

# Analysis of the Bis(benzoylacetato)zirconium(IV) Chloride Complex Compound Mulliken Charge Used As a Catalyst in the Ring Opening Polymerization of $\epsilon$ -Caprolactone

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**Abstract**—Poly( $\epsilon$ -caprolactone) (PCL) is one of the promising polymers because it can be utilized as a substitute for petroleum-based polymers that are difficult to biodegrade in nature. PCL has non-toxic properties, high crystallinity, and biodegradable. Therefore, this polymer is widely used for medical purposes and environmentally friendly packaging. The purpose of this study was to compare the degree of polymerization, catalytic activity and thermal properties between PCL produced using bis(benzoylacetato)zirconium(IV) catalyst (**2a**) with the PCL produced using other bis( $\beta$ -diketonato)zirconium(IV) chloride catalyst (**2b**, **2c**). In this research, ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) was performed by using complex **2a** as a catalyst. The polymerization reaction lasts for 4 h at 100°C. The results of the research showed that  $\epsilon$ -CL was successfully polymerized as proven in the results of its characterization. The molecular structure of the obtained PCL was analyzed by using FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, XRD, DSC, and TGA. The PCL produced in this study was a semicrystalline polymer. Meanwhile, a Mulliken charge of zirconium central atom in complex **2a–2c** was also measured. In Mulliken charge analysis, the Mulliken charge of complex **2c** has the highest Lewis acidity in comparison with complex **2a** and **2b**.

**Keywords:** Bis(benzoylacetato)zirconium(IV) Chloride, ring opening polymerization,  $\epsilon$ -caprolactone, Poly( $\epsilon$ -caprolactone), Mulliken charge

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## INTRODUCTION

At present, petroleum-based polymers have polluted the environment due to they cannot be decomposed by microorganisms. To overcome this problem, many scientists are involved in polymer synthesis that are readily biodegradable and environmentally friendly [1]. One of the biodegradable and environmentally friendly polymers is PCL. PCL also has other unique properties such as non-toxic, biocompatibility [2, 3], permeability, thermoplastic, mechanical properties that are easily controlled, high crystallinity [2], and has long-term

degradation properties. Based on these advantages, PCL is applied in a variety of purposes including as implantable devices, composites, packaging [2], materials [4, 5], surgical sutures, bone screws [6–8], reinforcing agents [3], vascular grafts, and drug delivery systems [9].

The ring opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) was usually carried out by using altered Lewis acid complexes catalyst through a coordination-insertion mechanism. This method is very effective for the synthesis of biodegradable polymers. Some of the catalysts and initiators that have been

used in the ROP of  $\epsilon$ -CL are bis-ligated magnesium complex [6], nanopori alumina membrane[7], alkali metal salts [8], distannoxane [10], Ti Al-MCM-41 [11], metanesulfonic acid [12], zinc complex [13], aluminum complex [14], tetrakis(acetylacetonato) zirconium [15], and bis(acetylacetonato)zirconium(IV) (**2b**), bis(dibenzoylmethanato)zirconium(IV) (**2c**) [16]. However, some of these catalysts have some drawback such as being exposed to corrosive, sensitive to air and moisture. These drawbacks make catalyst handling during ROP of  $\epsilon$ -CL become difficult. Besides that, it is rather complicated to manage the Lewis acidity of the complex compound.

In producing PCL, the previous research by the Dobrinsky research group used the same Zr metal centre and  $\beta$ -diketonate ligand as this current study. The difference between these two researches is the previous research conducted by the Dobrinsky research group used Zr  $\beta$ -diketonate with coordination number 8 (CN = 8), meanwhile this current research used Zr  $\beta$ -diketonate **2a** with CN = 4.

Previously, the researcher also had made the research about Zr  $\beta$ -diketonate **2b**, **2c** complex which was applied as a catalyst in the ROP of  $\epsilon$ -CL [16]. The complexes **2b**, **2c** have CN = 4 which is the same as complex **2a**. The ligand in the complex **2b**, **2c** were **1b** and **1c**. The ligand **1b** consists of electron donor group solely (methyl) while the ligand **1c** consists of electron withdrawing group solely (phenyl). Then, this research is the development of the Zr  $\beta$ -diketonate complex which is used as a catalyst to produce PCL. The ligand in this catalyst was **1a** which consist of the combination between ligand **1b** and **1c**; i.e. electron withdrawing group and electron donor group. The catalysts difference can be seen in the Schemes 1 and 2.

