 2      | 8500                    | 1.11   | -96.0                      | -41.8           |

<sup>a</sup> By SEC in tetrahydrofuran at 40°C.





FIGURE 4 DSC thermogram of PHIC (Table 1, sample 1).

known that the persistence length of the helical structure of polyisocyanates is quite big, meaning that our polymer chain maintains its left-handedness in full length.<sup>12b</sup>



**FIGURE 5** (a) Derivative weight loss with temperature for PHIC and (b) TGA curve of PHIC  $M_w = 10100$ .

**TABLE 2** Kinetic Study Data of HIC Polymerization

| Time (s) | Yield (%) <sup>a</sup> | <b>M</b> w <sup>b</sup> | ا ( <i>M</i> w/ <i>M</i> n) <sup>b</sup> |
|----------|------------------------|-------------------------|--|
| 2700     | 12.5                   | 3000                    | 1.07                                     |
| 5400     | 27                     | 5200                    | 1.13                                     |
| 9000     | 50                     | 9300                    | 1.12                                     |
| 10,200   | 58                     | 9700                    | 1.17                                     |

<sup>a</sup> Calculated by <sup>1</sup>H NMR spectra.

<sup>b</sup> By SEC in THF in 40°C.

From the TGA [Fig. 5(a)], PHIC begins to degrade at 141.7°C, displays maximum rate in mass loss at 231.1°C and reaches complete degradation at 254.6°C. The two shoulders at 174. and 209.1°C reveal the presence of a complicated degradation mechanism. It has been reported that thermal degradation proceeds either through formation of the amide anion, or through an intermolecular mechanism. In both cases, the cyclotrimer is the main product and monomer is produced in smaller quantities.<sup>13</sup> The thermogram [Fig. 5(b)] is quite different from others. One difference is the absence of a fast mass loss (10%) at the beginning of the process, which appears to be characteristic for all poly(alkyl isocyanates),<sup>14-16</sup> and is attributed to the loss of monomer.<sup>15</sup> Another difference is the temperature where decomposition is completed (254.5°C), since it has been reported that the decomposition is completed with the evaporation of the cyclotrimer, which occurs above 300°C. These remarks lead to the assumption that there is a different, more complex, mechanism for the decomposition of the polymers produced by the present complex. These differences may be attributed to the different end groups and/or the pure left-handed helical structure. These observations apply also to PBIC produced by the same complex, as will be discussed later (Fig. 11).

In order to clarify the mechanism for the polymerization of HIC with the complex  $[CpTiCl_2(O-(S)-2-Bu)]$ , a kinetic study



**FIGURE 6** Temporal evolution of yield ( $\alpha$ ) determined by <sup>1</sup>H NMR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 7** Temporal evolution of  $M_{w}$ . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was conducted. From the data in Table 2 and the graphs in Figures 6 and 7, the linear function between yield,  $\alpha$ , and time and between molecular weight,  $M_{w}$  and time as well becomes apparent. The good control of the molecular characteristics of the product is confirmed by the low molecular weight distribution values, which increase slightly over time (Fig. 8). When a large degree of polymerization is reached, the polymer is insoluble in the small amount of solvent used. The mixture becomes heterogeneous and, thus, the molecular weight distribution is increased dramatically (yield 72%, I = 1.21).



**FIGURE 8** SEC chromatograms in THF (40°C) of PHIC kinetic study (curves from right to left: 2700, 5400, 9000, and 10,200 s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 9  $^{1}$ H NMR spectrum of PBIC bearing (S)–2-butoxy end group.

