# Ring-Opening Polymerization of $\epsilon$-Caprolactone Initiated with Titanium *n*-Propoxide or Titanium Phenoxide

**Julien Cayuela, Véronique Bounor-Legaré,* Philippe Cassagnau, and Alain Michel**

*Laboratoire des Matériaux Polymères et des Biomatériaux, UMR−CNRS 5627: Ingénierie des Matériaux Polymères, ISTIL, Université Claude Bernard, Lyon 1, 15 Boulevard Latarjet 69622 Villeurbanne Cedex, France*

*Received June 17, 2005; Revised Manuscript Received December 6, 2005*

ABSTRACT: Ring-opening polymerization of $\epsilon$-caprolactone initiated by titanium *n*-propoxide Ti(O-*n*-Pr)$_4$ was compared to the one initiated by titanium phenoxide or Ti(OPh)$_4$. Polymerization was confirmed to proceed via a coordination−insertion mechanism for both initiators after end groups analysis by $^1$H and $^{13}$C NMR (nuclear magnetic resonance) spectroscopy. Bulk polymerization at 100 °C and with a $M_0/I_0$ (monomer/initiator ratio) equal to 300 was studied and compared with both initiators. The polymerization with Ti(OPh)$_4$ exhibits a slower kinetic of reaction and the polymer synthesized an higher number-average molecular weight and higher polydispersity than with Ti(OPr)$_4$. These results are consistent with evolution of the average number of active aryloxide groups per initiator ($\overline{N}_{aag}$) during polymerization for this initiator. Indeed, $\overline{N}_{aag}$ determined by $^1$H NMR increases gradually during the polymerization to 2 for around 70% conversion and then decreases at the end of the polymerization and even over the time required for total conversion. This decrease of $\overline{N}_{aag}$ at the end of the conversion may be explained by important transesterification reactions with phenoxyl end groups of the polymer, which lead to the formation of larger poly($\epsilon$-caprolactone) chains. That is consistent with the increase in the number-average molecular weight of the polymer beyond the end of the conversion. The rheological study also confirms this result.

## Introduction

Ring-opening polymerization (ROP) of $\epsilon$-caprolactone has been widely studied, and many efficient catalysts or initiators have been developed.[1−5] According to the initiator, the polymerization proceeds according to three different major reaction mechanisms, cationic,[6−8] anionic[9−11] or coordination−insertion[12,13] mechanisms.

Among them, the coordination−insertion ring-opening polymerization was thoroughly investigated since it may yield well-defined poly($\epsilon$-caprolactone) through living polymerization. A large variety of compounds, such as alkyl, oxides, carboxylates, and alkoxide metal are effective for the controlled ring-opening of lactones.[14−22] By careful selection of metal and ligands, reactions can be generated to form polyester with controlled architecture and tailor-made properties. The polymerization proceeds via acyl−oxygen cleavage of the lactone with insertion of the monomer into the metal−oxygen bond of initiator. The first step of the reaction corresponds to the formation of a complex between the lactone and the initiator through interactions between the carbonyl group of the lactone and the metal atom. Then in a second step, opening of the cycle occurs with cleavage of the acyl−oxygen bond. The most widely used initiators for ROP of cyclic esters are various tin[14−17] and aluminum alkoxides.[18−21] A major difference between tin and aluminum based initiators is that tin initiators are good transesterification catalysts. Other initiators were tested, such as zinc,[23] titanium,[12] magnesium,[24] and calcium[25] derivatives. More recently rare earth metal compounds[26−29] showed a very high activity in ROP of lactones and gave higher molecular weights. Yu et al.[30] compared different rare earth metal tris(4-*tert*-butylphenolates), Ln(OTBP)$_3$, and demonstrated that the lanthanide derivatives are the most efficient. In the same way that research is carried on a new central initiator atom, research on well-defined ligand environments that potentially facilitate more control on the molecular and physical properties of the polyester produced is significant. Indeed the ring-opening polymerization of lactones at high temperature or long reaction times leads to both inter- and intramolecular transesterification reactions. Both types of transesterifications lead to an increasing in polydispersity of polyesters.

Therefore, beside the well-known relative reactivity of different metal alkoxide initiators for transesterification reaction ($Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$) the use of bulky coordinated groups reduced the side reactions (e.g., transesterification, macrocycle formation, and racemization), and polymers with narrow molecular weight distribution and high molecular weight could be obtained. Indeed taking into consideration that the volume of the polymer chain is much larger than that of the monomer, it is supposed that bulky groups surrounding the active center of catalyst might hinder the polymer chain from access to the active center so that transesterification are reduced. For example, Takeuchi et al.[31] using bulky titanium bis(phenolate) complexes such as {2,2′-$CH_2$(4-Me-6-$^t$Bu$C_6H_2O)_2$}Ti($O^i$Pr)$_2$(OAr)$_2$ showed that only the isoproproxide group is able to initiate $\epsilon$-caprolactone polymerization at 25 °C and that, by changing the nature of the hindered group, a much narrower molecular weight distribution (MWD) is obtained. These results suggest that the hindered phenolates decrease the occurrence of transesterification. Chen et al.[32] demonstrated the preparation of well-defined polyester by using the high activity of aminebis(phenolate)aluminum complexes. The substitution in the phenyl rings of bisphenol affect the reactivity of the aluminum center and allow the controlled synthesis of various poly($\epsilon$-caprolactone)s or copolymers.[33]

The aim of the present paper is to show the influence of phenyl groups on the bulk ring-opening polymerization of

* Corresponding author: Veronique.Bounor-Legare@univ-lyon1.fr.

10.1021/ma051272v CCC: $33.50 
Published on Web 01/28/2006

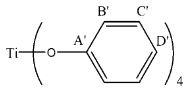
$\epsilon$-caprolactone initiated by titanium derivatives. The polymerization was studied with two initiators: titanium *n*-propoxide and titanium phenoxide. The polymerization was checked to proceed through a ring-opening reaction with selective cleavage of the acyl−oxygen bond. The influence of the phenoxide ligand on kinetic of polymerization, average molecular weight of the polymer synthesized, evolution of the average number of active alkoxide or aryloxide groups per initiator, and evolution of rheological parameters during polymerization was discussed. The characterization methods used were NMR, size exclusion chromatography (SEC), and rheological measurements.

## Experimental Section

**Materials.** $\epsilon$-Caprolactone (Lancaster, 99%) was dried over calcium hydride ($CaH_2$) for 2 days at room temperature, vacuum distilled, and stored under argon and on molecular sieves.

Titanium *n*-propoxide (Aldrich, 98%) was stored under argon and used without further purification.

Titanium phenoxide, $Ti(OPh)_4$, was synthesized by the method described by Yoshino et al.[34] Typically, titanium *n*-propoxide and phenol (99%, 1:4 molar ratio, Aldrich) were mixed in dry toluene (Aldrich, 99,8%). After 1 h 30 min of heating with reflux, a dark red-orange solution was obtained. After elimination of propanol on fractional distillation at reduced pressure to complete the reaction, washing with dry *n*-hexane (Aldrich, > 95%) and drying under vacuum at 40 °C, an orange powder of titanium phenoxide




was identified by $^1H$ and $^{13}C$ NMR spectroscopy. It was stored under argon.

$^1H$ NMR (250 MHz, $CDCl_3$, 57 °C): $\delta = 6.62$ ppm (B′, d, 8H), $\delta = 6.80$ ppm (D′, t, 4H), $\delta = 6.98$ ppm (C′, t, 8H).

$^{13}C$ NMR (62.9 MHz, $CDCl_3$, 57 °C): $\delta = 165.15$ ppm (A′), $\delta = 128.90$ ppm (C′), $\delta = 122.35$ ppm (D′), $\delta = 119.48$ ppm (B′).