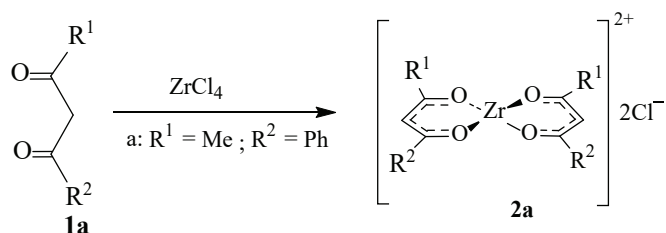
Furthermore, these bis( $\beta$ -diketonate)Zr(IV) (**2b**, **2c**) catalysts have some advantages like resistance to moisture and air, non-corrosive, a controlled Lewis acidity in the central atom (Zr) which was not found in the catalyst from the previous researchers [16]. Working with these catalysts will be much easier especially in tropical countries since they are resistance to moisture and air. Catalyst **2a** which was the development from catalysts **2b** and **2c** was expected to be much better in producing PCL specifically in high degree polymerization (DP), high decomposition temperature, high crystallinity, high melting temperature, high yield and also high catalytic activity.

## EXPERIMENTAL

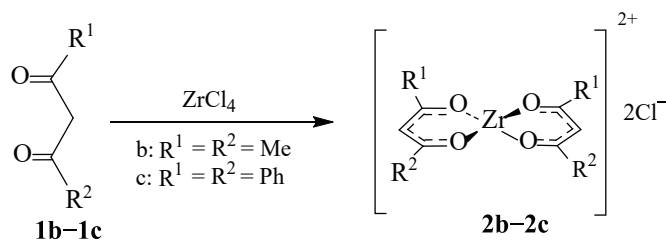
**Material and methods.** ROP of  $\epsilon$ -CL using bis(benzoylacetonato)zirconium(IV) chloride (**2a**), **2b** and **2c** as catalyst were conducted at the Inorganic Research Laboratory. PCL characterizations were carried out at the BSC-A Institut Teknologi Bandung, Physics Laboratory Universitas Negeri Medan, and Material Test and Electron Microscope Laboratory PTKI Medan. Materials used such as  $\epsilon$ -CL, bis( $\beta$ -diketonate) ligands and zirconium tetrachloride were bought from Sigma-Aldrich. The equipment used for characterization such as FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, XRD, DSC, and TGA have the same specifications as we reported in the previous report [16].

**Synthesis of bis(benzoylacetonato)zirconium(IV) chloride.** Synthesis of bis(benzoylacetonato) zirconium(IV) chloride was carried out by reacting 0.35 g zirconium tetrachloride (1.5 mmol) with 0.567 g benzoilacetonato (**1a**) (3.5 mmol) ligands. Meanwhile, 20 mL of benzene is used as a solvent. The reaction was carried out by reflux method for 14 h at 85°C. The reaction product is cooled and allowed to form product precipitate while the filtrate is discarded. The product formed was washed using 8 mL of *n*-hexane three times. The next step is drying process by using vacuum pump to produce complex compound **2a**. The same process was also performed to produce **2b–2c** complex compounds by using ligand **1b** and ligand **1c** [16–18]. Bis(benzoylacetonato)zirconium(IV) chloride

