

Continuous Polymerization of ϵ -Caprolactone Initiated by Titanium Phenoxide in a Twin-Screw Extruder

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ABSTRACT: The continuous polymerization of ϵ -caprolactone initiated by titanium phenoxide was carried out in both an internal mixer and a twin-screw extruder. The polymerization was performed under different processing conditions, including various temperatures and screw speeds. To perform a kinetic study, samples were collected along the time axis (internal mixer) and along the screw axis (extruder). Size exclusion chromatography and proton nuclear magnetic resonance were used to study the evolution of the conversion degree with mixing time and with the extruder. The rheological behavior was also character-

ized. Temperature had a strong effect on conversion in the internal mixer, whereas in the twin-screw extruder, both temperature and screw speed played major roles. The specificity of the titanium phenoxide to lead to high-molar-mass poly(ϵ -caprolactone) under these processing conditions was also confirmed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3480–3487, 2008

Key words: degree of polymerization (DP); kinetics (polym.); NMR; reactive extrusion; ring-opening polymerization

INTRODUCTION

The ring-opening polymerization of ϵ -caprolactone by coordination–insertion mechanism has been thoroughly investigated because it provides direct and easy access to the corresponding high-molar-mass poly(ϵ -caprolactone) (PCL).^{1,2} The most widely used initiators are various and include tin^{3–6} and aluminum alkoxides as well as carboxylates.^{7–10} However, initiators such as zinc,¹¹ titanium,¹ magnesium,¹² and calcium¹³ derivatives have also been tested. With regard to the mechanism, the covalent metal alkoxide or, carboxylate with empty *d* orbitals, reacts as a coordination initiator. The polymerization proceeds via an acyloxygen cleavage of the lactone with insertion of the monomer into the metal–oxygen bond of the initiator (Fig. 1).

The influence on this process by natural metals and ligands has been studied extensively.^{14–16} Through the comparison of both titanium *n*-propoxide and titanium phenoxide [Ti(OPh)₄], it was shown that it was possible to obtain high-molar-mass PCL with Ti(OPh)₄ for the same monomer/initiator

molar ratio. This difference was due to a lower amount of the phenoxide group involved in the growth of the polymer chains. Specific intermolecular transesterification with phenoxyl ester end groups (Fig. 2) was highlighted. As demonstrated by analysis of the evolution of the number of active phenoxide sites during polymerization with those after complete monomer conversion, there was an increase in the molar mass.¹⁷

With regard to the process of polymerization, this living polymerization has already been conducted by reactive extrusion.^{18–25} Indeed, reactive extrusion is an attractive route for polymerization because of its numerous advantages, including a solvent-free melt process, a continuous reaction, and the ability to start from a monomer to obtain the desired polymer.

Raquez et al.²⁶ recently published a review of specific polymerizations carried out by reactive extrusion. In particular, they showed that, in approximately 2 min, 99% of ϵ -caprolactone conversion is obtained at 150°C with Al(O_{sec}Bu)₃ as an initiator.²⁷ Kim and White^{28,29} described the influence of the screw speed, feed rate, and monomer over the initiator ratio on the evolution of the PCL molar mass obtained at the die. Balakrishnan et al.³⁰ reported the synthesis of three-arm PCL with aluminum tri-*sec*-butoxide as the initiator. They found that a screw configuration composed of entirely conveying elements allowed them to obtain high-molecular-weight PCL. Hamaide and Lavit³¹ polymerized ϵ -

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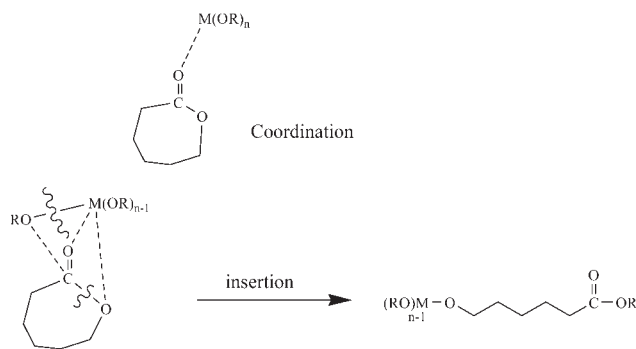


Figure 1 Coordination–insertion mechanism of ϵ -caprolactone polymerization.

caprolactone in a mini-extruder in the presence of benzyl alcohol as a transfer agent. They showed that this device allowed them to obtain functionalized polymer chains.

With regard to the work that has been performed by our group, it was previously shown that the use of $\text{Ti}(\text{OPh})_4$ in bulk led to high-molar-mass PCL because of the specificity of the phenoxide ligands. The key point in this case is to take advantage of both the specificity of this new initiator and the continuous extrusion process to obtain high-molar-mass PCL. A fundamental approach with ϵ -caprolactone polymerization in the extruder is to follow the kinetics along the extruder. Samples were collected along the extruder with devices inserted along the barrel of the extruder, which were developed for this purpose.³² The kinetics of polymerization were followed by proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy and size exclusion chromatography (SEC) analysis and compared to similar procedures carried out in internal mixer. The rheological properties were also compared.