Anhydrous solvents [dichloromethane ($CH_2Cl_2$, 99,8%), toluene, *n*-hexane] were purchased from Aldrich Chemicals and stored under argon and on molecular sieves. Others solvents [$CH_2Cl_2$ (99,9%), MeOH (99,9%)] were also purchased from Aldrich Chemicals and have high performance liquid chromatography (HPLC) grades. Deuterated chloroform $CDCl_3$ (Aldrich) was used as received.

**$\epsilon$-Caprolactone Polymerization Procedure.** Bulk polymerization of $\epsilon$-caprolactone is described with an example as follows with $Ti(OPh)_4$ as initiator: First 7.33 g of $\epsilon$-caprolactone and 90 mg of $Ti(OPh)_4$ were placed at room temperature under argon in a 20 mL Schlenk flask. $M_0/I_0$ is consequently equal to 300, $M_0$ corresponding to the number of moles of $\epsilon$-caprolactone and $I_0$ to the initial number of moles of initiator. $Ti(OPh)_4$ was dispersed with a combination of stirring (magnetic stirrer) and ultrasound. Then 2 mL of the mixture was injected with a syringe between the parallel plates (diameter $\phi = 25$ mm) of a Rheometrics mechanical spectrometer (RMS 800) used as reactor and preheated at 100 °C. Nitrogen was used to prevent hydrolysis of titanate bonds and the thickness of the sample (gap of the parallel-plate) was about 1 mm. The polymerization was carried out at a frequency $\omega = 10$ rad/s beyond the end of the conversion. In the case of polymerization with titanium *n*-propoxide, the initiator was dispersed in $\epsilon$-caprolactone just by stirring.

A complementary solution polymerization was studied under argon in toluene with $Ti(OPh)_4$ at 100 °C for $M_0/I_0 = 300$ ($[Ti(OPh)_4] = 12$ mmol·L$^{-1}_{\text{toluene}}$). $\epsilon$-caprolactone and $Ti(OPh)_4$ were respectively dissolved in two Schlenk flasks in toluene and heated at 100 °C prior to react.

To check the ring opening mechanism of the monomer, polymerizations were carried out in Schlenk flask for lower temperatures and $M_0/I_0$ ratios [$T = 50$ °C and $M_0/I_0 = 45$ for $Ti(O\text{-}n\text{-}Pr)_4$; $T = 40$ °C and $M_0/I_0 = 110$ for $Ti(OPh)_4$]. In that last case, the initiator was first dissolved in $CH_2Cl_2$ ($[Ti(OPh)_4] = 27$ mmol·L$^{-1}_{\text{methylene chloride}}$) and the polymerization stopped at 18% conversion (determined by $^1H$ NMR spectroscopy) to enhance the visualization of end groups by NMR spectroscopy.

The polymer synthesized, when specified along the text, was isolated after dissolution of the final reaction mixture in $CH_2Cl_2$, precipitation in cold methanol and drying under vacuum at room temperature during 5 h.

**Characterizations.** High-resolution liquid NMR spectroscopy was carried out with a Bruker AC 250 instrument working at 250 MHz for $^1H$ and 62.9 MHz for $^{13}C$. Deuterated chloroform, $CDCl_3$ was used as solvent for analysis. Chemical shifts values ($\delta$) are in ppm with reference to internal tetramethylsilane (TMS).

The number-average molecular weight ($M_n$), the weight-average molecular weight ($M_w$), and the polydispersity ($I_p$) were measured by size exclusion chromatography. Solutions of the polymer that was isolated, prepared in tetrahydrofuran (THF, 99,9%), were prefiltered on a filter plate (hydrophobic poly(tetrafluoroethylene), 0.45 $\mu$m pore size) before injection. The SEC apparatus was equipped with two Waters UltraStyragel columns (HR1 and HR4; inner diameter = 7.8 mm, length = 300 mm, and particle size = 5 $\mu$m) and a Waters R410 refractometer detector. THF was used as eluent with a flow rate of 1 mL/min and at 22 °C. The polystyrene calibration used was then corrected with the Mark−Houwink coefficients ($a = 0.786$, $k = 0.00014$ mg/1).[35]

The rheological kinetics of bulk polymerization were carried out at a frequency $\omega = 10$rad/s in the domain of the linear viscoelasticity. It allowed to measure in real time and in situ the storage modulus $G'$ and the loss modulus $G''$ of the reaction mixture. The modulus of the complex shear viscosity ($|\eta^*(\omega)|$) was measured at 140 °C on the reaction mixture after a heating at 140 °C for several minutes beyond the end of the conversion and after the hydrolysis of titanate bonds.

## Results and Discussion

**Mechanism of Ring-Opening of the Monomer. Nature of the End Groups.** The first step in a coordination−insertion reaction corresponds to the formation of a coordination complex between the lactone and the initiator with interaction between the carbonyl group and the metal atom. Then, the ring opening reaction occurs with a selective cleavage of the acyl−oxygen bond [Figure 1]. Numerous metal alkoxides lead to such mechanism such as magnesium, tin, titanium, zirconium and aluminum derivatives.[12,14,18,24] Our previous works[36] carried out with the titanium *n*-propoxide showed that the ring-opening polymerization of $\epsilon$-caprolactone proceeds via an acyl−oxygen bond cleavage. In our present conditions ($T = 50$ °C and $M_0/I_0 = 45$), we confirmed by $^1H$ and $^{13}C$ NMR spectroscopy the presence of signals corresponding to the methylene and methyl group of propyl ester function (−COO$CH_2CH_2CH_3$) respectively at 4.03, 1.65, and 0.94 ppm on $^1H$ NMR spectrum and respectively at 65.91, 21.97, and 10.41 ppm on $^{13}C$ NMR spectrum.The methylene group of an ethoxyl group HO$CH_2$-

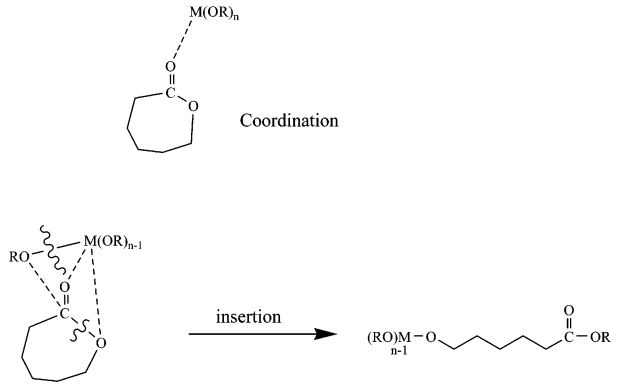
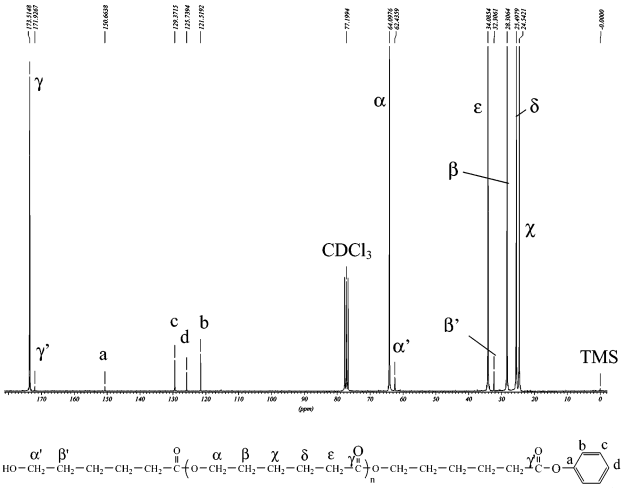



**Figure 1.** Coordination−insertion mechanism of $\epsilon$-caprolactone polymerization.

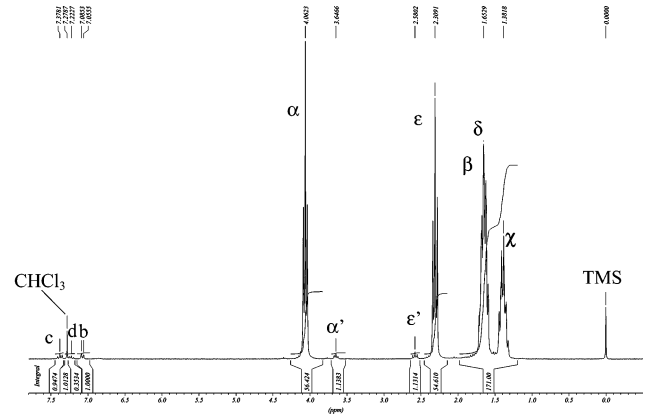



α' β' α β χ δ ε γ γ' a b c d
62.44 32.31 64.10 28.31 24.54 25.50 34.09 173.51 171.93 150.66 121.52 129.37 125.79

**Figure 2.** $^{13}$C NMR spectrum (measured in $CDCl_3$, 62.9 MHz) of the polymer isolated from the polymerization of $\epsilon$-caprolactone initiated with titanium phenoxide ($M_0/I_0 = 110$) at 40 °C by first dissolving the initiator in dry $CH_2Cl_2$ and then stopping the polymerization at 18% conversion.