**Scheme 1.** Synthesis of bis( $\beta$ -diketonato)zirconium(IV) chloride **2a** from current research.



**Scheme 2.** Synthesis of bis( $\beta$ -diketonato)zirconium(IV) chloride **2b–2c** from the previous research [16–18].



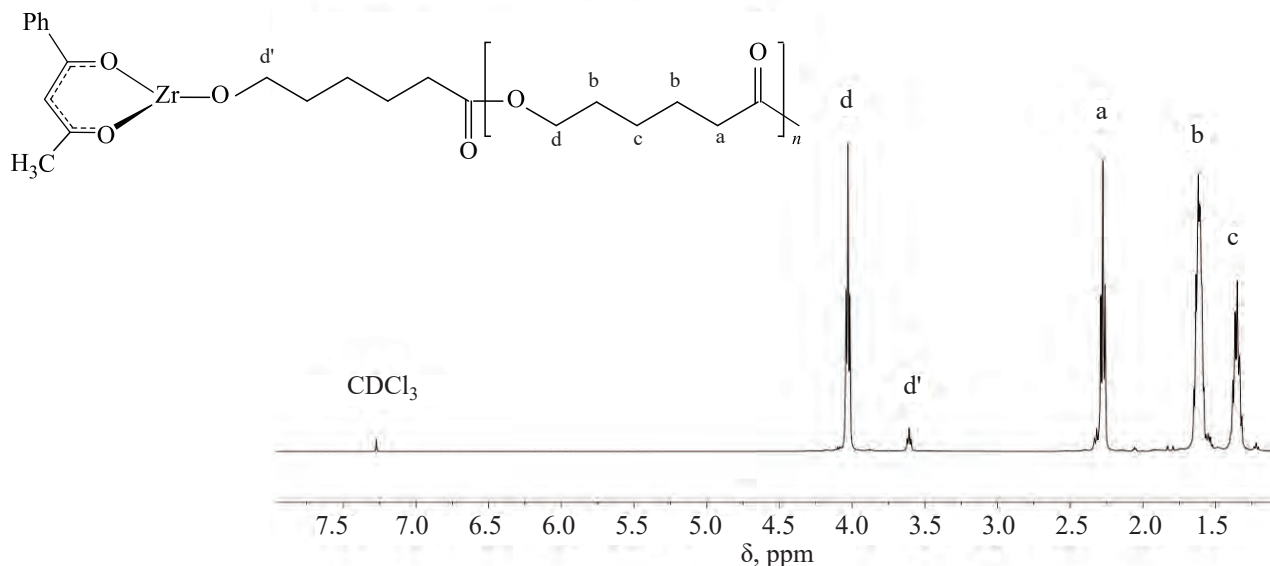


Fig. 1.  $^1\text{H}$ NMR Spectrum of PCL.

$[\text{Zr}(\text{bzac})_2]\text{Cl}_2$ : Yield 61%; NMR,  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ), 2.217 (s, 3H); 6.195 (s, 1H); 7.435–7.490 (t, 2H), 7.505–7.560 (t, 1H); 7.866–7.912 (d, 2H).

#### Ring-opening polymerization of $\epsilon$ -caprolactone.

The ROP procedure of  $\epsilon$ -CL in this study is the same as the method we have reported in previous reports [16]. A total of 0.065 g of the is(benzoylacetato) zirconium(IV) chloride complex (0.13 mmol) was mixed with 2.4 g of  $\epsilon$ -CL (21 mmol) monomer. The resulting mixture is then polymerized for 4 h at  $100^\circ\text{C}$ . Furthermore, the product formed is dissolved using 15 mL of chloroform and then stirred for 3 h. After that, the solution is refluxed for 1 h to create a transparent solution. The solution is then precipitated using 20 mL diethyl ether. The precipitate of the product is dried by using vacuum pump until the white solid PCL is produced. The equipment used for PCL characterization is FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, XRD, DSC, and TGA. In this study, ROP of  $\epsilon$ -CL was also applied by using bis(acetylacetonato)zirconium(IV) chloride (**2b**) and bis(dibenzoylmethanato)zirconium(IV) chloride (**2c**) complex compounds as catalysts [16]. FTIR PCL ( $\text{cm}^{-1}$ ): 3434 (OH), 2949 ( $\text{CH}_2$ , asym), 2865 ( $\text{CH}_2$ , sym), 1724 ( $\text{C}=\text{O}$ ), 1473 (CH, asym elongation), 1368 ( $\text{CH}_2$ , bending), 1295 (C-C), 1245 (C-O), 729 (long chain methylene rock).

**Computational method.** Mulliken charge analysis and optimization of the **2a–2c** complex was calculated by using the semi-empirical method PM3. Molecular calculations and visualizations were carried out by

using the HyperChem 8.0 program package. The Operating System is using Windows 07 [19–21]. The semi-empirical method PM3 has been used by other researchers to calculate the tetrakis(acetylacetonato) zirconium(IV) complex [15]. Polak-Ribiere is the algorithm used in this calculation with a maximum cycle calculation approximately 32 767.

## RESULTS AND DISCUSSION

**$^1\text{H}$  NMR spectroscopies.** The PCL produced using catalyst **2a** was analyzed by using  $^1\text{H}$ NMR spectrum with  $\text{CDCl}_3$  solvent as seen in the Fig. 1. Previously, another group of researchers had also obtained similar  $^1\text{H}$  NMR PCL spectra to those PCL obtained in this study [22–24]. The peak obtained in the range of 3.95–4.12 ppm is the  $-\text{CH}_2$  proton attached to oxygen in the ester ( $\text{H}^{\text{d}}$ ) bond. While the peak obtained in the range of 2.23–2.37 ppm is the proton  $-\text{CH}_2$  attached to the carbonyl group ( $\text{H}^{\text{a}}$ ). Meanwhile, the peaks obtained at 1.51–1.69 ppm and 1.29–1.42 ppm are protons  $-\text{CH}_2$  at the center of the PCL polymer ( $\text{H}^{\text{b}}$  and  $\text{H}^{\text{c}}$ ). In addition, the peak obtained in the range of 3.63–3.69 ppm is the proton  $-\text{CH}_2$  at the end of the PCL chain ( $\text{H}^{\text{d}'}$ ). Based on the result of the  $^1\text{H}$  NMR spectra,  $\epsilon$ -CL has been perfectly polymerized in the presence of the catalyst **2a**. In this research, the degree polymerization (DP) of PCL was also determined based on  $^1\text{H}$  NMR spectrum analysis. The method was carried out by comparing the ratio of the methylene integration at the PCL center ( $\text{H}^{\text{d}}$ )