EXPERIMENTAL

Materials

$\text{Ti}(\text{OPh})_4$ was synthesized by the method described by Yoshino et al.³³ As in the typical method, titanium *n*-propoxide and phenol (99%, molar ratio = 1 : 4; Aldrich, France) were mixed in dry toluene (99.8%,

Aldrich). After 1 h 30 min of heating with reflux, a dark red-orange solution was obtained. After the elimination of propanol with fractional distillation at reduced pressure to complete the reaction, washing with dry *n*-hexane (>95%, Aldrich), and drying *in vacuo* at 40°C, an orange powder of $\text{Ti}(\text{OPh})_4$ was identified by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy.¹⁷ It was stored under argon.

Anhydrous solvents (toluene and *n*-hexane) were purchased from Aldrich and stored under argon and on molecular sieves. Deuterated chloroform CDCl_3 (Aldrich), titanium *n*-propoxide (98%, Aldrich), and ϵ -caprolactone (99%, Lancaster, France) were used as received.

Polymerization procedure of ϵ -caprolactone in the internal mixer

For the bulk polymerization of ϵ -caprolactone in the internal mixer, namely, a Haake Rheomixer (Germany), the initiator was dispersed in ϵ -caprolactone in a Schlenk flask under argon at room temperature for an M_0/I_0 ratio equal to 300 (where I_0 is the initial number of moles of the initiator and M_0 is the number of moles of ϵ -caprolactone). Then, around 45 mL of the mixture was introduced in the Haake reactor, which was preheated to either 80 or 100°C. The polymerization was carried out with a roller rotation speed of 50 rpm. Samples were collected along the time of mixing without stopping the rotors.

Polymerization procedure of ϵ -caprolactone in the extruder

The polymerization of ϵ -caprolactone was performed in a laboratory modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder (Germany) (Fig. 3). The initiator was dispersed in ϵ -caprolactone in a Schlenk flask under argon at room temperature with an M_0/I_0 ratio equal to 300. An Ismatec MS-REGLO peristaltic pump was used to feed the mixture into the extruder. Experiments were performed under two different processing conditions: the barrel set temperatures were 150 and 100°C, the screw speeds were 15 and 50 rpm, and the flow rates were

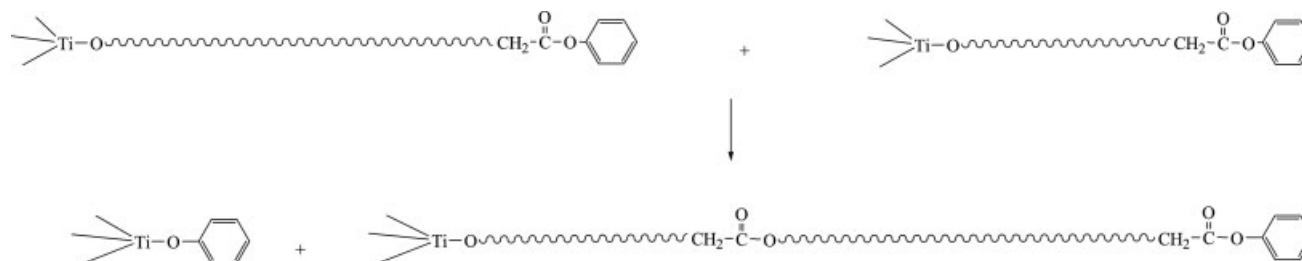


Figure 2 Intermolecular transesterification reactions with phenoxy ester end groups of PCL.

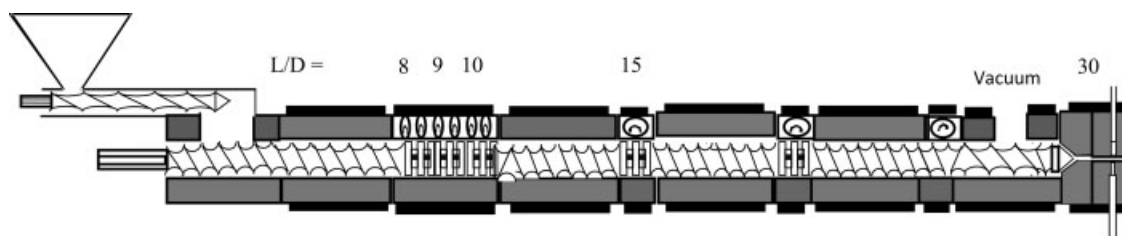


Figure 3 Extruder layout and sampling locations

10 and 15 mL/min (i.e., 150°C, 15 rpm, and 10 mL/min and 100°C, 50 rpm, and 15 mL/min, respectively). Samples for subsequent offline characterization were collected quickly along the extruder axis with a series of sampling devices. The location of these devices is also shown in Figure 3.

