The Use of Aluminum Trialkoxide for Synthesis of Poly(ε-Caprolactone) and Poly(δ-Valerolactone): A Comparative Study

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<td>bulk ring-opening polymerization, lactone, aluminum trialkoxide, biodegradable polymer, characterization</td>
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</table>
Abstract

Four aluminum (III) trialkoxides, namely, Al(III) ethoxide (1), Al(III) isopropoxide (2), Al(III) tert-butoxide (3), and Al(III) sec-butoxide (4), were employed as initiators for the bulk ring-opening polymerizations of δ-valerolactone (VL) and ε-caprolactone (CL). Chemical structure and properties of the prepared polymers was proven through different techniques such as FTIR, 1H-NMR, GPC, TGA and DSC. The effects of initiator concentrations and solubility as well as temperature were investigated for optimum polymerization conditions. It was found that the optimal condition is at 120 °C for 72 hours with 0.2%mol of initiator. However, 1 and 3 only partially dissolved in the CL monomer and gave no polymerization at low initiator concentration. In contrast, 4 was completely soluble in CL monomer and possess the highest percent yield (92%) and molecular weight ($\bar{M}_n = 2.83 \times 10^4$ g/mol). Both polymers exhibited the same melting characteristic, with PCL being thermally more stable than PVL.

Keywords: bulk ring-opening polymerization; lactone; aluminum trialkoxide; biodegradable polymer; characterization

1. Introduction

Polylactones such as poly(ε-caprolactone) (PCL) and poly(δ-valerolactone) (PVL) have still been gained great attention over the past decades due to their widespread applications in the biomedical, agricultural and pharmaceutical industries, including drug delivery (Jerome and Lecomte, 2008; Uhrich et al., 1999), medical implants and scaffolds for tissue engineering (Martina and Hutmacher, 2007). Ring-opening polymerization (ROP) (Duda et al., 2014; Nuyken and Pask, 2013) of lactones is a well-known synthetic method for producing such polymers with high molecular weight, good mechanical properties, hydrolyzability and biocompatibility (Albertsson and Varma, 2003; Lecomte and Jérôme, 2012; Penczek et al., 2007). Despite new and various initiators/catalysts (Labet and Thielemans, 2009) have been used for the synthesis of polylactone, metal alkoxides are still
useful for both academic and industrial purpose as they are very effective initiators for the 
ROP and a wide range of metals can be adopted. Of these initiators, Al trialkoxides have been 
extensively investigated (Dubois, Jacobs et al., 1991; Dubois, Jérôme et al., 1991; Duda and 
Penczek, 1995; Eguiburu et al., 1999; Ouhadi et al., 1975; Penczek and Duda, 1996). They 
are considered to be less reactive than its Sn analogous but their high selectivity, low toxicity 
as well as their versatile structure make them an attractive catalyst for producing aliphatic 
polyesters with designed macromolecular architecture. However, it is commonly known to be 
aggregated in solution which limits their applications. Very recently, a number of studies 
have shown its useful application in the synthesis of PCL through the bulk ROP (i.e., 
performed in the absence of any solvent). Balakrishnan et al. reported a bulk polymerization 
process to manufacture three-arm PCL using Al tri-sec-butoxide as initiator (Balakrishnan et 
al., 2004). Using the commercially available Al(O"Bu)₃, Limwanich et al. (Limwanich et al., 
2015) have analyzed several kinetic parameters for the same polymerization using differential 
scanning calorimetry. The mechanism of the Al trialkoxides mediated ROP has been 
proposed for decades to proceed via a two-step coordination-insertion (Duda and Penczek, 
1991; Löfgren et al., 1995; Ouhadi et al., 1975) and our recent DFT study (Jitonnom et al., 
2016) put it forward in more detail and predicts a unique penta-O-coordinated Al transition 
state as a key species of the initiation (see Scheme 1), which is somewhat different from the 
previously proposed mechanism of other related metal alkoxides (Sattayanon et al., 2013; 
Sattayanon et al., 2014; Sattayanon et al., 2015).

This paper focuses on the synthesis of PCL and PVL, via the ROP, with aluminum 
trialkoxides. Four different Al trialkoxides are considered as initiators, namely, 
aluminum(III) ethoxide Al(OEt)₃; aluminum(III) isopropoxide, Al(O"Pr)₃; aluminum(III) tert-
butoxide, Al(O"Bu)₃; aluminum(III) sec.-butoxide, Al(O"Bu)₃. The polymerizations were 
carried out in bulk under an inert nitrogen atmosphere. The effects of initiator concentrations,
solubility as well as reaction temperature on the percent yield, molecular weight and PDI value were investigated. The structural and thermal properties of the resultant polymers were further characterized by different techniques, such as Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (1H-NMR), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

2. Experimental

2.1 Materials

Commercial Al(OEt)$_3$ (Sigma-Aldrich), Al(O'Pr)$_3$ (Sigma-Aldrich), Al(O'Bu)$_3$ (Fluka), and Al(O'Bu)$_3$ (Sigma-Aldrich) were used as supplied. Commercial VL (Acros Organics) and CL (Acros Organics) monomers (see Figure 1) were purified by fractional distillation under reduced pressure over calcium hydride (b.pt. 50-55 °C and 60-65 °C / 2-3 mm Hg, respectively) and was stored over molecular sieves 4 Å in a refrigerator until required for use.