$CH_2-$ was observed at 3.64 ppm on $^1$H NMR spectrum and at 62.57 ppm on $^{13}$C NMR spectrum.

To evidence such a mechanism in the $Ti(OPh)_4$ case, the identification of end groups of the polymer synthesized and isolated was carried out at 40 °C ($M_0/I_0 = 110$) by first dissolving initiator in dry $CH_2Cl_2$ and stopping the polymerization at 18% conversion. The polymerization was stopped at a low conversion rate to enhance end groups concentration. Typically the $^1$H and $^{13}$C NMR spectra of the polymer synthesized (Figures 2 and 3) shows important signals α, $\beta$, $\chi$, $\delta$, $\epsilon$, and $\gamma$ due to repeating $-C(O)(CH_2)_5O-$ units of poly($\epsilon$-caprolactone) and relatively weak signals corresponding to end groups. By comparison with NMR spectra of phenyl propionate and 1-hexanol, ester and hydroxyl end group model compounds, $^{13}$C spectrum (Figure 2) presents 5 weak signals $\gamma'$ ($\delta = 171.93$ ppm), a ($\delta = 150.66$ ppm), b ($\delta = 121.52$ ppm), c ($\delta = 129.37$ ppm) and d ($\delta = 125.74$ ppm) corresponding to the phenoxyl ester end groups and two weak signal α′ ($\delta = 62.44$ ppm) and $\beta'$ ($\delta = 32.31$ ppm) assignable to the hydroxyl end groups. Furthermore, no evidence of phenyl ether end groups was observed. Consequently these observations confirm that polymerization of $\epsilon$-caprolactone with $Ti(OPh)_4$ proceeds also with cleavage of the acyl−oxygen bond in $\epsilon$-caprolactone. The $^1$H spectrum (Figure 3) confirms results of $^{13}$C NMR analysis. Four weak signals b ($\delta = 7.07$ ppm), c ($\delta = 7.38$ ppm), d ($\delta = 7.22$ ppm) and $\epsilon'$ ($\delta = 2.58$ ppm) are assignable to aromatic protons




α' α β χ δ ε ε' b c d
3.65 4.06 1.65 1.38 1.65 2.31 2.58(t) 7.07 7.38 7.22

**Figure 3.** $^1$H NMR spectrum (measured in $CDCl_3$, 250 MHz) of the polymer isolated from the polymerization of $\epsilon$-caprolactone initiated with titanium phenoxide ($M_0/I_0 = 110$) at 40 °C by first dissolving initiator in dry $CH_2Cl_2$ and stopping the polymerization at 18% conversion.

in ortho, para and meta position of the terminal −COOPh and to protons $CH_2$ of the terminal -$CH_2$COOPh. It also appears a weak signal α′ ($\delta = 3.65$ ppm) corresponding to the proton resonance of the methylene group in α position of the hydroxyl end group.

**Kinetic of Polymerization.** A kinetic study was carried out for bulk polymerization at 100 °C and for $M_0/I_0 = 300$ by carrying out the polymerization in situ between the rheometer plates at frequency $\omega = 10$ rad/s. The evolution of the degree of conversion $C$ (%) vs time was evaluated from the quantitative analysis $^1$H NMR of aliquots extracted from the reactive medium at different times and immersed immediately in a solution ($CDCl_3$ + few microliters of $CH_3COOH$) to stop the polymerization. It was calculated from the ratio of number of moles of monomer that reacted to the initial number of moles of monomer molecules ((1) for polymerization with Ti(O-*n*-Pr)$_4$ and (1′)) for polymerization with $Ti(OPh)_4$).

$$C\,(\%) = \frac{\text{area of triplet } \epsilon \text{ at 2.31 ppm}}{\text{area of triplet } \epsilon \text{ at 2.31 ppm} + \text{area of triplet } \epsilon_c \text{ at 2.64 ppm}} \times 100 \qquad (1)$$

$$C\,(\%) = \frac{\text{area of triplet } \alpha \text{ at 4.06 ppm} + \text{area of triplet } \alpha' \text{ at 3.64 ppm}}{\text{area of triplet } \alpha \text{ at 4.06 ppm} + \text{area of triplet } \alpha' \text{ at 3.64 ppm} + \text{area of triplet } \alpha_c \text{ at 4.23 ppm}} \times 100 \qquad (1')$$

The signal $\epsilon$ at 2.31 ppm and $\epsilon_c$ at 2.64 ppm correspond to the proton resonance of the methylene group $-O-(CH_2)_4-CH_2-(C{=}O)-$ respectively in the repeat unit of the polymer and in the monomer. The signal α at 4.06 ppm, α′ at 3.64 ppm, and $\alpha_c$ at 4.23 ppm correspond to the proton resonance of the methylene group $-O-CH_2-(CH_2)_4$-(C=O)- respectively in the repeat unit of the polymer, next to the terminal hydroxyl of the polymer and in the monomer.

Figure 4 shows the time−conversion curves of $\epsilon$-caprolactone polymerization with both Ti(O-*n*-Pr)$_4$ and $Ti(OPh)_4$. Both polymerizations proceed rapidly up to 100% conversion at 100 °C but in a different range of time (200s and 480s for Ti(O-*n*-Pr)$_4$ and $Ti(OPh)_4$ respectively). To go further in the $\epsilon$-caprolactone polymerization kinetics, the plots of ln(100 $-C(t)$) vs

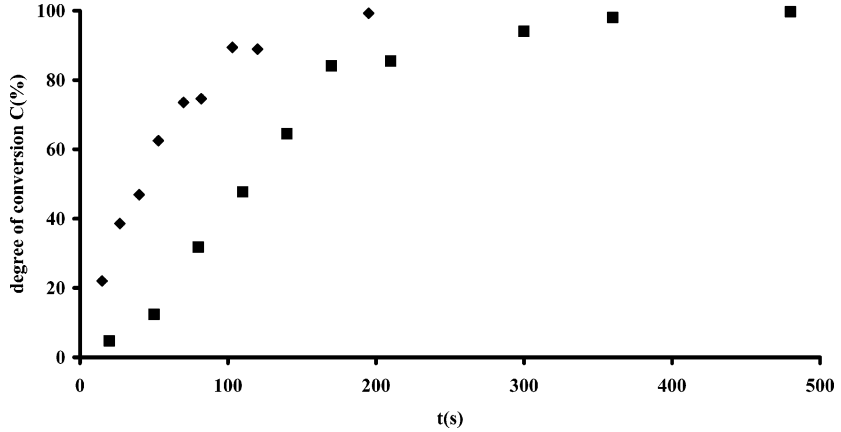



**Figure 4.** Time−conversion curves for the bulk polymerization of ϵ-caprolactone between the rheometer plates at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium *n*-propoxide (◆) or titanium phenoxide (■).