Characterization

High-resolution liquid $^1\text{H-NMR}$ spectroscopy was carried out with a Bruker AC 250 instrument (Germany) at 250 MHz for ^1H . Deuterated chloroform, CDCl_3 , was used as the solvent for analysis. Chemical shift (δ) values are presented in parts per million with reference to internal tetramethylsilane.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (I_p) were measured by SEC. Solutions were prepared in tetrahydrofuran (THF; 99.9%) and prefiltered on a filter plate (hydrophobic polytetrafluoroethylene, pore size = 0.45 μm) before injection. The SEC apparatus was equipped with two Waters Ultrastaygel columns (France) (HR1 and HR4; inner diameter = 7.8 mm, length = 300 mm, particle size = 5 μm) and a Waters R410 refractometer detector. THF was used as the 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 ($a = 0.786$, $k = 0.00014 \text{ mg}/1$).³⁴ To follow the ϵ -caprolactone conversion, a calibration curve was established from different monomer concentrations in THF.

Oscillatory rheological measurements were carried out in a stress-controlled Reologica StressTech HR rotational rheometer (Sweden) at 140°C with parallel-plate geometry. The gap and diameter of the plates were 0.8 mm and 2.0 cm, respectively. A frequency sweep from 0.04 to 100 rad/s under a constant shear stress of 10 Pa was performed for each sample.

Kinetics of polymerization

The evolution of the conversion degree [$C(\%)$] versus time of mixing in the internal mixer or along the

extruder was evaluated by both SEC and $^1\text{H-NMR}$ quantitative analysis.

From the $^1\text{H-NMR}$ spectrum (Fig. 4), C was calculated by the ratio of the number of moles of monomer that reacted to the initial number of moles of monomer molecules with the following equation:

$$C(\%) = \frac{A_{\alpha 4.06} + A_{\alpha' 3.64}}{A_{\alpha 4.06} + A_{\alpha' 3.64} + A_{\alpha_c 4.23}} \quad (1)$$

where $A_{\alpha 4.06}$, $A_{\alpha' 3.64}$, and $A_{\alpha_c 4.23}$ are the areas of the triplet at α (4.06 ppm), α' (3.64 ppm), and α_c (4.23 ppm). The signals α at 4.06 ppm, α' at 3.64 ppm, and α_c at 4.23 ppm correspond to the proton resonance of the methylene groups $-\text{O}-\text{CH}_2-(\text{CH}_2)_4-\text{C}(=\text{O})-$ in the repeat unit of the polymer, next to the terminal hydroxyl of the polymer, and in the monomer, respectively.^{1,17,35}

Nevertheless, with a calibration curve obtained under the same analysis conditions but with different concentrations of monomer, ϵ -caprolactone conversion could be obtained from SEC analysis and compared to the conversion calculated by NMR.

The degree of polymerization determined by NMR ($\overline{\text{DP}}_{\text{NMR}}$), which corresponded to the average number of monomer units polymerizing per active aryloxide group, was determined by Eq. (2), with α and α' as previously defined:

$$\overline{\text{DP}}_{\text{NMR}} = \frac{A_{\alpha 4.06} + A_{\alpha' 3.64}}{A_{\alpha' 3.64}} \quad (2)$$

The degree of polymerization determined by SEC ($\overline{\text{DP}}_{\text{SEC}}$) was obtained by the division of M_n by the molar mass of the repetitive unit, which was 114 g/mol. M_n , M_w , and I_p were measured by SEC in THF as previously described.

RESULTS AND DISCUSSION

Polymerization in an internal mixer

The time-conversion curves of ϵ -caprolactone polymerization with $\text{Ti}(\text{OPh})_4$ obtained at both 80 and 100°C in the internal mixer are reported in Figure 5.

It is possible to notice the accuracy of both $^1\text{H-NMR}$ and SEC analysis to follow the conversion of ϵ -caprolactone in the internal mixer. At 100°C, the

