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Original Article

The use of aluminum trialkoxide for synthesis of poly (ε-caprolactone) and poly (δ-valerolactone): A comparative study

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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 were assessed by various techniques, such as FTIR, ^{1}H-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 conditions were 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 gave the highest yield (92%) and molecular weight ($\overline{M}_n$ = 2.83 x 10^4 g/mol). Both polymers exhibited similar melting characteristics, 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 gained a great deal of attention over the past decades due to their widespread applications in biomedical, agricultural and pharmaceutical industries, including drug delivery (Jerome & Lecomte, 2008; Uhrich *et al.*, 1999), medical implants and scaffolds for tissue engineering (Martina & Hutmacher, 2007). Ring-opening polymerization (ROP) (Duda *et al.*, 2014; Nuyken & Pask, 2013) of lactones is a well-known synthesis method for producing such polymers with high molecular weight, good mechanical properties, hydrolyzability and biocompatibility (Albertsson & Varma, 2003; Lecomte & Jérôme, 2012; Penczek *et al.*, 2007). Despite the various initiators/catalysts (Labet & Thielemans, 2009) that have been used for the synthesis of polylactone, metal alkoxides are still useful for both academic and industrial purposes 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, Jérŏme *et al.*, 1991; Duda & Penczek, 1995; Eguiburu *et al.*,

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1999; Ouhadi *et al.*, 1975; Penczek & Duda, 1996). They are considered to be less reactive than their Sn analogs, but their high selectivity, low toxicity as well as their versatile structure make them attractive catalysts for producing aliphatic polyesters with designed macromolecular architecture. However, it is commonly known that they tend to agglomerate in solution, which limits their applications. Very recently, a number of studies have shown their useful applications 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 the initiator (Balakrishnan *et al.*, 2004). Using commercially available $Al(O^sBu)_3$, 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 trialkoxide mediated ROP has been proposed to proceed via a two-step coordination-insertion (Duda & Penczek, 1991; Löfgren *et al.*, 1995; Ouhadi *et al.*, 1975) and our recent DFT study (Jitonnom *et al.*, 2016) explored this in more detail, also predicting a unique penta-*O*-coordinated Al transition state as a key species in the initiation (Scheme 1), which is somewhat different from the previously proposed mechanism for 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 Altrialkoxides are considered as initiators, namely aluminum(III) ethoxide $Al(OEt)_3$; aluminum(III) isopropoxide, $Al(O^iPr)_3$; aluminum(III) *tert*-butoxide, $Al(O^tBu)_3$; and aluminum(III) sec.-butoxide, $Al(O^sBu)_3$. The polymerizations were carried out in bulk under an inert nitrogen atmosphere. The effects of initiator concentration, solubility, as well as reaction temperature on yield, molecular weight and PDI were investigated. The structural and thermal properties of the resultant polymers were further characterized by multiple techniques, such as Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