2.2 Synthesis

Ring-opening polymerizations of VL and CL were carried out in bulk at 120 °C in a round-bottomed flask with ground-glass joints and magnetic stirring. 0.2 and 1.0 mol% of the initiators and the monomers were weighed accurately into the reaction flask in a controlled atmosphere glove box under dry nitrogen at room temperature. After removing the flask from the glove box, it was immersed in a silicone oil bath at a constant temperature of 120 °C for 72 hours. At the end of the polymerization period, the flask was allowed to cool to room temperature. The crude polymer was purified by dissolving in chloroform, re-precipitating in ice-cooled methanol before finally drying in a vacuum oven at 45 °C to constant weight. To test the effect of temperature on the percent yield, further polymerizations of CL and VL
under the same condition were performed at various temperatures as 100, 110, 120, 130, 140 °C using 0.2 mol% of Al(O\text{Bu})_3.

2.3 Characterizations

**GPC**

The number-average molecular weights ($\overline{M}_n$) and polydispersity index (PDI) of the purified polymers were determined by gel permeation chromatography (GPC) using a Waters e2695 separations modules and employing polystyrene standard calibration (model 3580 refractive index detector). Tetrahydrofuran was used as the solvent at 35 °C at a flow rate of 1.0 ml/min. The GPC curves and the molecular weights were included in Figures S1-S4 and Table S1 of the Supplementary Material.

**NMR**

Proton nuclear magnetic resonance (\textsuperscript{1}H-NMR) spectra were recorded in chloroform-D (CDCl\textsubscript{3}) as solvent on a Bruker Avance 400 NMR Spectrometer operating at 400 MHz and 25 °C. Proton chemical shifts were recorded relative to tetramethylsilane (TMS) as internal standard.

**FTIR**

A Thermo Scientific Nicolet iS5 FT-IR spectrometer was used for the recording of FT-IR spectra with the range 400 – 4000 cm\textsuperscript{-1}.

**DSC**

Differential scanning calorimetry (DSC) measurements of dried samples were performed from 20 °C to 100 °C at a heating rate of 10 °C/min on a Perkin-Elmer DSC7
instrument with Pyris software. The samples with a typical mass of 3-5 mg were encapsulated in sealed aluminum pans and were heated and cooled under nitrogen atmosphere.

**TGA**

Thermal gravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA7 thermal analyzer. TGA analyses were performed at 50 °C to 550 °C at a rate of 10 °C/min in a nitrogen atmosphere.

**SCHEME 1:** Proposed ROP mechanism of lactone by aluminum trialkoxide based on Jitonnom et al. (Jitonnom et al., 2016)

**FIGURE 1:** Chemical structures of monomers and initiators under this study.

3. Results and Discussion

3.1. Effects of initiator concentration and solubility.

In our previous studies (Limwanich et al., 2015; Meelu et al., 2012), we demonstrated that PCL could be well prepared, via bulk ROP, by varying initiator concentration in ranges of 0.01−1.0 %mol. Similarly, we start our experiment on the bulk polymerizations of CL by tuning the amount of each initiator on the polymer properties (i.e., percent yield (%), number-average molecular weight (\( \bar{M}_n \)) and polydispersity index or PDI). Table 1 lists the effect of concentrations (0.2 and 1.0 %mol) of four different Al(OR)₃ initiators (R = Et, Pr, Bu, sBu) on the CL polymerization. As shown, all polymerizations
were achieved at 120 °C for 72 hours under an inert nitrogen atmosphere, except those using 0.2 %mol of Al(OEt)₃ and Al(O’Bu)₃ as initiators, due possibly to their poor solubility in CL. It is notable that Al(O’Bu)₃ is a slightly viscous liquid whereas all the other initiators are solids. Furthermore, polymerizations at low initiator concentration (0.2 %mol) exhibited higher number-average molecular weights ($\bar{M}_n = 9.19 \times 10^3 - 2.83 \times 10^4$ g/mol) than those ($\bar{M}_n = 4.81–8.34 \times 10^3$ g/mol) obtained at high initiator concentration (1.0 %mol). The decreased molecular weight of PCL at higher initiator concentration can be expected when CL is initiated by aluminum triisopropoxide (via $A_3$) (Meelu et al., 2012). One should consider this as an indirect effect according to the presence of non-reacting aggregated species. Notably, all aluminum trialkoxides provide narrow molecular weights with low PDI values (1.19-1.87), demonstrating their initiating efficiency towards the polymerizations of CL at 120 °C.