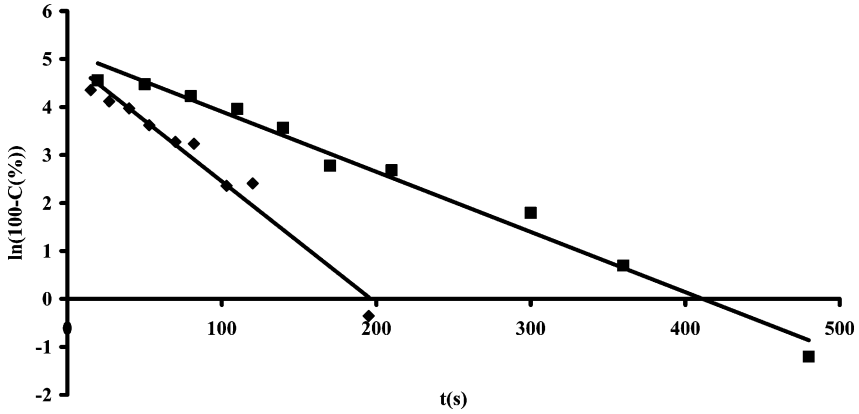



**Figure 5.** Plot of ln(100 − *C* (%)) as a function of time in bulk ϵ-caprolactone polymerization between the rheometer plates at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium *n*-propoxide (◆) or titanium phenoxide (■). *C* (%) corresponds to the degree of conversion in percent.

time were studied (Figure 5). The linearity obtained indicated that the polymerization is first-order in monomer, which is consistent with the living character of this polymerization. Therefore, the polymerization of ϵ-caprolactone initiated by both titanium derivatives under the conditions studied obey eq 2 where [M] is the monomer concentration and $K_{app}$ the apparent polymerization rate.

$$-\frac{d[M]}{dt} = K_{app}[M] \qquad (2)$$

From the slope of the previous plots, $K_{app}$ deduced is equal respectively to 0.0254 and 0.0125 $s^{-1}$ for Ti(O-*n*-Pr)$_4$ and Ti(OPh)$_4$. The value found for Ti(O-*n*-Pr)$_4$ is consistent with the apparent polymerization rate obtained in our previous work.[36] Indeed Gimenez et al.[36] showed that for $T = 100$ °C and $M_0/I_0$ ratio equal to 400, $K_{app}$ was a little lower, equal to 0.0183 $s^{-1}$, due to the different initial $M_0/I_0$ ratio. The value of $K_{app}$ found for Ti(OPh)$_4$ is divided by 2 with respect to the one found with Ti(O-*n*-Pr)$_4$ which could be consistent with a lower average number of active ligands with the titanium phenoxide. Besides, this assumption is also in accordance with the higher number-average molecular weight, $M_n = 21\,550$ g/mol for the polymer synthesized with Ti(OPh)$_4$ and isolated at 99% of conversion against 10 350 g/mol for the one synthesized with Ti(O-*n*-Pr)$_4$ (Table 1).

Few hypothesis could explain the lower number of active ligands for polymerization with Ti(OPh)$_4$. First, Ti(OPh)$_4$ is a solid at 100 °C and its solubility in ϵ-caprolactone not determined. Therefore, the polymerization of the ϵ-caprolactone could occur in an heterogeneous medium (at least at the beginning of the reaction). The solubility of the growing species from the initiator may increase during the reaction. This phenomenon could also explained the slight induction time below 50 s. The observation of an induction period was already pointed out by Storey et al.[37] in the case of ϵ-caprolactone polymerization initiated by stannous octoate. They demonstrated that the delay corresponded to the formation of a "true" active species. Second, physical properties of aryloxide titanium were studied by several authors and compared with the ones of alkoxides titanium.[38−41] Aryloxide ligands are poorer p-donors than their aliphatic counterparts due to delocalization of the electrons within the phenyl ring. This results in larger and weaker Ti−O bond but also in the ability of TiOPh to form large Ti−O−C angle and then to relieve steric strain at the metal.[39] The metal atom is then more prone to coordination with

**Table 1. SEC Results of Isolated Polymer Obtained from Bulk ϵ-caprolactone Polymerization at 100 °C ($M_0/I_0 = 300$) Initiated by Ti(O-*n*-Pr)$_4$ or Ti(OPh)$_4$**

| initiator | | $M_n$ (g/mol) | $M_w$ (g/mol) | $I_p$ |
|---|---|---|---|---|
| Ti(O-*n*-Pr)$_4$ | polymer isolated at 98.2% of monomer conversion | 10350 | 19550 | 1.89 |
| Ti(O-*n*-Pr)$_4$ | polymer isolated beyond total conversion after thermal treatment at 140 °C for a few minutes | 9400 | 18350 | 1.95 |
| Ti(OPh)$_4$ | polymer isolated at 99.8% of monomer conversion | 21550 | 67450 | 3.13 |
| Ti(OPh)$_4$ | polymer isolated beyond total conversion after thermal treatment at 140 °C for a few minutes | 43600 | 92350 | 2.12 |

**Table 2. Average Number of Active Groups ($\overline{N_{aag}}$) Determination from $^1$H NMR Spectra for Bulk $\epsilon$-caprolactone Polymerization at 100 °C ($M_0/I_0 = 300$) Initiated by Ti(O-*n*-Pr)$_4$[a]**

| $C$ (%) $100[I(\epsilon)/(I(\epsilon)+I(\epsilon_c))]$ | $M_0/I_0[I(\epsilon)+I(\epsilon_c)]/(I(\alpha')/4)$ | PCL-OH $I(\alpha')/2$ | propanol $I(a')/2$ | monomer $I(\epsilon_c)/2$ | repetitive unit $I(\epsilon)/2$ | $\overline{N_{aag}}$ $4[I(\alpha')/(I(\alpha')+I(a'))]$ |
|---|---|---|---|---|---|---|
| 31.4 | 318 | 1.0 | 0.0 | 54.5 | 25.0 | 4.0 |
| 39.8 | 307 | 1.0 | 0.0 | 46.2 | 30.5 | 4.0 |
| 46.9 | 307 | 1.0 | 0.0 | 40.8 | 36.0 | 4.0 |
| 56.9 | 313 | 1.0 | 0.0 | 33.8 | 44.6 | 4.0 |
| 63.2 | 311 | 1.0 | 0.0 | 28.6 | 49.1 | 4.0 |
| 75.1 | 314 | 1.0 | 0.0 | 19.6 | 59.0 | 4.0 |
| 84.6 | 318 | 1.0 | 0.0 | 12.3 | 67.2 | 4.0 |
| 92.6 | 322 | 1.0 | 0.0 | 6.0 | 74.5 | 4.0 |
| 95.9 | 331 | 1.0 | 0.0 | 3.4 | 79.5 | 4.0 |
| 98.2 | 316 | 1.0 | 0.0 | 1.4 | 77.6 | 4.0 |
| *b* | 316 | 1.0 | 0.0 | 0.0 | 79.1 | 4.0 |
| | av 316 | | | | | |

[a] $I(\alpha')$: integral of the signal HO−C$H_2$− of poly($\epsilon$-caprolactone). $I(a')$: integral of the signal HO−C$H_2$− of 1-propanol. $I(\epsilon)$: integral of the signal −C$H_2$−(C═O)−O− in the repeating unit of poly($\epsilon$-caprolactone). $I(\epsilon_c)$: integral of the signal −C$H_2$−(C═O)−O− of $\epsilon$-caprolactone. [b] Beyond total conversion and after thermal treatment at 140 °C.