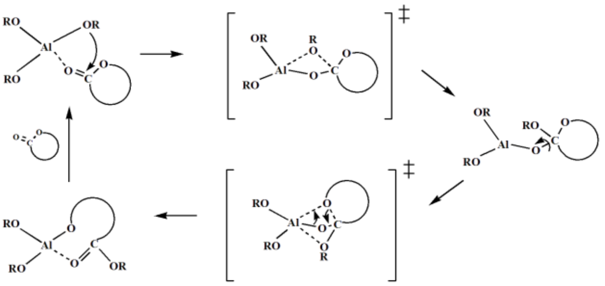
2. Experimental

2.1 Materials

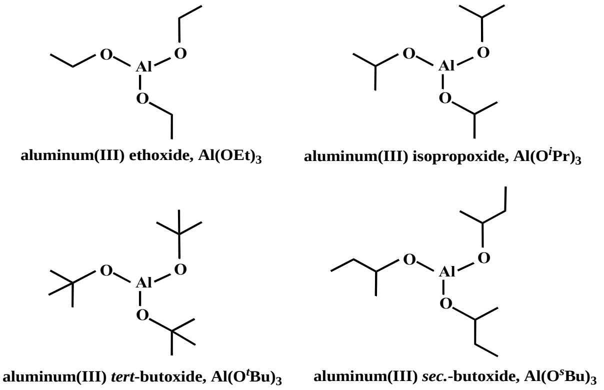
Commercial $Al(OEt)_3$ (Sigma-Aldrich), Al $(O^iPr)_3$ (Sigma-Aldrich), Al $(O^tBu)_3$ (Fluka), and Al $(O^sBu)_3$ (Sigma-Aldrich) were used as supplied. Commercial VL (Acros Organics) and CL (Acros Organics) monomers (Figure 1) were purified by fractional distillation under reduced pressure over calcium hydride (b.pt. 50-55 °C and 60-65 °C / 2-3 mm Hg, respectively) and were 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 and re-precipitating in ice-cooled methanol before finally drying in a vacuum oven at 45 °C to constant weight. To test the effects of temperature on yield, further polymerizations of CL and VL under the same conditions otherwise were performed at various temperatures: at 100, 110, 120, 130, 140 °C using 0.2 %mol of $Al(O^sBu)_3$.



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


aluminum(III) ethoxide, $Al(OEt)_3$ aluminum(III) isopropoxide, $Al(O^iPr)_3$

aluminum(III) *tert*-butoxide, $Al(O^tBu)_3$ aluminum(III) *sec.*-butoxide, $Al(O^sBu)_3$

Figure 1. Chemical structures of monomers and initiators used in this study.

2.3 Characterizations

2.3.1 GPC

The number-average molecular weights (‾) and polydispersity indexes (PDI) of the purified polymers were determined by gel permeation chromatography (GPC) using a Waters e2695 separations module 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 are included as Figures S1-S4 and Table S1 in the Supplementary Material.

2.3.2 NMR

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded in chloroform-D ($CDCl_3$) as the 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 the internal standard.

2.3.3 FTIR

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

2.3.4 DSC

Differential scanning calorimetry (DSC) measurements of dried samples were performed from 20 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.

2.3.5 TGA

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

3. Results and Discussion

3.1. Effects of initiator concentration and solubility

In our previous studies (Limwanich *et al.*, 2015; Meelua *et al.*, 2012), we demonstrated that PCL could be prepared via bulk ROP, by varying the initiator concentration in the range 0.01−1.0 % mol. Similarly, we start our current experiments on the bulk polymerization of CL by tuning the amount of each initiator for best results (*i.e.*, percent yield (%), number-average molecular weight (¯) and polydispersity index or PDI). Table 1 lists the effects of concentration (0.2 or 1.0 %mol) for four alternative $Al(OR)_3$ initiators (R = **Et**,***^{i}*Pr**,**^{t}Bu**,**^{s}Bu**) on the CL polymerization. As shown, all the polymerizations were successful at 120 °C for 72 hours under an inert nitrogen atmosphere, except those using 0.2 % mol of $Al(OEt)_3$ and $Al(O^tBu)_3$ as initiators, due possibly to their poor solubility in CL. It is notable that $Al(O^sBu)_3$ 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 (¯ = 9.19 x 10^3– 2.83 x 10^4 g/mol) than those (¯ = 4.81–8.34 x 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) (Meelua *et al.*, 2012). One should consider this as an indirect effect in the presence of non-reacting aggregated species. Notably, all aluminum trialkoxides provide narrowly distributed molecular weights with low PDI (1.19-1.87), demonstrating their initiating efficiency in the polymerization of CL at 120 °C.