**TABLE 1**: Effects of initiator concentration on percent yields, number-average molecular weights and PDI value obtained from the bulk ROP of CL with different aluminum trialkoxides

The data in Table 1 further indicates that the activities of the initiators decrease in the following sequence: Al(O’Bu)₃ > Al(O’Pr)₃ > Al(O’Bu)₃ > Al(OEt)₃. Considering the high percent yield and molecular weight, both Al(O’Pr)₃ and Al(O’Bu)₃ initiators are highly active toward the CL polymerization and the latter is likely the most effective one in terms of small initiator concentration, high percent yield (> 90%) and high number-average molecular weight ($\bar{M}_n = 8.34 \times 10^3 - 2.84 \times 10^4$ g/mol). These values are much improved from the work (%yield = 85 and $\bar{M}_n = 2.40 \times 10^4$ g/mol) reported earlier by Limwanich et al.
(Limwanich et al., 2015) on the same polymerization. It can be argued that such high reactivity of Al(O\text{Bu})\text{3} over the others is mainly a matter of solubility where its liquid form can be readily soluble in CL and thus minimize the molecular aggregation.

3.2. Structural characterization.

The PVL and PCL samples were obtained from the polymerization and their structures were confirmed by FTIR and \textsuperscript{1}H-NMR. Figure 2 shows the FTIR spectra of PVL and PCL measured at room temperature (25 °C), which indicates the characteristic bands of the biodegradable polyesters at 1721.32 and 1720.92 cm\textsuperscript{-1}, respectively, for the carbonyl (C=O) band. Both polymers also exhibit the same peaks at 3000-2800 cm\textsuperscript{-1}, 1470-1360 cm\textsuperscript{-1} which corresponds to the C-H stretching and bending in methylene carbon (–CH\textsubscript{2}–), respectively, while the C–O stretching of polymer chain appears at 1300-1000 cm\textsuperscript{-1}. \textsuperscript{1}H-NMR is shown in Figure 3 which indicates similar proton signals between the two polymers. The methylene proton (–CH\textsubscript{2}–) connected to the Al–O bond is shown as a triplet signal at 3.60 ppm (H\textsubscript{a}). The methine proton (–CH–) of the O\text{Bu} group appeared as a multiplet at 4.80 ppm (see H\textsubscript{i} and H\textsubscript{k} for PVL and PCL, respectively). The triplet signal at 0.90 ppm (see H\textsubscript{f} and H\textsubscript{m} for PVL and PCL, respectively) was assigned to the methyl chain end (–CH\textsubscript{3}). While another methyl proton displayed as a doublet at 1.20 ppm (H\textsubscript{g}). These observations are consistent with the proposal that the bulk ROP of CL proceeds via a coordination-insertion mechanism for all initiators studied. The results of both FTIR and \textsuperscript{1}H-NMR clearly proves that PVL and PCL samples were successfully prepared.

FIGURE 2: FTIR of PVL (upper) and PCL (lower) samples.

FIGURE 3: \textsuperscript{1}H-NMR spectrums of PVL (upper) and PCL (lower) samples.
3.3. The effect of reaction temperature on the molecular weights of PCL and PVL.

To study the effect of reaction temperature on the percent yield, molecular weight and PDI value, the bulk polymerizations of the PVL and PCL were performed for 24 h using 0.2 %mol Al(OrBu)3 at temperatures ranging from 100 to 140 °C. The results are listed in Table 2. As shown, the percent yield of VL and CL starts to decrease at 100 and 120 °C, respectively, which corresponds well to its ceiling temperature (Tc) reported in the literature (Duda et al., 2005). As a result, at the temperatures greater than the Tc values the lower yield and molecular weight were obtained. This is mainly due to the increase of the backbiting side reactions (Mecerreyes et al., 1999), which make the molecular weight distributions broader at high temperature. Overall, the CL polymerizations exhibited higher molecular weight (1.92 x 10^4–3.91 x 10^4 g/mol) compared to that (1.70x10^4 – 2.43x10^4 g/mol) of VL polymerizations.