**Table 3. Average Number of Active Groups ($\overline{N_{aag}}$) Determination from $^1$H NMR Spectra for Bulk $\epsilon$-Caprolactone Polymerization at 100 °C ($M_0/I_0 = 300$) initiated by Ti(OPh)$_4$**

| $C$ (%) $100[(I(\alpha)+I(\alpha')+I(\alpha_c))/2]/[(I(b)/2)+(I(d'+b')/3)]/4$ | $M_0/I_0$ | PCL−OPh $I(b)/2$ | phenol $I(d'+b')/3$ | monomer $I(\alpha_c)/2$ | repetitive unit $[I(\alpha)+I(\alpha')]/2$ | PCL-OH $I(\alpha')/2$ | $\overline{DP_{NMR}}$ $[I(\alpha)+I(\alpha')]/I(b)$ | $\overline{N_{aag}}$ $3C\,(\%)/\overline{DP_{NMR}}$ |
|---|---|---|---|---|---|---|---|---|
| 12.7 | 374 | 1.0 | 2.2 | 264.7 | 38.4 | 1.1 | 38.4 | 1.0 |
| 19.5 | 374 | 1.0 | 1.6 | 196.3 | 47.7 | 1.0 | 47.7 | 1.2 |
| 27.3 | 351 | 1.0 | 1.2 | 142.4 | 53.6 | 1.0 | 53.6 | 1.5 |
| 45.7 | 366 | 1.0 | 0.8 | 91.1 | 76.8 | 1.1 | 76.8 | 1.8 |
| 70.6 | 363 | 1.0 | 0.7 | 45.0 | 107.9 | 1.0 | 107.9 | 2.0 |
| 85.3 | 362 | 1.0 | 0.7 | 22.9 | 133.0 | 1.0 | 133.0 | 1.9 |
| 88.2 | 377 | 1.0 | 0.9 | 20.8 | 155.2 | 1.0 | 155.2 | 1.7 |
| 96.0 | 350 | 1.0 | 1.1 | 7.5 | 179.6 | 1.0 | 179.6 | 1.6 |
| 98.7 | 327 | 1.0 | 1.3 | 2.5 | 187.2 | 0.9 | 187.2 | 1.6 |
| 99.8 | 350 | 1.0 | 1.7 | 0.5 | 233.0 | 1.0 | 233.0 | 1.3 |
| *b* | 357 | 1.0 | 6.2 | 0.0 | 645 | 1.0 | 645 | 0.5 |
| | av 359 | | | | | av 1.00 | | |

[a] $I(\alpha)$: integral of the signal −C$H_2$−O−(C═O)− in the repeating unit of poly($\epsilon$-caprolactone). $I(\alpha_c)$: integral of the signal −C$H_2$−O−(C═O)- of $\epsilon$-caprolactone. $I(b)$: integral of the signal corresponding to proton in ortho position in the terminal −(O═C)-O*Ph* of poly($\epsilon$-caprolactone). $I(d'+b')$: Sum of integrals of the signals corresponding to proton in para and ortho position in phenol respectively at 6.92 and 6.82 ppm. $I(\alpha')$: integral of the signal HO−C$H_2$− of poly($\epsilon$-caprolactone). $\overline{DP_{NMR}}$: average degree of polymerization calculated from NMR data. [b] Beyond total conversion and after thermal treatment at 140 °C.

carbonyl group of $\epsilon$-caprolactone than in the case of Ti(O-*n*-Pr)$_4$. Actually, this phenomenon is not observed. For example when Takeuchi et al.[31] studied $\epsilon$-caprolactone polymerization at 25 °C initiated by {2,2′-CH$_2$(4-Me-6-$^t$BuC$_6$H$_2$O)$_2$}Ti(O$^i$Pr)$_2$-(OAr)$_2$, only the isoproproxide end groups are identified by NMR spectroscopy. Therefore, even if the Lewis base−adduct formation with Ti(OPh)$_4$ should be easier than that with Ti(O-*n*-Pr)$_4$, this difference in our polymerizations conditions on number of active site may provide from the steric hindrance or complex structure of this initiator.

**Evolution of the Average Number of Active Alkoxide or Aryloxide Groups per Initiator during Polymerization.** To check the hypothesis of a lower average number of active ligands for polymerization with Ti(OPh)$_4$, the evolution of the average number of active alkoxide or aryloxide groups per initiator ($\overline{N_{aag}}$) vs conversion rate was studied for bulk polymerization (100 °C, $M_0/I_0 = 300$) for both initiators. To determine $\overline{N_{aag}}$, polymerizations were carried out in the same conditions than for kinetic study. The only difference was that the aliquots were not immediately immersed in a solution ($CDCl_3$ + few microliters of $CH_3COOH$) but only in deutered chloroform ($CDCl_3$) in order to avoid possible further reactions.

For bulk polymerization with Ti(O-*n*-Pr)$_4$, $\overline{N_{aag}}$ was determined from $^1$H NMR spectrum of aliquots by comparing the integral of the signal $\alpha'$ defined as before to the one of the signal a′ at 3.60 ppm corresponding to HOC$H_2$− of the 1- propanol (3).

$$\overline{N_{aag}} = 4 \times \frac{\text{(area of triplet } \alpha' \text{ at 3.64 ppm)}}{\text{(area of triplet } \alpha' \text{ at 3.64 ppm + area of triplet } \alpha' \text{ at 3.60 ppm)}} \quad (3)$$

This method is correct if the hydrolysis reaction of bonds Ti−O−CH$_2$∼ is complete. Table 2, which presents results of $^1$H NMR quantitative analysis for Ti(O-*n*-Pr)$_4$, shows that the $M_0/I_0$ value measured for each aliquot is about constant and close to 300 which demonstrates that the hydrolysis reaction of Ti−O−CH$_2$∼ bonds is complete in $CDCl_3$.

For bulk polymerization with Ti(OPh)$_4$, $\overline{N_{aag}}$ was determined from $^1$H NMR spectrum of aliquots by first calculating the average degree of polymerization by NMR, $\overline{DP_{NMR}}$, corresponding to the average number of monomer unit polymerizing per active aryloxide group and determined with the relation in (4). $\alpha$ and $\alpha'$ are defined as before and the signal b at 7.07 ppm corresponds to the resonance of the proton in ortho position in COOPh polymer end group.

$$\overline{DP_{NMR}} = \frac{\text{area of triplet } \alpha \text{ at 4.06 ppm + area of triplet } \alpha' \text{ at 3.64 ppm}}{\text{area of doublet b at 7.07 ppm}} \quad (4)$$

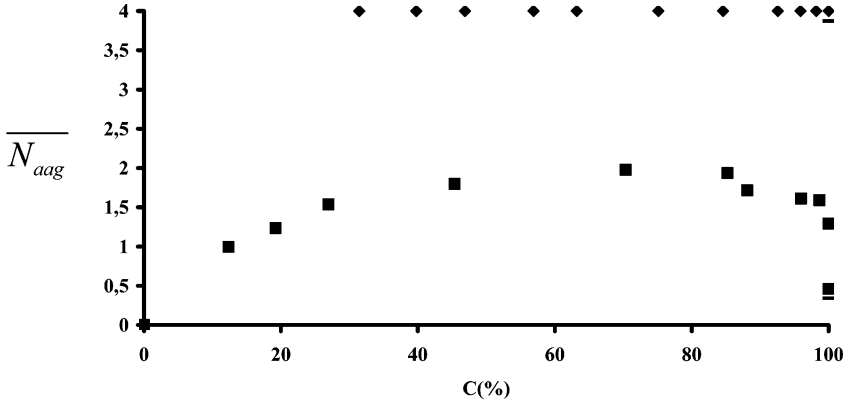



**Figure 6.** Evolution of average number of active alkoxide groups per initiator ($\overline{N_{aag}}$) vs monomer conversion for bulk $\epsilon$-caprolactone polymerization between the rheometer plates at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium *n*-propoxide (◆) or titanium phenoxide (■). The underlined points correspond to a further thermal treatment at 140 °C for few minutes.