The data in Table 1 further indicates that the activities of the initiators decrease in the following sequence: $Al(O^sBu)_3$>$Al(O^iPr)_3$>$Al(O^tBu)_3$>$Al(OEt)_3$. Considering high yield and molecular weight, both $Al(O^iPr)_3$ and $Al(O^sBu)_3$ initiators are highly active in the CL polymerization and the latter is likely the most effective one in terms of small initiator concentration, high yield (> 90%) and high number-average molecular weight (¯ = 8.34 x 10^3 -2.84 x 10^4 g/mol). These values are much improved from the work (%yield = 85 and ¯ = 2.40 x 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 $(O^sBu)_3$ over the others is mainly a matter of solubility: as liquid it can be readily soluble in CL and thus minimizes the molecular aggregation.

Table 1. Effects of initiator concentration on yields, number-average molecular weights and PDI obtained from the bulk ROP of CL with alternative aluminum trialkoxides^a

Initiator	Concentration (% mol)	Yield (%)	¯ ^{b} (g/mol)	PDI
$Al(OEt)_3$	0.2	–^{c}	–^{c}	–^{c}
	1.0	49.64	4.81 × 10^3	1.19
$Al(O^iPr)_3$	0.2	34.19	9.19 × 10^3	1.37
	1.0	93.62	7.35 × 10^3	1.73
$Al(O^tBu)_3$	0.2	–^{c}	–^{c}	–^{c}
	1.0	77.82	5.68 × 10^3	1.26
$Al(O^sBu)_3$	0.2	92.13	2.83 × 10^4	1.70
	1.0	90.15	8.34 × 10^3	1.87

^{a} Polymerizations were conducted at 120 °C for 72 hours
^{b} Obtained using GPC technique
^{c} Not detected

3.2. Structural characterization

For the PVL and PCL samples obtained from the polymerization, their structures were confirmed by FTIR and^{1}H-NMR. Figure 2 shows the FTIR spectra of PVL and PCL measured at room temperature (25 ºC), with the characteristic bands for the carbonyl (C=O) of biodegradable polyesters at 1721.32 and 1720.92cm^{-1}, respectively. Both polymers also exhibit the same peaks at 3000-2800 cm^{-1} and 1470-1360 cm^{-1}, which correspond to the C-H stretching and bending in methylene carbon($–CH_2–$), respectively, while the C–O stretching of polymer chain appears at 1300-1000 cm^{-1}. ^{1}H-NMR is shown in Figure 3, which indicates similar proton signals for the two polymers. The methylene proton ($–CH_2–$) connected to the Al–O bond is shown as a triplet signal at 3.60 ppm (H^a). The methine proton (–CH–) of the O^sBu group appeared as a multiplet at 4.80 ppm (H^i and H^k for PVL and PCL, respectively). The triplet signal at 0.90 ppm (sH^k and H^m for PVL and PCL, respectively) was assigned to the methyl chain end ($–CH_3$), while another methyl proton displayed as a doublet at 1.20 ppm (H^z). These observations are consistent with the proposal that the bulk ROP of CL proceeds via a coordination-insertion mechanism for all the initiators studied. The results of both FTIR and ^{1}H-NMR clearly prove that PVL and PCL samples were successfully prepared.

3.3. The effects of reaction temperature on the molecular weights of PCL and PVL

To study the effects of reaction temperature on yield, molecular weight and PDI, bulk polymerizations of PVL and PCL were performed for 24 hours using 0.2 %mol $Al(O^sBu)_3$ at temperatures ranging from 100 to 140 °C. The