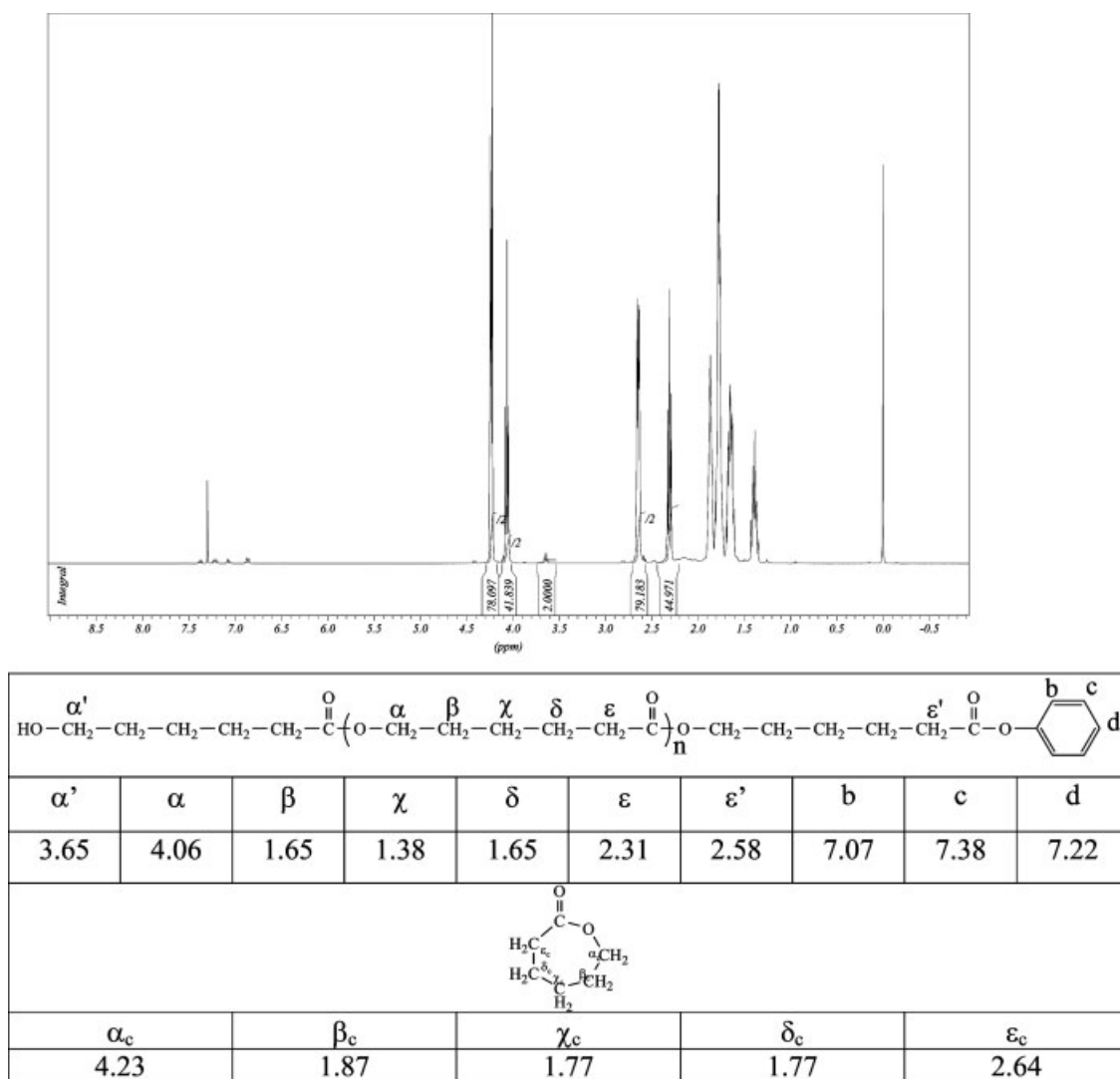


Figure 4 $^1\text{H-NMR}$ spectrum (measured in CDCl_3 at 250 MHz) of the reaction medium from the polymerization of ϵ -caprolactone initiated with $\text{Ti}(\text{OPh})_4$ ($M_0/I_0 = 300$) at 100°C during 100 s in an internal mixer.

polymerization proceeded rapidly, taking approximately 200 s to reach almost 100% conversion. However, at 80°C , this reaction speed was slower, and the maximum conversion is reached after approximately 1000 s. These results were directly related to the influence of the temperature on the polymerization conversion; higher temperatures resulted in higher conversions. A similar effect was observed by Kim and White³⁶ in a study of the polymerization of ω -lauryl lactam. With respect to the effect of mixing, an experiment carried out between plates of a rheometer at 100°C (Fig. 6)¹⁷ demonstrated a higher degree of conversion in a shorter range of time (400 s to reach the highest conversion at 100°C in the rheometer) when shearing was applied on the reaction medium. The effect of shearing may have increased the diffusion of the reactants and enhanced the reaction. A minor side effect may have included slight self-heating in the Haake plasticorder. Navarchian et al.³⁷

studied the effect of shear rate on the kinetics of linear polyurethane formation and found an increase in conversion with shear.

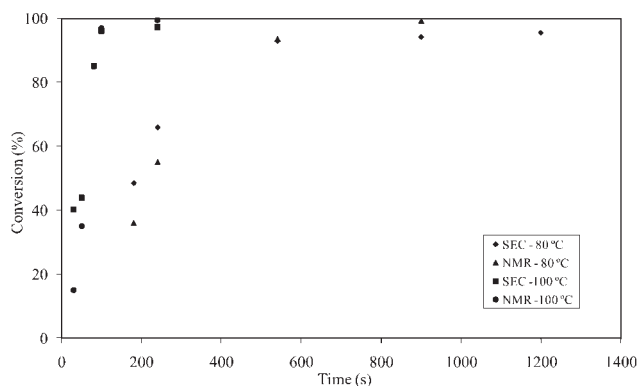


Figure 5 Evolution of the conversion of ϵ -caprolactone as a function of the reaction time in an internal mixer at 80 and 100°C , 50 rpm, and $M_0/I_0 = 300$.