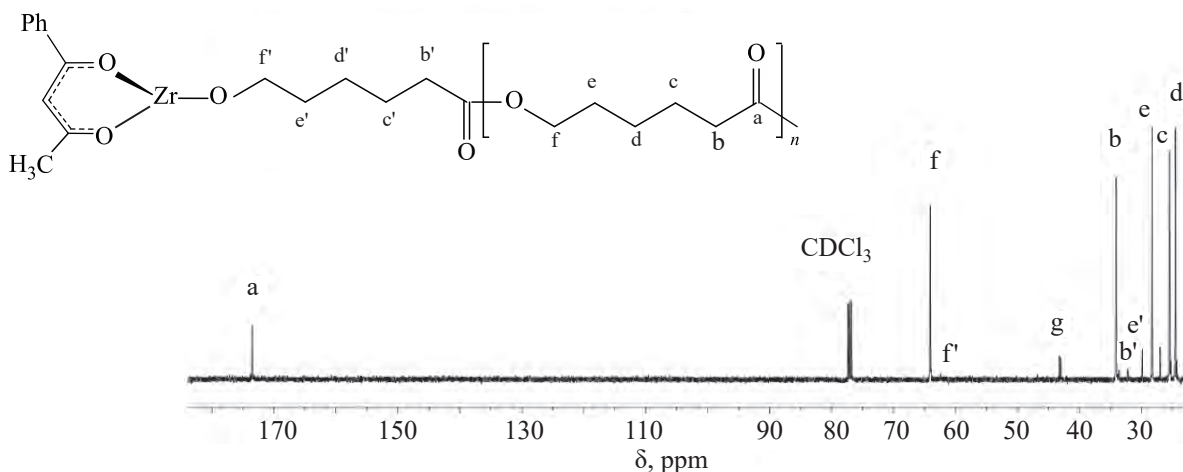


Fig. 2.  $^{13}\text{C}$ NMR Spectrum of PCL.

with the methylene integration at the end of PCL chain ( $\text{H}^{\text{d}}$ ) [24]. The calculations are illustrated in Eq. (1):

$$\text{DP} = \frac{\text{Methylene integration at the PCL center } (\text{H}^{\text{d}})}{\text{Methylene integration at the end of PCL chain } (\text{H}^{\text{d}'})} \quad (1)$$

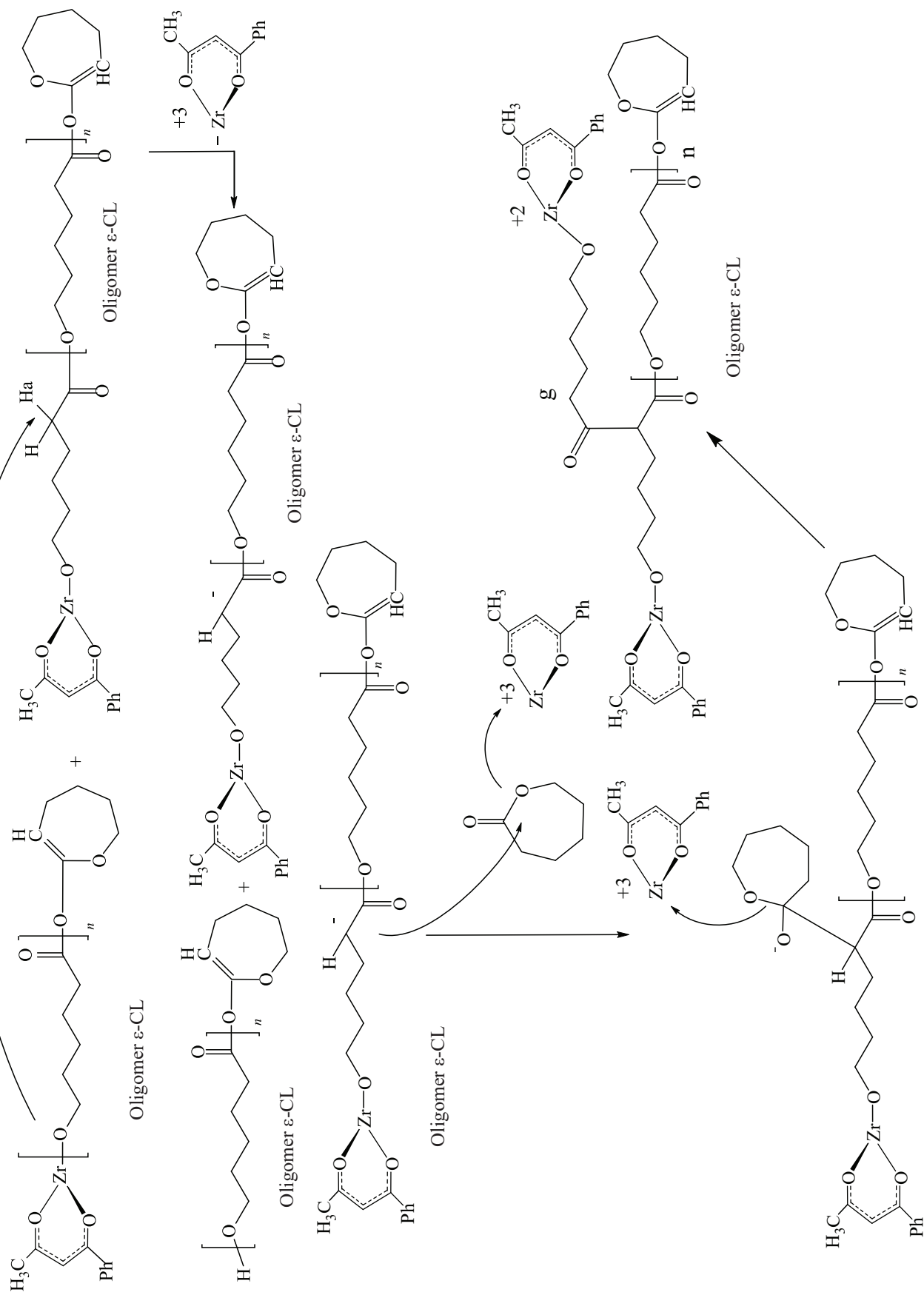
DP PCL obtained using catalyst **2a** and **2c** is 10. PCL produced using catalyst **2b** produces a higher DP (14) compared to that obtained using catalyst **2a** and **2c**. The existence of phenyl rings on the complex **2a** and **2c** ligand frame due to steric factors so that  $\epsilon$ -CL is difficult to coordinate with complex **2a** and **2c** [16]. The PCL with low DP (DP: 5–10) can be utilized to increase the degree of ester exchange reaction between PCL using high DP (DP: 701) with PET. In that PET/PCL blend, PCL with low DP serves as the third component in melt mixture which can be speed up the mixing time. This method would be very helpful to produce PET/PCL blends which have a good mechanical properties and combinations of miscibility [25].