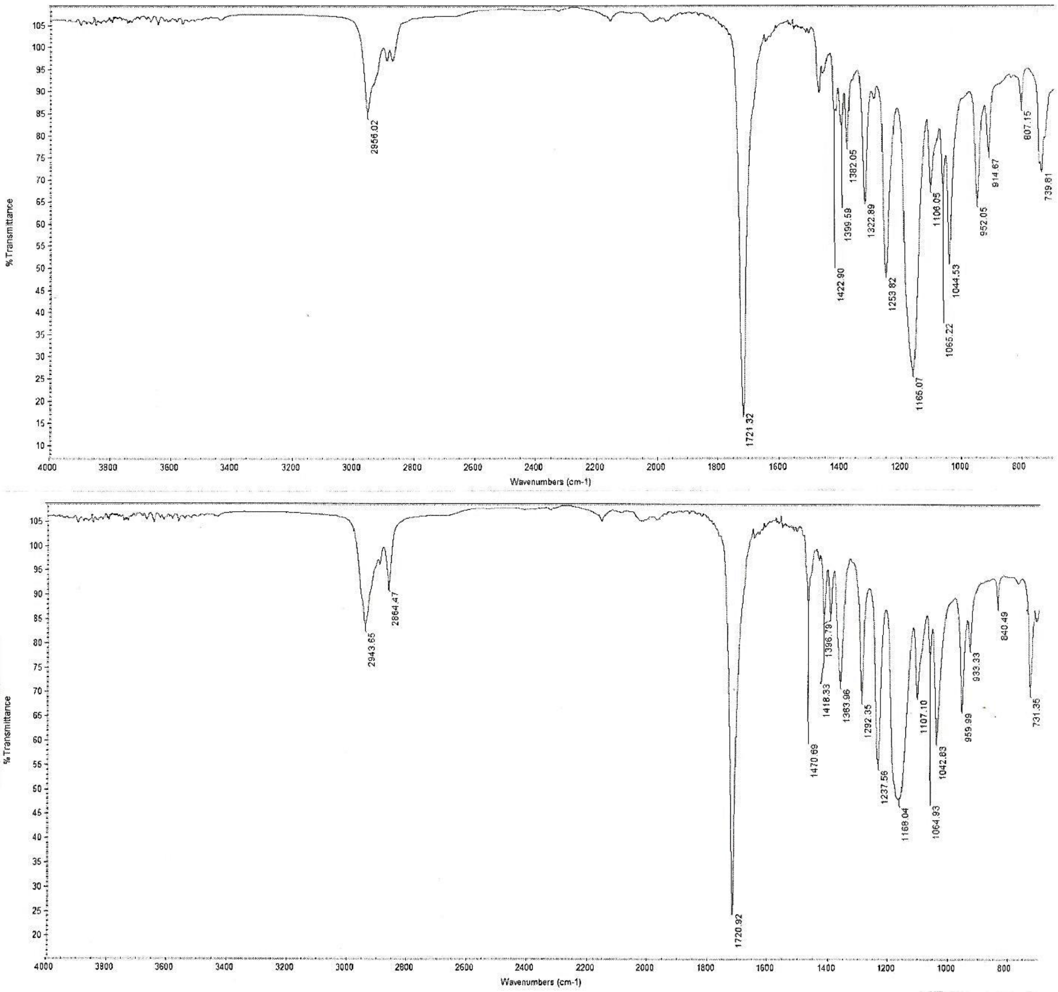


Figure 2. FTIR of PVL (upper) and PCL (lower) samples.

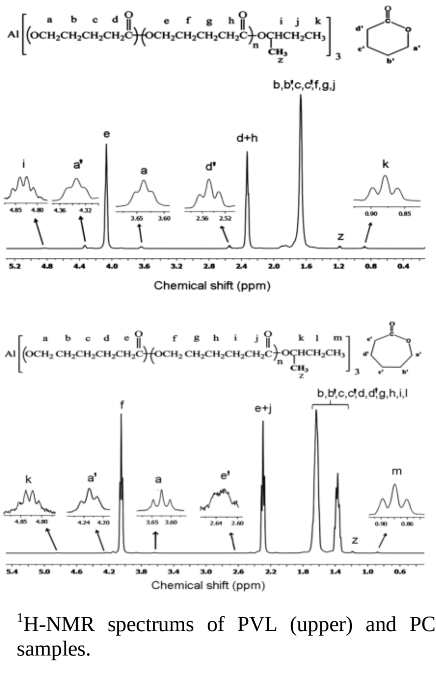


Figure 3. ^{1}H-NMR spectrums of PVL (upper) and PCL (lower) samples.

results are listed in Table 2. As shown, the yields of VL and CL start to decrease at 100 and 120 °C, respectively, which corresponds well to the ceiling temperature (T_c) reported in the literature (Duda *et al.*, 2005). As a result, at temperatures exceeding T_c, lower yield and molecular weight were obtained. This is mainly due to increased 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 10^4–3.91x 10^4 g/mol) compared to the VL polymerizations (1.70x10^4– 2.43x10^4 g/mol).