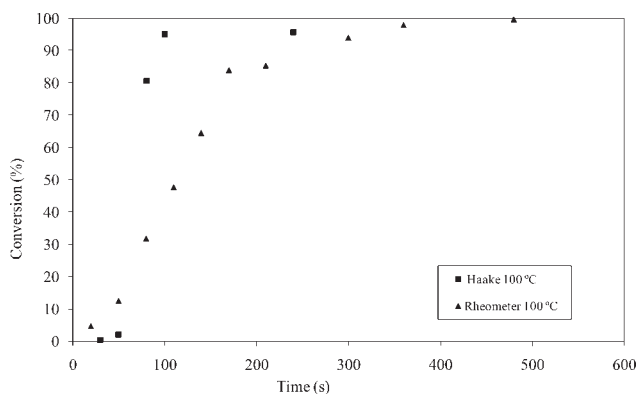


Figure 6 Time-conversion curves for the bulk polymerization of ϵ -caprolactone ($M_0/I_0 = 300$) initiated with $\text{Ti}(\text{OPh})_4$ (\blacktriangle) between rheometer plates at 100° or (\blacksquare) in an internal mixer at 100°C . The conversion was calculated on the basis of $^1\text{H-NMR}$ spectroscopy.

To go further into the ϵ -caprolactone polymerization kinetics, the good linearity of $\text{Ln}[100 - C(\%)]$ versus time obtained at 80 and 100°C indicated that polymerization was first-order in the monomer, which was consistent with the living character of this polymerization (Fig. 7). The polymerization of ϵ -caprolactone initiated by titanium derivatives under the conditions studied obeyed Eq. (3), where $[M]$ is the monomer concentration and K_{app} is the apparent polymerization rate:

$$-\frac{d[M]}{dt} = K_{\text{app}}[M] \quad (3)$$

The K_{app} values deduced were equal to 0.046 and 0.006 s^{-1} at 100 and 80°C , respectively. The evolution of these values was consistent with the increase in temperature. These values also highlighted the influence of shearing on the polymerization kinetics. Actually, the value found when the polymerization was carried out between the plates of a rheometer under the same experimental conditions (100°C) was

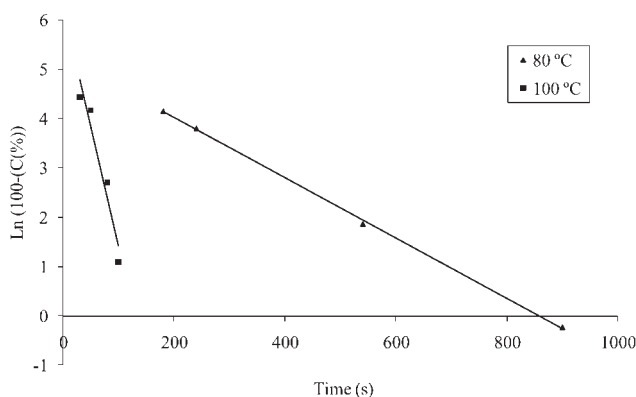


Figure 7 $\text{Ln}[100 - C(\%)]$ as a function of time in bulk ϵ -caprolactone polymerization in an internal mixer at (\blacktriangle) 80°C and (\blacksquare) 100°C , 50 rpm, and $M_0/I_0 = 300$.

0.0125 s^{-1} .¹⁷ All of these observations confirmed the role of shearing on the ring-opening polymerization of ϵ -caprolactone by $\text{Ti}(\text{OPh})_4$.

The effect of temperature was also pronounced in the evolution of $\overline{DP}_{\text{NMR}}$, as depicted in Figure 8. At 100°C in the internal mixer, $\overline{DP}_{\text{NMR}}$ increased strongly and reached a value of 325 at 240 s. At 80°C , it increased progressively and reached a value of 180 at 900 s. The difference in the evolution of $\overline{DP}_{\text{NMR}}$ at the two different temperatures was in line with the conversion and the specificity of the initiator. As expected, the effect of mixing was also evident on the evolution of $\overline{DP}_{\text{NMR}}$ along the time. As for conversion, a higher $\overline{DP}_{\text{NMR}}$ was obtained at a lower reaction time when mixing was applied. Generally, the average number of active ligands for polymerization ($\overline{N}_{\text{aag}}$) for titanium alkoxide is constant along the polymerization. However, we previously demonstrated¹⁷ that, in the case of $\text{Ti}(\text{OPh})_4$, this value evolved with the monomer conversion. When bulk polymerization (100°C , $M_0/I_0 = 300$) was carried out between the plates of a rheometer, $\overline{N}_{\text{aag}}$ gradually increased to reach a maximum of approximately 2 before decreasing at the end of the conversion and even more down to 0.5. In this case, a $\overline{DP}_{\text{NMR}}$ of 325 corresponded roughly to 1 in $\overline{N}_{\text{aag}}$, as calculated with Eq. (4):

$$\overline{N}_{\text{aag}} = \frac{M_0}{I_0} \times \frac{C(\%)}{100} = \frac{3C(\%)}{DP_{\text{NMR}}} \quad (4)$$

At 80°C , the $\overline{DP}_{\text{NMR}}$ reached after 900 s of polymerization was 185, which corresponded to a $\overline{N}_{\text{aag}}$ value of 1.6. The value was slightly higher than the one obtained at 100°C for shorter times. This highlights the specific intermolecular transesterification with phenoxy ester end groups (Fig. 2), which was predominant at high degrees of conversion and enhanced by temperature. Indeed, among the factors affecting the transesterification reactions, we can cite