The  $^{13}\text{C}$  NMR analysis was used to determine the PCL structure produced using catalyst **2a** as presented in Fig. 2. Previously, the other research groups had obtained similar  $^{13}\text{C}$  NMR PCL spectra to those obtained in this study [26–28]. The peak obtained in the range of 173.5 ppm was carbon in the carbonyl group ( $-\text{C}^{\text{a}}$ ). Next, the peak obtained in the range of 64.1 ppm and 62.5 ppm is carbon attached to oxygen in the ester bond and the carbon at the end of the PCL chain ( $-\text{CH}_2^{\text{f}}$  and  $-\text{CH}_2^{\text{f}'}$ ). After that, the peak obtained at 34.06 and 32 ppm is the carbon close to the carbonyl group

( $-\text{CH}_2^{\text{b}}$  and  $-\text{CH}_2^{\text{b}'}$ ). Furthermore, the peak at 30 ppm is the carbon close to the carbon at the end of PCL chain ( $-\text{CH}_2^{\text{e}}$ ). Meanwhile, the peak obtained at 28.29, 25.46, and approximately 24.55 ppm are carbon atoms at the center of the PCL ( $-\text{CH}_2^{\text{e,c,d}}$ ). The peak at 43 ppm was also detected in the  $^{13}\text{C}$  NMR spectroscopy. This peak was assumed to be the carbon atom adjacent to the carbonyl group in the  $\epsilon$ -CL oligomer ( $-\text{CH}_2^{\text{g}}$ ). The results of  $^{13}\text{C}$  NMR indicated that apart from producing PCL,  $\epsilon$ -CL oligomeric products were also produced in small amounts. The proposed reaction steps for the formation of  $\epsilon$ -CL oligomers are shown in Scheme 3. Based on the PCL chemical shift obtained from the  $^{13}\text{C}$  NMR spectra, ROP  $\epsilon$ -CL has succeeded in the presence of catalyst **2a**.

**Catalytic activity.** The catalytic activity of complex **2a–2c** was calculated from the mass of PCL obtained divided by the bis( $\beta$ -diketonate)zirconium(IV) catalyst mole and the reaction time of 4 h (Table 1) [18]. Complex **2c** shows the higher catalytic activity which is  $4.31 \text{ kg mol}^{-1} \text{ h}^{-1}$  compared to complexes **2b** and **2a**, each of  $4.01 \text{ kg mol}^{-1} \text{ h}^{-1}$  and  $2.44 \text{ kg mol}^{-1} \text{ h}^{-1}$ . While the  $\text{ZrCl}_4$  precursor does not react. Meanwhile, the PCL obtained using catalyst **2c** (91) also produce higher yields than those obtained using catalysts **2b** (87) and **2a** (54).

The difference in catalytic activity is caused by the difference in Lewis acidity of complexes **2a–2c**. The presence of phenyl ring groups in complex compounds **2c** which have an electron withdrawal character in the ligand frame reduces electron density in the zirconium central atom so that the Lewis acidity of zirconium was increases [18]. Complex compound **2c**

Scheme 3. The proposed reaction steps for the formation of  $\epsilon$ -CL oligomers.