#### **Butyl Isocyanate**

The polymerization of BIC was also studied, employing the same half-titanocene chiral complex. The calculated molecular weight of PBIC from the <sup>1</sup>H NMR spectrum, integrating the peaks of the end group (f) and the side group (d), was  $M_n = 1660$ . Size exclusion chromatography provides  $M_w = 2960$ ,  $M_n = 2650$ , I = 1.12. The difference is due to instrument calibration with polystyrene standards and the difference in hydrodynamic volumes between PBIC and polystyrene. A correction factor of 0.58 due to the difference in hydrodynamic volume is given in the literature. In this sample, applying the correction factor  $M_n = 1540$ , which is in good agreement with the value calculated from the <sup>1</sup>H NMR spectrum (Fig. 9). The calculated molecular weight from the yield of the reaction,  $M_n = 1868$ , is also in good agreement with the experimental data.

PBIC is insoluble in hexane, in contrast to poly(hexyl isocyanate). For this reason, tetrahydrofuran was used to prepare the samples for CD measurements. However, the observation area became narrower (>220 nm) and therefore, it was



FIGURE 10 CD spectra of PBIC at 20°C.



**FIGURE 11** (a) Derivative weight loss with temperature for PBIC and (b) TGA curve of PBIC.

impossible to observe the expected Cotton effect at  $\sim 205$  nm, due to the arrangement of the chiral amide linkages along the main chain (Fig. 10). In the CD spectrum, the synthesis of the left-handed helix was verified by the negative Cotton effect at 257 nm, which is due to the n- $\pi$ \* transitions of the amide chromophore group. The variable temperature study of the structure by CD revealed that the helical structure remains intact up to 45°C, as in the case of low molecular weight PHIC.

TGA analysis (Fig. 11) reveals that the polymer starts to degrade at  $136.4^{\circ}$ C, has maximum mass loss rate at  $207.6^{\circ}$ C and reaches complete degradation at  $223.5^{\circ}$ C. The bulkier side group of PHIC provides the polymer more protection from thermal degradation than PBIC, which has a smaller side group. For this reason, the degradation of PBIC begins ( $136.4^{\circ}$ C) and is completed ( $223.5^{\circ}$ C) at lower temperatures than that of PHIC (141.7 and  $254.6^{\circ}$ C, respectively). The behavior is similar to that of PHIC, which has been discussed previously.

#### 2-Ethylhexyl Isocyanate

EHIC was employed in order to study the monomer's steric hindrance effect on the activity of the half-titanocene chiral



FIGURE 12 <sup>13</sup>C NMR spectrum of the cyclotrimerization product of triphenyl isocyanate (triphenyl isocyanurate).

complex. A lower polymerization rate of this monomer was expected. However, even after several days of reaction no polymer was detected. In fact, only the cyclotrimer was formed. It can, thus, be concluded that bulky monomers cannot be homopolymerized by this complex. Nevertheless, they can be selectively cyclotrimerized. Even though cyclotrimerization was not the goal of this research, isocyanurates are still useful compounds with industrial applications, such as pesticides (chlorinated isocyanurates), crosslinking agents (triallyl isocyanurate), electronics (triglycidyl isocyanurate), food preservatives [(2,3-dibromopropyl) isocyanurate], etc. The synthetic procedures for some of these compounds might be simplified using this or similar catalysts with bulky isocyanates.

#### **Phenyl Isocyanate**

PhIC is a bulky monomer, which, however, has different electronic effects from those of alkyl isocyanates due to the aromatic ring. When phenyl isocyanate reacts with the complex no polymer is produced. After 7 days of reaction, triphenyl isocyanurate is recognized as the only product by <sup>13</sup>C NMR spectroscopy (Fig. 12).<sup>16</sup> This result indicates that the steric factors prevail over any electronic effect. Therefore, phenyl isocyanate behaves in a similar manner as EHIC during the reaction with the chiral half-titanocene.