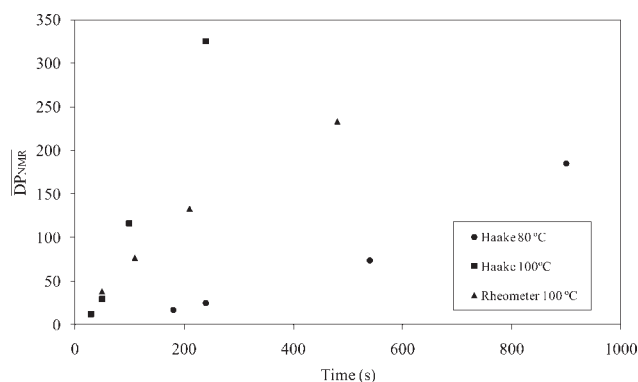


Figure 8 Evolution of $\overline{DP}_{\text{NMR}}$ and the conversion as a function of the reaction time in an internal mixer at 80 and 100°C , 50 rpm, and $M_0/I_0 = 300$.

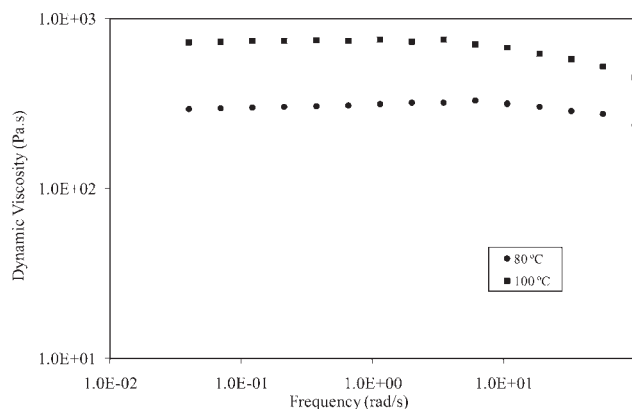


Figure 9 Dynamic viscosity of ϵ -caprolactone polymerized in an internal mixer at 80 and 100°C, 50 rpm, and $M_0/I_0 = 300$.

temperature,³⁸ reaction time,³⁹ type and concentration of the catalyst or initiator,¹ and the nature of the ester cyclic monomer.⁴⁰

In accordance with previous data, the viscosity was higher when polymerization was performed at 100°C (728 Pa s) than when it was performed at 80°C (295 Pa s; Fig. 9). Because \overline{DP}_{NMR} at this temperature was higher, this behavior was expected. These values were consistent with those obtained in the rheometer,¹⁷ where 1200 Pa s was obtained for the zero-shear viscosity measured at 140°C on polymers treated for a few minutes at 140°C after polymerization was carried out at 100°C.

Polymerization in the twin-screw extruder

The polymerization of ϵ -caprolactone in the twin-screw extruder was performed at different barrel temperatures (150 and 100°C) and different screw

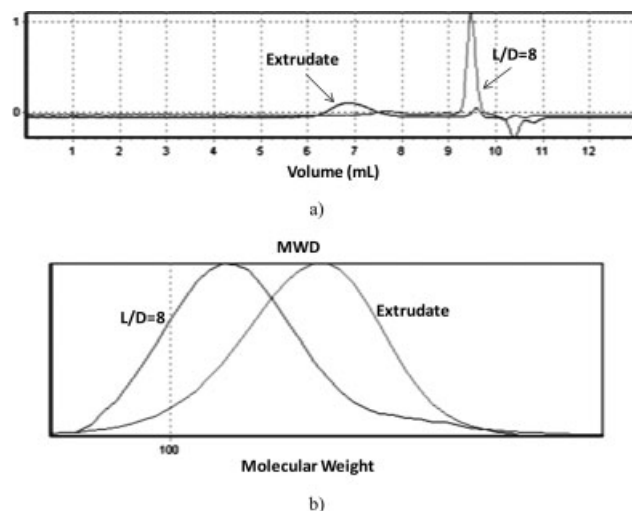


Figure 10 (a) SEC results and (b) MWDs of two samples collected at different locations ($L/D = 8$ and for the extrudate) and polymerized at 100°C and 50 rpm.

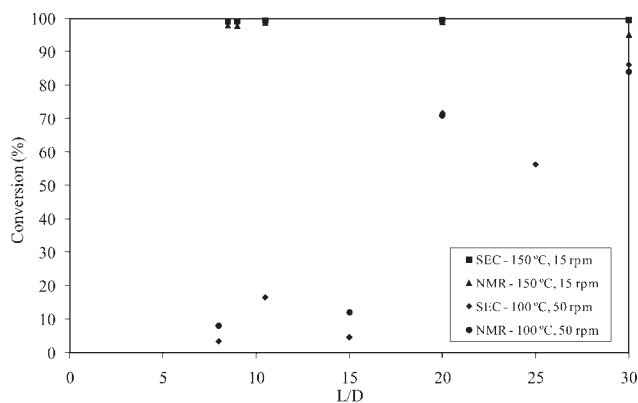


Figure 11 Evolution of the conversion of ϵ -caprolactone as a function of L/D in a twin-screw extruder at $M_0/I_0 = 300$.

speeds (15 and 50 rpm). In all cases, the samples were collected along the extruder during continuous polymerization. The conversion was then analyzed by SEC and NMR. Figure 10 shows an example of the SEC results and corresponding molecular weight distributions (MWDs) of two samples collected at different locations along the barrel [length/diameter (L/D) = 8] and for the extrudate polymerized at 100°C with 50 rpm. The difference between the samples was significant. The sample collected at $L/D = 8$ had a very high amount of monomer (peak at 9.5 min), and almost no peak for the polymer can be detected [Fig. 9(a)]. On the other hand, the sample collected from the die showed a very small peak for the monomer and a significant peak for the polymer. With regard to the molar mass distribution, a shift was observed, which indicated a strong increase in molar mass.