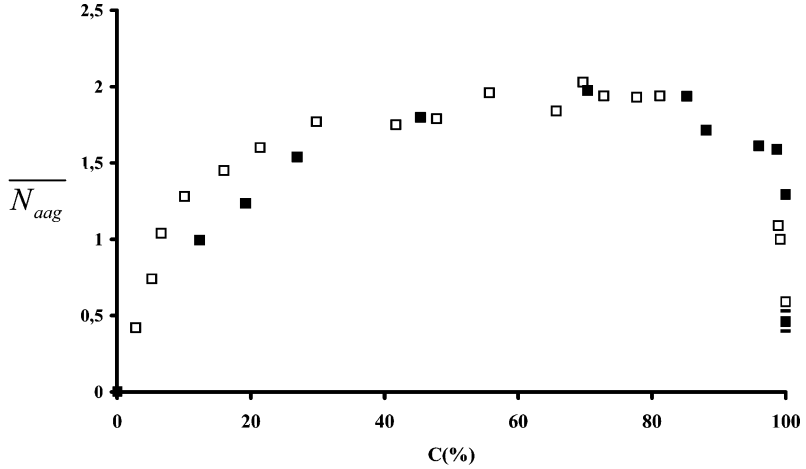



**Figure 7.** Evolution of average number of active alkoxide groups per initiator ($\overline{N_{aag}}$) vs monomer conversion ($C$) for bulk (■) and solution (□) $\epsilon$-caprolactone polymerization at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium phenoxide. The underlined points correspond respectively to a further thermal treatment at 140 °C for few minutes (■) for the bulk polymerization and to the polymerization beyond the total conversion for solution polymerization (□).

$\overline{N_{aag}}$ was then connected with $\overline{DP_{NMR}}$ by the eq 5.

$$\overline{N_{aag}} = \frac{\dfrac{M_0}{\overline{I_0}}}{\overline{DP_{NMR}}} \times \frac{C\,(\%)}{100} = \frac{3C\,(\%)}{\overline{DP_{NMR}}} \qquad (5)$$

Table 3, which shows results of $^1$H NMR quantitative analysis for Ti(OPh)$_4$, demonstrates two important points. First, the $M_0/I_0$ ratio measured for each aliquot is in average equal to 359, which is superior to the theoretical ratio determined by weighing. This suggests an incomplete hydrolysis of Ti−OPh bonds in $CDCl_3$. Nevertheless, the determination of $\overline{N_{aag}}$ is always correct because eq 5 does not depend on the degree of hydrolysis of titanate bonds. Second, as hydrolysis of Ti−O−$CH_2$∼ bonds is complete (integral of the signal $\alpha' = 1.00$ on the average), $\overline{DP_{NMR}}$ could be also calculated by replacing the integral of the signal b at 7.07 ppm relative to terminal COOPh of the polymer by the one of the signal $\alpha'$ at 3.64 ppm relative to the terminal HO−$CH_2$− of the polymer. From NMR approach, the comparison between integrals of aromatic and aliphatic protons is possible in our conditions by proper angle pulse and time between two pulses.

Figure 6 represents the evolution of $\overline{N_{aag}}$ vs monomer conversion in percent for both initiators.

With Ti(O-*n*-Pr)$_4$, $\overline{N_{aag}}$ is constant and is equal to 4 from 30% to 100% conversion. Aliquots could not be extracted before 30% conversion because of the polymerization rate. This result allows concluding that all the ligands of the initiator are active at least from 30% conversion, and it can be supposed that this is true from the first percentages of conversion. This value is the same that the one found by Kricheldorf et al.[12] with Ti(OBu)$_4$ (bulk polymerization with first dissolution Ti(OBu)$_4$ in $CH_2Cl_2$ (1 mol/L), $T = 100$ °C, $M_0/I_0 = 400$).

With Ti(OPh)$_4$, $\overline{N_{aag}}$ increases gradually during polymerization to reach a maximun (2.0) for around 70% conversion and then decreases down to 1.3 until 99.8% of conversion. The first conclusion is that only half of the phenoxide ligands are active during the polymerization, which is in agreement with the slower kinetic of polymerization and the higher number-average molecular weight of the polymer obtained with this initiator.

On both curves, a last point was added corresponding to the $\overline{N_{aag}}$ value if the reaction mixture is kept in situ after complete conversion and heated at 140 °C over several minutes. This point was determined during the rheological study. It can be observed that $\overline{N_{aag}}$ is still equal to 4 with Ti(O-*n*-Pr)$_4$ whereas continues to decrease with Ti(OPh)$_4$ ($\overline{N_{aag}} = 0.5$).

More precisely, the increase of $\overline{N_{aag}}$ during the first 70% of conversion means that a progressive initiating step is consistent

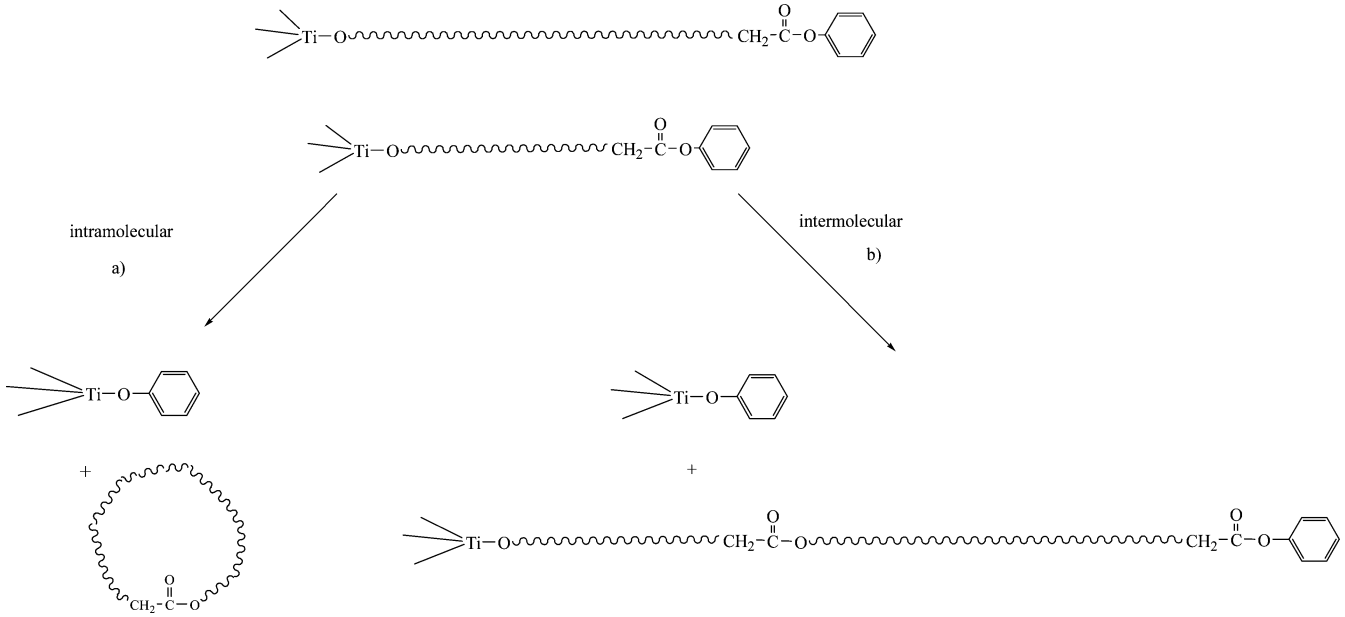



**Figure 8.** Inter- (a) and intramolecular (b) transesterification reactions with phenoxyl ester end groups of poly($\epsilon$-caprolactone).