**Table 1.** ROP of CL using catalysts **2a–2c**<sup>a</sup>

Catalyst	R <sup>1</sup>	R <sup>2</sup>	DP	Activity <sup>b</sup> , kg mol <sup>-1</sup> h <sup>-1</sup>	Yield, % <sup>c</sup>	T <sub>d</sub> , °C <sup>d</sup>	T <sub>m</sub> , °C <sup>e</sup>	Enthalpy, J/g <sup>e</sup>
ZrCl <sub>4</sub>			–	No reaction	–	–	–	–
<b>2a</b>	Me	Ph	10	2.44	54	274-439	63.73	140.8
<b>2b</b>	Me	Me	14 <sup>f</sup>	4.01	87	274-438 <sup>f</sup>	63.18 <sup>f</sup>	111.2 <sup>f</sup>
<b>2c</b>	Ph	Ph	10 <sup>f</sup>	4.31	91	295-435 <sup>f</sup>	59.62 <sup>f</sup>	109.0 <sup>f</sup>

<sup>a</sup> Reaction condition: 100°C; 4 h; catalyst 0.6 mol%; ε-CL 21 mmol;

<sup>b</sup> Determined based on PCL yield in kg per mol catalyst per hour;

<sup>c</sup> Determined from the mass of PCL formed divided by the mass of the ε-CL monomer used and multiplied by 100;

<sup>d</sup> Determined by TGA analysis;

<sup>e</sup> Determined by DSC analysis;

<sup>f</sup> Taken from Ref. [16].

has the highest Lewis acidity in the central atom due to two electron withdrawing ligands (phenyl) bound to the central atom (Table 2). While complex compound **2b** has the lowest Lewis acidity due to two electron donor ligands (Methyl) attached to the central atom. The highest catalytic activity of complex **2c** obtained based on the polymerization reaction is due to increased Lewis acidity in the zirconium central atom compared to complexes **2a** and **2b**. In addition, PCL produced using the **2c** complex also produces high yields.

The lower catalytic activity was shown by complex **2a** which has one phenyl ring, thereby causing steric hindrance of the complex. As a result, ε-CL is difficult to coordinate with the central atom of zirconium. Meanwhile, complex **2b** has two methyl ligands which do not have steric hindrance when coordinating with the central atom, so that its catalytic activity is higher compared to complex **2a**.

**Mulliken charge analysis of 2a–2c complex.** Nowadays, Mulliken charge analysis is one of the most widely charge analysis method that it is used. This analysis is used to describe the tendency of an atom to draw electrons based on an average calculation of the first ionisation energy and electron affinity [29]. On a small basis sets, this analysis is very effective.

Mulliken analysis in this study was conducted to observe the electron charging of the central atom in the bis(β-diketonate)zirconium (**2a–2c**) complex compound as illustrated in the Table 2. The Lewis acidity strength order of complex **2a–2c** will be obtained according to Mulliken charge analysis predictions. The complex **2c** has the highest Lewis acidity compared to complex **2a** and **2b**. Complex **2b** has the lowest Lewis acidity due to

two electron donors (Methyl) bound to the ligand frame. Although **2c** complex has the highest Lewis acidity, the value of the Mulliken charge does not reflect the ease of ε-CL being coordinated with the zirconium central atom. Ligand steric factor is also a factor that influences the ease of ε-CL coordinated with the central atom. The optimized geometry structure of **2a–2c** complex illustrated in the Fig. 3 [16].

**X-Ray giffraction (XRD) analysis.** PCL is a semicrystalline polymer because it consists of crystalline and amorphous phases. Semicrystalline polymers have a well-organized chain on the polymer re-unit. To find out the amorphous and crystalline structure of PCL can be observed by using XRD analysis. A sharp peak at XRD intensity will produce a crystalline polymer while a wide peak will produce an amorphous polymer. In addition, the XRD analysis can also done to examine the crystallinity size of PCL.

Figure 4 illustrate the XRD profile of PCL produced using catalyst **2a**. The sharp crystal peak is to be found at 2θ = 21.5°; 22.2°; and 23.8°. This peak conforms to the plane of reflection (110), (111) and (200) [30]. Meanwhile, the amorphous peak of PCL overlaps at a broad peak between 2θ = 15° to 45°. Previously, the other research groups had obtained similar PCL XRD pattern to those obtained in this research. Meanwhile, the degree

**Table 2.** Mulliken charge of Zr in **2a–2c** complex

Complex	R <sup>1</sup>	R <sup>2</sup>	Mulliken charge of Zr
<b>2a</b>	Me	Ph	1.124
<b>2b</b>	Me	Me	1.155
<b>2c</b>	Ph	Ph	1.093