#### **Benzyl Isocyanate**

BzIC is also a bulky monomer. The aromatic ring affects the electronic properties of the molecule compared to those of alkyl isocyanates. The  $^1$ H NMR spectrum (Fig. 13) of a sample taken from the reaction solution of BzIC has a broad

peak at 3.8–5.5 ppm, which is attributed to the polymer. The peak at 4.51 ppm is assigned to the monomer and the peak at 5.05 ppm is attributed to the cyclotrimer.<sup>17</sup> The peaks of the aromatic rings of each compound overlap and cannot be assigned separately. The polymerization reaction is much slower compared to alkyl isocyanates, as expected. The main feature of this particular polymerization reaction is the fact that, unlike the polymerization of BIC and HIC, cyclotrimer is produced as a byproduct during the polymerization reaction. The polymer has very low molecular weight, probably due to cyclotrimerization reactions, which are essentially termination reactions. This is the only monomer which exhibits both polymerization and cyclotrimerization reactions simultaneously. This behavior can be attributed to the intermediate flexibility of BzIC compared with PhIC and EHIC.

Taking into consideration the results from all the monomers discussed previously, it can be concluded that the reaction with the chiral complex depends almost exclusively on the stereochemical properties of the monomer and not on its electronic properties.

#### 3-(Triethoxysilyl)propyl isocyanate

This compound is commonly used as a linker molecule and not a monomer. PTEOSiPIC has been reported to be prepared by anionic polymerization.<sup>18</sup> The size exclusion chromatogram of our product is bimodal with a broad distribution. In the <sup>1</sup>H NMR spectrum of a sample of the polymerization solution (Fig. 14), the characteristic peak of the polymer appears in the 3.40–3.70 ppm region (e).<sup>17</sup> Although, during the polymerization reaction the polymer is soluble, after the



**FIGURE 13** <sup>1</sup>H NMR spectrum of the polymerization reaction mixture.

termination with acidic methanol, it is insoluble in common solvents. The polymer is cross-linked due to rapid hydrolysis of the triethoxysilyl group and the formation of siloxane linkages. As was revealed in the IR spectrum (Si-O-Si  $1050 \text{ cm}^{-1}$ ), the cross-linking is quite extensive, in agreement with literature data.<sup>17</sup> Taking into account this initial



**FIGURE 14** <sup>1</sup>H NMR spectrum of the polymerization reaction mixture.



FIGURE 15 <sup>13</sup>C NMR spectrum of PHIC-co-PEHIC, \*peaks attributed to EHIC units.

result, other efficient procedures for the termination of the polymerization without involving cross-linking reactions are tested.

# Cyclotrimerization Versus Polymerization in Anionic and Coordination Polymerization

The polymerization of isocyanates has been studied extensively using anionic initiators.<sup>19</sup> Backbiting reactions of the active chain end take place during the polymerization leading to the formation of inactive trimers of the isocyanate monomer. Cyclotrimerization is not a termination reaction in anionic polymerization, because the anion is still active at the polymer chain end. However, this side reaction leads to low polymer yields and broad molecular weight distributions. In order to prevent cyclotrimerization, the polymerization has to be conducted at low temperatures in the presence of several additives, such as crown ethers or NaBPh<sub>4</sub>.<sup>13,20</sup>

In this study, the polymerization of stereochemically nonhindered monomers (HIC, BIC) proceeds without the production of cyclotrimers. On the other hand, the reaction of bulky monomers (PhIC, EHIC) leads exclusively to cyclotrimers. The case of BzIC, where both cyclotrimerization and polymerization occur simultaneously, is unique. It seems that the crucial parameter is the bulkiness close to the carbonyl group of the monomer. This conclusion is further supported by the behavior of TEOSiPIC. This is a sterically hindered monomer but the bulky triethoxysilyl group is connected to the nitrogen atom through a spacer, which is the propyl group. Therefore, TEOSiPIC is polymerized to a high yield without the formation of trimer. Even though a detailed mechanistic analysis is not available, it is assumed that, in the coordination polymerization of isocyanates, cyclotrimerization is a termination reaction.