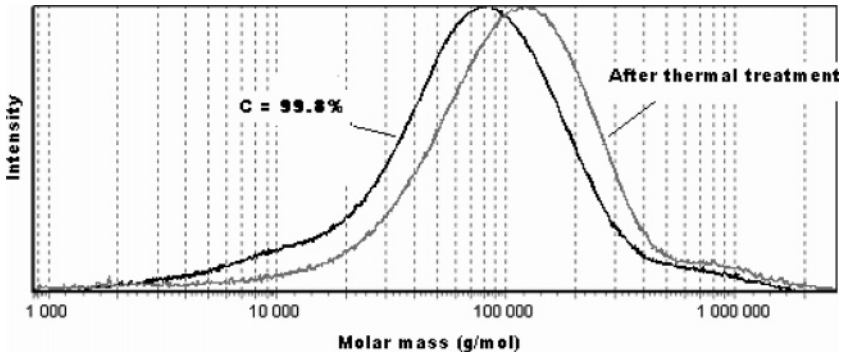



**Figure 9.** Size exclusion chromatograms of poly($\epsilon$-caprolactone) isolated obtained by bulk polymerization between the rheometer plates at $T$ = 100 °C ($M_0/I_0$ = 300) initiated with titanium phenoxide. Dark line: after 99.8% of monomer conversion; Grey line: after further thermal treatment at 140 °C during few minutes.

with the high polydispersity ($I_p$ = 3.1) found for the polymer isolated at the total conversion (Table 1). To determine if this increasing is linked to either a slow homogenization of the medium or is inherent to the $Ti(OPh)_4$ molecule, the evolution of $\overline{N_{aag}}$ vs monomer conversion was also studied for an isothermal solution polymerization in toluene (100 °C, $M_0/I_0$ = 300). $\overline{N_{aag}}$ was determined from $^1$H NMR spectrum of aliquots immersed immediately in $CDCl_3$ by first calculating $\overline{DP_{NMR}}$ defined by the relation (6) before calculating $\overline{N_{aag}}$ by relation 5, $\alpha$ and $\alpha'$ being defined as before.

$$\overline{DP_{NMR}} = \frac{\text{area of triplet } \alpha \text{ at 4.06 ppm} + \text{area of triplet } \alpha' \text{ at 3.64 ppm}}{\text{area of doublet } \alpha' \text{ at 3.64 ppm}} \qquad (6)$$

The signal $\alpha'$ at 3.64 ppm was used because the signal b at 7.07 ppm is hidden by signals of toluene.

Figure 7 represents the evolution of $\overline{N_{aag}}$ vs monomer conversion for respectively bulk and solution polymerization. A similar phenomenon is observed for solution polymerization with a little faster increase of $\overline{N_{aag}}$ in that case. Consequently, it can be concluded that this first evolution of $\overline{N_{aag}}$ is inherent to the $Ti(OPh)_4$ initial structure but also to its modification occurring during polymerization. The formation of $TiOCH_2$-polymer could enhance the coordination−insertion through another TiOPh bond.

The second part of the curve corresponding to the decrease of $\overline{N_{aag}}$ at the end of the consumption of the monomer and even beyond, observed for bulk and solution polymerization, means a diminution of the concentration of phenoxyl ester end groups of poly($\epsilon$-caprolactone) without disappearance of phenyl groups. It may be explained by intra- or intertransesterification reactions with phenoxyl ester end groups. These reactions lead to the formation of either macrocycles (Figure 8a) or larger poly($\epsilon$-caprolactone) chains (Figure 8b) and to the "regeneration" of titanate phenoxide bonds. These transesterification reactions are favored with end groups in the case of polymerization with $Ti(OPh)_4$ because the C−O bond of the terminal phenoxyl ester is more prone to nucleophilic substitution than the C−O bond in the repetitive unit due to the influence of the phenyl group on electronic delocalization. The results of the SEC analysis (Table 1) confirm this conclusion as the number-average molecular weight of the polymer isolated after thermal treatment at 140 °C ($M_n$ = 43 600 g/mol) is much higher than the one for the polymer isolated at 99.8% conversion ($M_n$ = 21 500 g/mol). For $Ti(O\text{-}n\text{-}Pr)_4$, the number-average molecular weight remains constant after total conversion. A few authors have already demonstrated[12,13,42,43] the role of the transesterification in polymerization of various lactones by coordination−insertion mechanisms. They showed that the molecular weight distribution is substantially broadened when the living chains are left in the reaction medium beyond the time required for complete

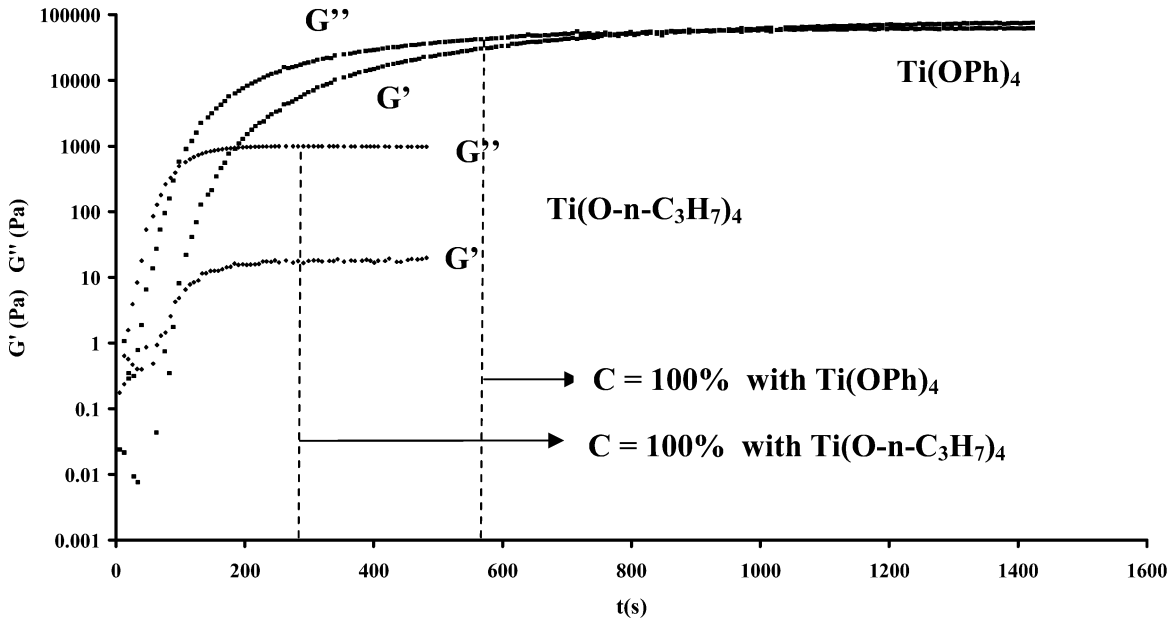



**Figure 10.** Evolution of $G'$ and $G''$ during bulk $\epsilon$-caprolactone in situ polymerization between the rheometer plates at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium *n*-propoxide or titanium phenoxide. Vertical dashed line corresponding to 100% monomer conversion.

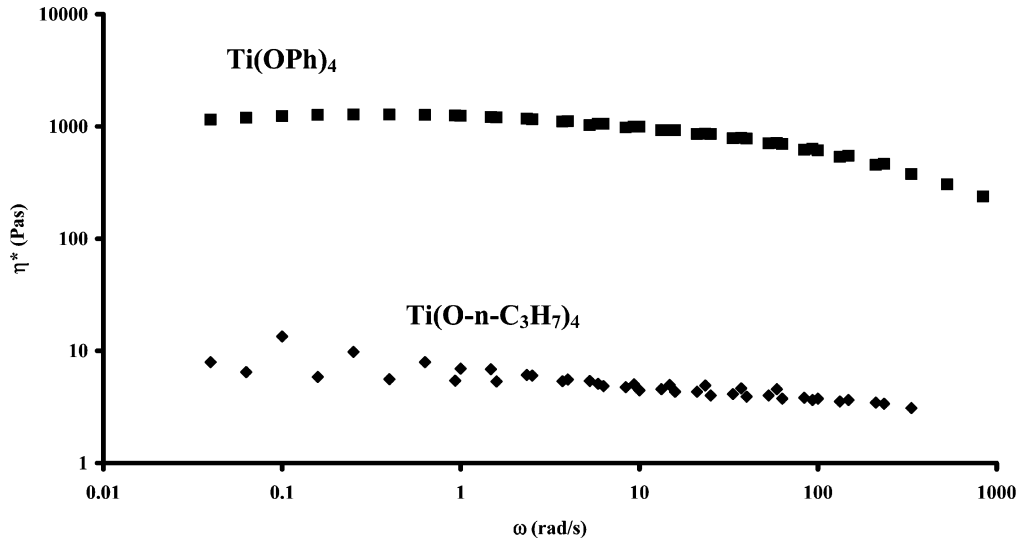



**Figure 11.** Evolution of complex shear viscosity at 140 °C of the polymer obtained after bulk $\epsilon$-caprolactone polymerization in situ between the rheometer plates at $T = 100$ °C ($M_0/I_0 = 300$) initiated with titanium *n*-propoxide (◆) or titanium phenoxide (■), treated few minutes at 140 °C and after hydrolysis of Ti−O-bonds.

monomer conversion. Generally, formation of cyclic oligomers is also observed. In our case, comparison of the chromatogram for $Ti(OPh)_4$ just at the end of total monomer conversion and after further thermal treatment (Figure 9) displayed a shift of the weight distribution toward higher average molecular weight but without appearance of others peaks. This observation is more consistent in our analytical conditions with intermolecular transesterification leading to the formation of larger chains.