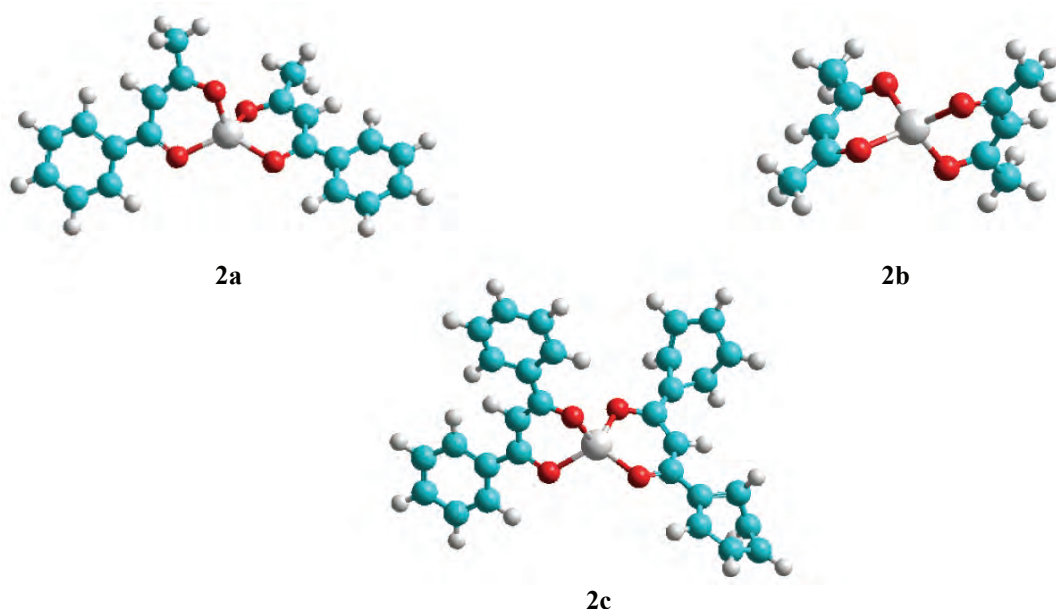


Fig. 3. Optimized geometry structure of complex 2a–2c.

of crystallinity ( $X_c$ ) of PCL produced using catalyst **2a** was 82% (Table 3) [30]. Based on XRD analysis, the PCL produced using catalyst **2a** has orthorhombic shape and semicrystalline structures.

Furthermore, the crystal size ( $D$ ) of the PCL crystal can be calculated by the Scherrer equation as illustrated in Eq. 2 [31].

$$D = \frac{k\lambda}{FWHM \cos\theta}, \quad (2)$$

where the constant value ( $k$ ) is 0.94 while the wavelength value is 0.15406. Whereas, the FWHM is a crystal grain size calculated from the top of the XRD plane. While the diffraction angle is depicted with the theta obtained from the Origin software [31]. The PCL crystal size corresponding to the calculation results of the Scherrer equation as illustrated in the Table 3.

In accordance to the calculation results from Eq. (1), it was found that the PCL crystal grain size in the orien-

tation plane 110 (D110) was 22.13 nm. While the PCL crystal grain size in the orientation plane 111 (D111) was 17.91 nm. Meanwhile, the crystal grain size of the PCL in the orientation plane 200 (D200) was 19.91 nm. Based on the results of the crystal grain size calculation, it can be assumed that in the amorphous matrix of PCL has embedded nanocrystalline grains. Previously, our research group also obtained PCL crystal grain size that was almost similar to what we reported in this study [16].

**Thermal analysis.** In the Fig. 5 was presented the DSC analysis of PCL. Furthermore, in this study has analyzed the melting behaviour of PCL at the heating rate of 10°C/min using DSC analysis. Meanwhile, the energy needed to change PCL solids into a liquid can be seen from the enthalpy measurements.

Based on the Fig. 5, The PCL endothermic process starts at 40°C where the peak is detected at 63.7°C. This temperature (63.7°C) was identified as the melting temperature ( $T_m$ ) of PCL. Subsequently, in the Table 1 also presents the enthalpy value ( $H_m$ ) of PCL produced using catalyst **2a** which is 140.8 J/g. The results from  $T_m$  and PCL enthalpy are in the same range as previously reported by researchers [32, 33].

Meanwhile,  $T_g$  PCL was detected in the range –67 to –62°C. These results also be obtained by using the DSC based on previous research reports.  $T_g$  PCL is the temperature at which PCL behaves like hard glass to become rubbery and elastic PCL [34, 35].