The conversion as a function of the screw length is plotted in Figure 11 for the different extrusion conditions. At 150°C and 15 rpm, the conversion was significantly high and almost complete at the first kneading disks. At 100°C and 50 rpm, it increased along the extruder, but at the die it was

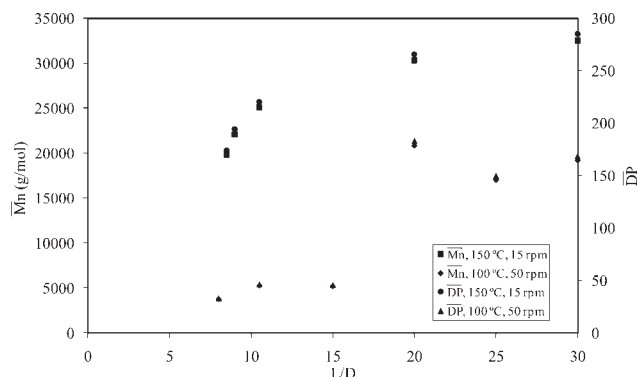


Figure 12 Evolution of M_n and \overline{DP}_{SEC} of ϵ -caprolactone as a function of L/D in a twin-screw extruder at $M_0/I_0 = 300$.

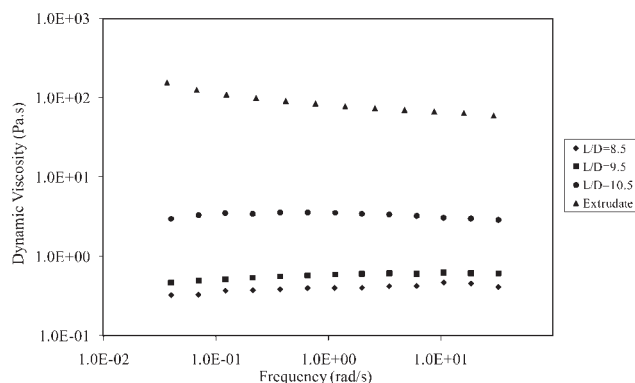


Figure 13 Dynamic viscosity along the barrel of ϵ -caprolactone polymerized in a twin-screw extruder at 150°C, 15 rpm, and $M_0/I_0 = 300$.

not complete. The different behavior was a result of both temperature and screw speed. Temperature had a strong effect on the conversion, which coincided with the results obtained in the internal mixer. Nevertheless, the increase in screw speed contributed to the decrease in conversion. When the screw speed increased, the residence time of the ϵ -caprolactone polymerization decreased, and thus, the conversion was lower.

The results obtained at the same temperature, 100°C, in the internal mixer and along the extruder were quite different. The lower conversion values along the extruder could be explained by the difference in real temperature in the internal mixer and in the extruder. Although, in the internal mixer, 100°C was the melting temperature, in the extruder, it was the barrel set temperature, with a melting temperature around 80–90°C. We measured the average melting temperature along the extruder by sticking a preheated needle-type fast-response thermocouple (penetration probe, type K, Coleparmer [Vernon Hills, Illinois (USA)], time constant ≈ 1 s) into the freshly collected material.

Figure 12 depicts the evolution of M_n and \overline{DP}_{SEC} of the polymer along the extruder for different extrusion conditions. As in the case of conversion, the evolution of M_n had different behaviors under the two conditions used. At 150°C and 15 rpm, it increased significantly in the first part of the extruder and then increased slightly and reached a plateau. At 100°C and 50 rpm, only a small increase was observed in the first kneading zone, and a progressive increase was detected downstream. As observed for conversion, the final value of M_n at 150°C was higher than the value at 100°C.

The values of M_n and degree of polymerization (DP) obtained in the internal mixer were quite different from the values obtained in the extruder. As discussed before, this might have been the result of temperature and residence time.

The viscosity measurements of the samples collected along the extruder at 150°C and 15 rpm are depicted in Figure 13. According to the M_n data, the viscosity increased along the extruder. In the beginning, the viscosity was very low, which could be explained by the large amount of monomer [Fig. 10(a)]. Along the extruder, as the polymerization continued, resulting in the high-molar-mass polymer, the viscosity increased.