The rheological kinetic study also confirms the formation of large chain beyond of the end of conversion in polymerization with $Ti(OPh)_4$. Indeed, for $Ti(O\text{-}n\text{-}Pr)_4$, $G'$ and $G''$ remains constant after the total consumption of the monomer, whereas $G'$ and $G''$ in polymerization with $Ti(OPh)_4$ go on rising after the end of polymerization (Figure 10). At the end of the conversion, reaction mixtures were kept in situ then heated at 140 °C for several minutes. Then reaction mixtures were immediately dissolved in chloroform and solutions were conserved several days in order to hydrolyze all titanate bonds, which were checked by $^1H$ NMR. Then the modulus of the complex shear viscosity ($|\eta^*(\omega)|$) were measured at 140 °C (Figure 11) on polymers collected after evaporation of solvent and dried at 40 °C. It logically appears that the zero shear viscosity is much higher with $Ti(OPh)_4$ (1200 Pas) than with $Ti(O\text{-}n\text{-}Pr)_4$ (7 Pas).

All the results suggest that it is possible to obtain high molecular weight poly($\epsilon$-caprolactone) with $Ti(OPh)_4$ first due to a lower number of active site and second to intermolecular transesterification with phenoxyl ester end groups as demonstrated by the analysis of the $\overline{N_{aag}}$ evolution.

## Conclusion

$\epsilon$-Caprolactone polymerization initiated by $Ti(OPh)_4$ or by titanium propoxide, $Ti(O\text{-}n\text{-}Pr)_4$, was compared. The kinetics of polymerization with $Ti(OPh)_4$ is slower and the polymer synthesized presents higher molecular weight and higher polydispersity. The molecular weight of the polymer still increases beyond the end of the conversion because of important

transesterification reactions with end groups that lead to the formation of larger poly($\epsilon$-caprolactone) chains and to the "regeneration" of titanate phenoxide bonds. All these results are consistent with the evolution of the average number of active aryloxide groups per initiator ($\overline{N}_{aag}$) during polymerization for this initiator, which gradually reaches a maximum before decreasing at the end of the conversion and even beyond.

**Acknowledgment.** The work was realized in the CPR "Contrat Program de Recherche du CNRS" program untitled "Reactive processing". The authors wish to thank the NMR department of the Fédération des Polymeristes Lyonnais (FR 2151), CNRS, for NMR analyses and the ADEME (Agence pour le Développement et la Maîtrise de l'Energie) for its financial support.

## References and Notes

(1) Loefgren, A.; Albertsson, A. C.; Dubois, P.; Jerome, R. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1995**, *C35*, 379−418.
(2) Penczek, S. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 1919−1933.
(3) Kubisa, P.; Penczek, S. *Prog. Polym. Sci.* **1999**, *24*, 1409−1437.
(4) Mecerreyes, D.; Jerome, R.; Dubois, P. *Adv. Polym. Sci.* **1999**, *147*, 1−59.
(5) Kricheldorf, H. R.; Kreiser-Saunders, I. *Macromol. Symp.* **1996**, *103*, 85−102.
(6) Kricheldorf, H. R.; Jonté, M.; Dunsing, R. *Makromol. Chem.* **1986**, *187*, 771−785.
(7) Kricheldorf, H. R.; Dunsing, R. *Makromol. Chem.* **1986**, *187*, 1611−1625.
(8) Hofman, A.; Szymanski, R.; Slomkowski, S.; Penczek, S. *Makromol. Chem.* **1984**, *185*, 655−667.
(9) Hofman, A.; Slomkowski, S.; Penczek, S. *Makromol. Chem.* **1984**, *185*, 91−101.
(10) Kricheldorf, H. R.; Kreiser-Saunders, I.; Scharnagl, N. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 285−298.
(11) Jedlinski, Z.; Kowalczuk, M. *Macromolecules* **1989**, *22*, 3242−3244.
(12) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286−293.
(13) Dubois, Ph.; Barakat, R. J.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 4407−4412.
(14) Storey, R. F.; Sherman, J. W. *Macromolecules* **2002**, *35*, 1504−1512.
(15) Lecomte, Ph.; Stassin, F.; Jerome, R. *Macromol. Symp.* **2004**, *215*, 325−338.
(16) Stridsberg, K.; Albertsson, A.-C. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 3407−3417.
(17) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689−695.
(18) Ouhadi, T.; Stevens, C.; Teyssié, P. *Makromol. Chem. Suppl.* **1975**, *1*, 191−201.
(19) Liu, Y. C.; Ko, B. T.; Lin, C. C. *Macromolecules* **2001**, *34*, 6196−6201.
(20) Chen, H. L.; Ko, B. T.; Huang, B. H.; Lin, C. C. *Organometallics* **2001**, *20*, 5076−5083.
(21) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114−2122.
(22) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176.
(23) Vivas, M.; Contreras, J. *Eur. Polym. J.* **2003**, *39*, 43−47.
(24) Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* **2004**, *23*, 3296−3302.
(25) Dobrzynski, P.; Kasperczyk, J.; Bero, M. *Macromolecules* **1999**, *32*, 4735−4737.
(26) Shen, Z. Q.; Shen, Y. Q.; Zhang, F. Y.; Zhang, Y. F. *Polym. J.* **1995**, *27*, 59−64.
(27) Agarwal, S.; Mast, C.; Dehnicke, K.; Greiner, A. *Macromol. Rapid Commun.* **2000**, *21* (5), 195−212.
(28) Yasmashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798−1806.
(29) Ling, J.; Zhu, W.; Shen, Z. *Macromolecules* **2004**, *37*, 758−763.
(30) Yu, C.; Zhang, L.; Shen, Z. *Eur. Polym. J.* **2003**, *39*, 2035−2039.
(31) Takeuchi, D.; Nakamura, T.; Aida, T. *Macromolecules* **2000**, *33*, 725−729.
(32) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968−7973.
(33) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763−5768.
(34) Yoshino Takeshi, Kijima Ichiro, Ochi Miyoshi, Sampei Akio, Sai Shoki. Synthesis of aryl titanate. *Tokyo Univ. Sci., Kogyo Kagaku Zasshi* **1957**, *60*, 1124−1125.
(35) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci.: Part A: Polym. Chem.* **1982**, *20*, 319−326.
(36) Gimenez, J.; Cassagnau, P.; Fulchiron, R.; Michel, A. *Macromol. Chem. Phys.* **2000**, *201*, 479−490.
(37) Storey, R. F.; Sherman, J. W. *Macromolecules* **2002**, *35*, 1504−1512.
(38) Malhotra, K.; Sharma, N.; Chaudhry, S. C. *Transition Met. Chem.* **1981**, *6*, 238−240.
(39) Coffindaffer, T. W.; Rothwell, I. A.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906−2910.
(40) Malhotra, K. C.; Martin, R. L. *J. Orgametal. Chem.* **1982**, *239*, 159−187.
(41) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wikinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, pp 335−364.
(42) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Symp.* **1997**, *123*, 93−101.
(43) Penczek, S.; Duda, A.; Szymanski, R. *Macromol. Symp.* **1998**, *132*, 441−449.

MA051272V