TABLE 2: Effect of reaction temperature on percent yield (%) and number-average molecular weight (\(\bar{M}_n\)) in bulk ROPs of VL and CL.\(^a\)

3.4. Thermal degradation and melting behavior.

The thermal properties of the resulting polymers, PVL and PCL, were also characterized by TGA and DSC techniques, and the results are shown in Figure 4. As expect, PCL is thermally more stable than PVL as supported by TGA analysis (see Figure 2a) of the PCL and PVL samples at a heating rate of 10 °C/min. The decomposition temperature of PCL started at 250 °C, and the remaining weight of the sample reached zero at 525 °C. In contrast, the weight loss of PVL started at lower temperature (around 168 °C), and the sample was completely loss at 398 °C. The thermal degradation/depolymerization of PVL and PCL can be explained via an unzipping mechanism, as suggested for the low molecular weight polymer in nitrogen (Unger et al., 2010), or, alternately, via a random chain cleavage through
ester pyrolysis reactions (Persenaire et al., 2001). From DSC peaks (Figure 4b), the two polymers exhibited similar melting behavior with PCL showing its $T_m$ value (60.2 °C) slightly higher than that of PVL ($T_m = 58.3$ °C), in accordance with the literature value for PCL ($T_m = 65$ °C (Mecerreyes et al., 1999)). The glass transition temperature ($T_g \approx -60$ °C) cannot be measured here as it is below the temperature limit ($\approx -25$ °C) of the DSC instrument used in this study. Such relatively low melting temperatures make PCL materials easy to fabricate or process into highly structured forms (Karimi et al., 2012).

**FIGURE 4:** TGA (a) and DSC (b) thermograms for PVL (grey) and PCL (black).

### 4. Conclusion

In this paper, the use of aluminum trialkoxides as initiators for the synthesis of PCL and PVL has been successfully applied through the bulk ROP. The structural and thermal properties of the polymers were further proved by various techniques, including FTIR, $^1$H-NMR, GPC, TGA and DSC. The effects of the amount of initiator and solubility as well as reaction temperature on the polymerization of lactone were examined and the optimal condition is found at 120 °C for 72 hours with low initiator concentration (0.2%mol). Thermal analysis by TGA and DSC shows that PCL is thermally more stable than PVL and both polymers have the same melting characteristic. Our results also showed that while both $\text{Al(O^{'Pr})_3}$ and $\text{Al(O^{'Bu})_3}$ are efficient initiators for the bulk ROP of lactone and the latter is the best in terms of better solubility and higher yield and molecular weight ($\%$yield $> 90$ and $\overline{M_n} = 2.83 \times 10^4$ g/mol).

### Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgements

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References


SCHEME AND FIGURES

SCHEME 1: Proposed ROP mechanism of lactone by aluminum trialkoxide based on

Jitonnom et al. (Jitonnom et al., 2016)
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FIGURE 3: $^1$H-NMR spectrums of PVL (upper) and PCL (lower) samples.
FIGURE 4: TGA (a) and DSC (b) thermograms for PVL (grey) and PCL (black).
**TABLE**

**TABLE 1**: Effects of initiator concentration on percent yields, number-average molecular weights and PDI value obtained from the bulk ROP of CL with different aluminum trialkoxides

<table>
<thead>
<tr>
<th>Initiators</th>
<th>Concentration (% mol)</th>
<th>Yield (%)</th>
<th>$\overline{M}_n$ (g/mol)</th>
<th>PDI</th>
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<tr>
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<td>–$^c$</td>
<td>–$^c$</td>
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<td>–$^c$</td>
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<tr>
<td>Al(O'Bu)$_3$</td>
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<td>90.15</td>
<td>$8.34 \times 10^3$</td>
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</table>

$^a$ Polymerizations were conducted at 120 °C for 72 hours  
$^b$ Obtained using GPC technique  
$^c$ Not detected
TABLE 2: Effect of reaction temperature on percent yield (%) and number-average molecular weight ($\bar{M}_n$) in bulk ROPs of VL and CL. $^a$

<table>
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<th>Monomer</th>
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<td>85.76</td>
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$^a$Polymerizations were conducted for 24 h using 0.2 %mol of Al(O'Bu)$_3$
Supplementary Materials

The Use of Aluminum Trialkoxide for Synthesis of Poly(ε-Caprolactone) and Poly(δ-Valerolactone): A Comparative Study

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⁴Demonstration School, University of Phayao, Phayao 56000, Thailand
GPC curves

Fig. S1 GPC curves print-out for purified PCL synthesized using Al(OEt)$_3$
Fig. S2  GPC curves print-out for purified PCL synthesized using Al(O\text{Pr})_3
Fig. S3 GPC curves print-out for purified PCL synthesized using Al(OtBu)₃.
Fig. S4 GPC curves print-out for purified PCL synthesized using Al(O' Bu)₃
Fig. S5 $^1$H-NMR for the bulk ROP of CL at different polymerization times (30, 60, 120, 180, 240 mins)
Fig. S6 Plot of %conversion for the bulk ROP of CL with 0.2% mol Al(O^tBu)_3 as a function of time as determined by ^1H-NMR and gravimetry techniques.

Data that is used in Fig. S6

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Table S1 GPC molecular weight average and polydispersity indices for PCL synthesized at 120 °C for 72 hours using different aluminum trialkoxides

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<th>Initiator used</th>
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