CONCLUSIONS

The continuous bulk polymerization of ϵ -caprolactone initiated by $Ti(OPh)_4$ was carried out in an internal mixer and in a twin-screw extruder. Conversion along both the time and extruder axes was followed by SEC and 1H -NMR. Although in the internal mixer, at 100°C, complete conversion was achieved after approximately 200 s; in the extruder, the reaction was not complete at the die. Thus, the DP obtained was also different, being higher in the internal mixer. Temperature and shearing seemed to have major effects on conversion in the internal mixer, whereas temperature and residence time appeared to be most important in the twin-screw extruder. This confirmed the potential of producing high-molar-mass PCL by single-stage continuous reaction extrusion. It also highlighted some parameters to consider, including shearing, temperature, and residence time. In addition, this study confirmed the advantage of the development of new inline tools, such as the sampling devices inserted along the barrel of the extruder, to allow the extraction of data on C (%) during the polymerization process.

References

- Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* 1988, 21, 286.
- Dubois, P.; Barakat, R. J.; Jérôme, R.; Teyssié, P. *Macromolecules* 1993, 26, 4407.
- Storey, R. F.; Sherman, J. W. *Macromolecules* 2002, 35, 1504.
- Lecomte, P.; Stassin, F.; Jerome, R. *Macromol Symp* 2004, 215, 325.
- Stridsberg, K.; Albertsson, A.-C. *J Polym Sci Part A: Polym Chem* 1999, 37, 3407.
- Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* 2000, 33, 689.
- Ouhadi, T.; Stevens, C.; Teyssié, P. *Makromol Chem Suppl* 1975, 1, 191.
- Liu, Y. C.; Ko, B. T.; Lin, C. C. *Macromolecules* 2001, 34, 6196.
- Chen, H. L.; Ko, B. T.; Huang, B. H.; Lin, C. C. *Organometallics* 2001, 20, 5076.
- Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* 1998, 31, 2114.
- Vivas, M.; Contreras, J. *Eur Polym J* 2003, 39, 43.
- Sarazin, Y.; Schormann, M.; Bochmann, M. *Organometallics* 2004, 23, 3296.

13. Dobrzynski, P.; Kasperczyk, J.; Bero, M. *Macromolecules* 1999, 32, 4735.
14. Takeuchi, D.; Nakamura, T.; Aida, T. *Macromolecules* 2000, 33, 725.
15. Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* 2004, 37, 7968.
16. Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* 2002, 35, 5763.
17. Cayuela, J.; Bounor-Legaré V.; Cassagnau, P.; Michel, A. *Macromolecules* 2006, 39, 1338.
18. Narayan, R.; Krishnan, M.; Snook, J. B.; Gupta, A.; Dubois, P. U.S. Pat. 5,801,224 (1998).
19. Narayan, R.; Krishnan, M.; Snook, J. B.; Gupta, A.; Dubois, P. U.S. Pat. 5,906,783 (1999).
20. Narayan, R.; Krishnan, M.; Snook, J. B.; Gupta, A.; Dubois, P. U.S. Pat. 5,969,089 (1999).
21. Gimenez, J.; Cassagnau, P.; Boudris, M.; Michel, A. *Réc Prog Gén Proc* 1999, 13, 231.
22. Gimenez, J.; Boudris, M.; Cassagnau, P.; Michel, A. *Polym React Eng* 2000, 8, 135.
23. Cassagnau, P.; Bounor-Legare, V.; Fenouillot, F. *Int Polym Proc* 2007, 22, 218.
24. Wautier, H. U.S. Pat. 5,468,837 (1995).
25. Wautier, H.; Detournay, L.; Kaszacs, M. U.S. Pat. 5,656,718 (1997).
26. Raquez, J. M.; Degee, P.; Nabar, Y.; Narayan, R.; Dubois, P. *C R Chim* 2006, 9, 1370.
27. Raquez, J. M.; Degee, P.; Dubois, P.; Balakrishnan, S.; Narayan, R. *Polym Eng Sci* 2005, 45, 622.
28. Kim, B. J.; White, J. L. *Int Polym Proc* 2002, 17, 33.
29. Kim, B. J.; White, J. L. *J Appl Polym Sci* 2004, 94, 1007.
30. Balakrishnan, S.; Krishnan, M.; Narayan, R.; Dubois, P. *Polym Eng Sci* 2006, 46, 235.
31. Hamaide, T.; Lavit, E. *Polym Bull* 2002, 48, 173.
32. Machado, A. V.; Covas, J. A.; Duin, M. *J Polym Sci* 1999, 71, 135.
33. Takeshi, Y.; Ichiro, K.; Miyoshi, O.; Akio, S.; Shoki, S. *Tokyo Univ Sci Kogyo Kagaku Zasshi* 1957, 60, 1124.
34. Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J Polym Sci Part A: Polym Chem* 1982, 20, 319.
35. Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* 1990, 23, 1640.
36. Kim, B. J.; White, J. L. *J Appl Polym Sci* 2005, 97, 1605.
37. Navarchian, A. H.; Picchioni, F.; Janssen, L. P. *Polym Eng Sci* 2005, 279.
38. Devaux, J.; Godard, P.; Mercier, J. P. *J Polym Sci Polym Phys Ed* 1982, 20, 1895.
39. Libszowski, J.; Kowalski, A.; Duda, A.; Penczek, S. *Macromol Chem Phys* 2002, 203, 1694.
40. Bero, M.; Kasperczyk, J. *Macromol Chem Phys* 1996, 197, 3251.