Table 3. Crystal grain size of PCL

Crystallite size	2θ	PCL-2a	
		nm	Xc, %
D 110	21.5	22.13	82
D 111	22.2	17.91	
D 200	23.8	19.91	

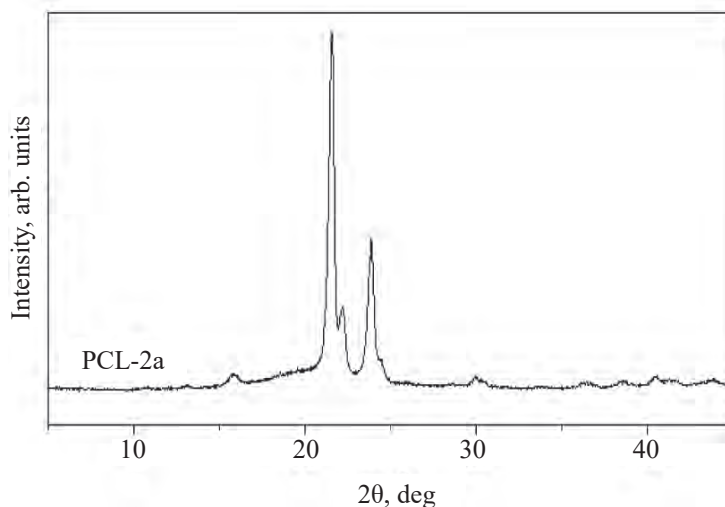


Fig. 4. XRD profile of PCL (PCL 2a).

Besides DSC analysis, TGA analysis is also used to investigate the thermal properties of PCL as presented in Fig. 6. The changes in PCL mass obtained using catalyst **2a** are measured from temperatures of 40 to 550°C. The TGA curve shows that the PCL mass is still stable at 100% when heated in the temperature range of 40–84.5°C. When heated in the temperature range of 84.6–274°C there is only a decrease in mass around 3%. Therewith the mass of PCL has decreased drastically to 90% when heated in the temperature range of 274–439°C. In addition, thermal decomposition ( $T_d$ ) of PCL begins at a temperature of 440°C and there is no change (plateau). These results are almost identical to the results of research obtained by previous research groups [26, 30].

After PCL characterization was performed, we found that the PCL obtained in this study was almost alike to the results obtained by previous researchers. Characterization was carried out by using FTIR,

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, XRD, DSC, and TGA. However, in this study we used complex **2a** as a catalyst in the ROP  $\epsilon$ -CL. Additionally, catalysts **2a–2c** are ideal for use in the tropics climate because they are not prone to moisture and air.

## CONCLUSIONS

ROP of  $\epsilon$ -CL using catalyst **2a** has been successfully conducted at temperature of 100°C for 4 h. The PCL produced by catalyst **2a** and **2c** resulted in degree of polymerization of 10, while the PCL produced by catalyst **2b** resulted in degree of polymerization of 14. Meanwhile, complex **2c** has the highest Lewis acidity relative among to complexes **2a** and **2b** by Mulliken charge analysis. However, this value does not imply the ease of  $\epsilon$ -CL converting to PCL product. Moreover, PCL produced by using catalyst **2a** is also a semi-crystalline polymer with a crystallinity level ( $X_c$ ) about 82%. The

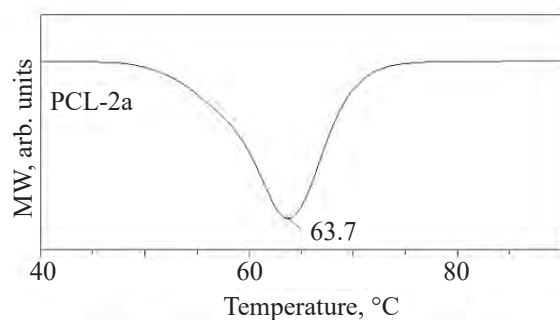


Fig. 5. DSC at the heating rate of 10°C/min for PCL.

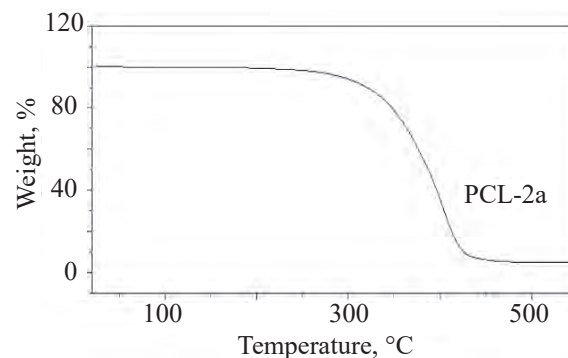


Fig. 6. TGA curve of PCL.



Xc of PCL indicates that the PCL produced has a high regularity. Additionally, PCL produced using catalyst **2a** has almost the same thermal properties as PCL produced using catalysts **2b** and **2c**. On the other hand, This PCL produced by catalyst **2a** can be applied as the third component in the melt mixture between PCL using high DP with PET so the result polyblend have a good mechanical properties and miscible combinations.

#### ACKNOWLEDGMENTS

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#### CONFLICT OF INTERESTS

The authors declare no conflict of interest requiring disclosure in this article.

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