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 expected, PCL is thermally more stable than PVL in the TGA analysis (Figure 2a) at a heating rate of 10 °C/min. The decomposition 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 a lower temperature (around 168 °C), and the sample was completely lost at 398 °C. The thermal degradation/depolymerization of PVL and PCL can

Table 2. Effects of reaction temperature on yield (%) and number-average molecular weight (¯) in bulk ROPs of VL and CL.[a]

Monomer	Temperature (°C)	Yield (%)	¯ (g/mol)	PDI
VL	100	91.53	2.43×10^4	1.79
	110	90.84	1.95×10^4	1.83
	120	85.09	1.97×10^4	1.95
	130	82.96	1.94×10^4	2.04
	140	81.09	1.70×10^4	2.34
CL	100	88.70	2.41×10^4	1.68
	110	89.81	2.91×10^4	1.85
	120	94.18	3.38×10^4	1.78
	130	91.71	3.91×10^4	2.13
	140	85.76	1.92×10^4	2.49

[a] Polymerizations were conducted for 24 h using 0.2 %mol of Al(O^{s}Bu)$_3$

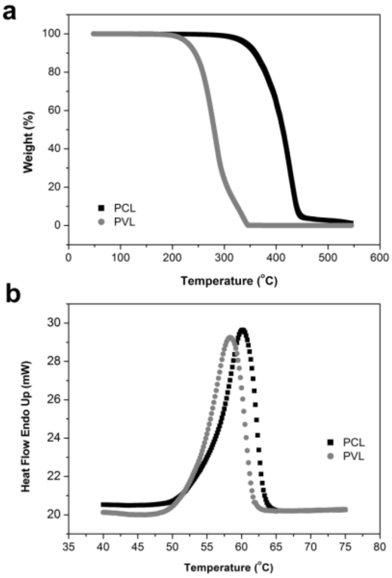


Figure 4. TGA (a) and DSC (b) thermograms for PVL (grey) and PCL (black).

be explained by an unzipping mechanism, as suggested for low molecular weight polymers in nitrogen (Unger *et al.*, 2010), or, alternately, via random chain cleavages through ester pyrolysis reactions (Persenaire *et al.*, 2001). Regarding the DSC peaks (Figure4b), the two polymers exhibited similar melting behavior, with the PCL showing a slightly higher T_m (60.2 °C) than the 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 (≈ -25 °C) of the DSC instrument used in this study. The relatively low melting temperatures make PCL materials easy to fabricate or process into highly structured forms (Karimi *et al.*, 2012).

4. Conclusions

In this paper, the use of aluminum trialkoxides as initiators for the synthesis of PCL and PVL was successful in bulk ROP. The structural and thermal properties of the polymers were further assessed by various techniques, including FTIR, ^{1}H-NMR, GPC, TGA and DSC. The effects of the amount of initiator and its solubility, as well as of reaction temperature on the polymerization of lactone were examined, and the optimal conditions found were 120 °C for 72 hours with low initiator concentration (0.2 %mol).Thermal analysis by TGA and DSC showed that PCL is thermally more stable than PVL, and these polymers have similar melting characteristic. Our results also show that while both Al(O^{i}Pr)$_3$ and Al(O^{s}Bu)$_3$ are efficient initiators for the bulk ROP of lactone, the latter is better in terms of better solubility and higher yield and molecular weight (yield > 90 % and ¯ = 2.83 x 10^4 g/mol).

Acknowledgements

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