#### Copolymers

Due to steric effects of the monomer, the homopolymerization of EHIC is impossible under the same reaction conditions as for the other alkyl isocyanates. However, efforts to copolymerize EHIC and HIC were rather successful. In the <sup>13</sup>C NMR spectrum (Fig. 15), the peaks attributed to PHIC are dominant but there are also several smaller and wider peaks (10.50, 30.04, and 38.61 ppm) attributed to EHIC units incorporated in the polymer chain. Therefore, a statistical copolymerization of the two monomers occurred. The intensity of the peaks attributed to PEHIC indicate that there were very few units of EHIC introduced in the polymer chain, even though the feed composition of the monomers (mol) was approximately 1:1. Therefore, the reactivity ratio for HIC is much higher than that of EHIC. The copolymer had relatively narrow molecular weight distribution  $(M_w = 16700, I = 1.11)$  revealing good control of the copolymerization reaction.

The copolymerization of BzIC with HIC was also examined. After reaction of the first monomer (BzIC), the second monomer was introduced in the reaction mixture, without removal of the first one. A bimodal distribution was revealed in the size exclusion chromatogram of the final product. Formation of the cyclotrimer during the polymerization reaction of BzIC possibly leads to termination of polymer molecules and

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 TABLE 3
 Molecular Characteristics of the Homo- and Copoly mers Synthesized

| Sample        | Yield (%)       | <b>M</b> <sub>w</sub> <sup>b</sup> | I ( <i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub> ) <sup>b</sup> |
|---------------|-----------------|------------------------------------|--|
| PHIC (1)      | 66              | 8500                               | 1.11   |
| PHIC (2)      | 21              | 9900                               | 1.17   |
| PHIC (3)      | 71              | 10100                              | 1.32   |
| PBzIC         | 40 <sup>a</sup> | Bimodal                            | -  |
| PTEOSiPIC     | 75 <sup>a</sup> | Insol.                             | -  |
| PEHIC-co-PHIC | 23              | 16,700                             | 1.11   |
| PBzIC-b-PHIC  | 20              | 4800                               | 1.21   |

<sup>a</sup> Calculated in <sup>1</sup>H NMR spectrum.

<sup>b</sup> By SEC in tetrahydrofuran at 40°C.

disengagement from the metal. The formation of a copolymer of the type PBzIC-b-P(BzIC-co-HIC) is more possible. The homopolymerization of HIC can be ruled out taking into account the SEC and NMR data.

A strong evidence for the copolymer formation is the solubility of the final product in chloroform, where PBzIC homopolymer is almost insoluble. From the <sup>1</sup>H NMR spectrum, the composition of the copolymer in BzIC is equal to 70%. Further studies are in progress to elucidate the structure of this copolymer. The molecular characteristics of the copolymers along with characteristic homopolymers are given in Table 3.

#### CONCLUSIONS

A new chiral, half-titanocene, alkoxy complex [CpTiCl<sub>2</sub>(0-(S)-2-Bu)] was synthesized. The aforementioned complex induces asymmetric polymerization of non chiral isocyanates. The (S)-2-butoxy group, which is ultimately covalently bonded to the end of the polymer chain, induces the polymerization of only the left-handed (M) helix. The products have relatively narrow molecular weight distributions, and the polymerization reaction is well controlled. Sterically hindered monomers, such as 2-ethylhexyl isocyanate and phenyl isocyanate are exclusively cyclotrimerized producing the corresponding isocyanurates. However, statistical copolymerization of 2-ethylhexyl isocyanate and hexyl isocyanate was achieved, but with limited incorporation of 2-ethylhexyl isocyanate units along the polymer chain. Benzyl isocyanate was polymerized to a low molecular weight polymer, due to termination reactions (cyclotrimerization). The product has limited solubility in common solvents and only a copolymer with hexyl isocyanate was dissolved in chloroform. The polymerization of 3-(triethoxysilyl)propyl isocyanate proceeds to a product which is less soluble in common solvents, probably due to partial hydrolysis of the triethoxysilyl groups during the termination process.

In conclusion, the monomer structure, or in other words the steric hindrance close to the isocyanate group influences the progress of the reaction with the chiral half-titanocene complex, leading either to polymerization or cyclotrimerization products.

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