

Synthesis of Bis(β - diketonato)Zirconium (IV) Chloride As A Catalyst In The Ring Opening Polymerizations of ϵ -Caprolactone

by Muhammad Yusuf

Submission date: 27-Nov-2019 04:28PM (UTC+0530)

Submission ID: 1222766761

File name: RJC_5463_814_publish_2019.pdf (613.03K)

Word count: 3907

Character count: 19377

SYNTHESIS OF BIS(β -DIKETONATO)ZIRCONIUM (IV) CHLORIDE AS A CATALYST IN THE RING OPENING POLYMERIZATIONS OF ϵ -CAPROLACTONE

M. Yusuf^{1,*}, D. Roza¹, M.urfajriani¹, H. Gunawan¹ and N. Dari¹

¹Department of Chemistry, Universitas Negeri Medan, Jl. Willem Iskandar, Medan, 20221, Indonesia

*E-mail: yusuf.6423@gmail.com

ABSTRACT

Poly(ϵ -caprolactone) (PCL) is a biodegradable polymer that is very attractive because of its properties such as high crystallinity, high permeability, and non-toxic. In this research, a series of bis(β -diketonato)zirconium (IV) chloride have been synthesized to be performed as a catalyst in the ring-opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL). The polymerization reaction was performed at 100 °C by stirring the mixture in the oil bath for 4 hours. The results showed that the PCL has been successfully polymerized using bis(β -diketonato)zirconium (IV) chloride catalysts complex and its molecular structure has been determined by Fourier Transform Infrared (FTIR), Proton nuclear magnetic resonance (¹HNMR), Carbon Nuclear Magnetic Resonance (¹³CNMR), X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). On the other hand, the plausible reaction mechanism of the use of bis(β -diketonato)zirconium (IV) chloride catalyst in the ROP of ϵ -CL was also proposed in this research.

Keywords: Bis(β -diketonato)zirconium(IV) Chloride, Ring Opening Polymerization, ϵ -Caprolactone, Poly(ϵ -caprolactone), Plausible Mechanism.

© Rasayan, All rights reserved

INTRODUCTION

Recent years, many researchers are interested in the synthesis of biodegradable polymers to reduce environmental pollution as a result of the inability of microorganisms to degrade petroleum base polymers.¹⁻⁴ Unlike synthetic polymers, PCL is one of the biodegradable polymers that are easy to decompose.⁵⁻⁶ PCL also has long term degradation so it's widely used for drug delivery systems and long-term implant devices. In addition, PCL has other interesting properties such as high crystallinity⁵, thermoplastic and mechanical properties that can be controlled⁵, biocompatibility⁵⁻⁶, permeability, and non-toxic materials. Hence, PCL has been adopted in various applications including packaging materials, implants, surgical sutures, vascular grafts, composite⁵, reinforcing agent⁶, and bone screws.⁷⁻⁹

ROP of ϵ -CL is called living polymerization⁷ because as long as there is still a monomer, its reaction occurs continuously. Because of that, this polymerization has been widely interesting for many researchers for the last many years. They also have conducted ROP ϵ -CL by using modified Lewis acid complex as a catalyst and initiators.⁷⁻¹⁵ They have employed some of the catalysts and initiators such as nanoporous alumina membranes⁷, alkali metal salts⁸, bis-ligated magnesium complexes⁹, Ti Al-MCM-41¹⁰, tetrakis (acetylacetonato)zirconium¹¹, metanesulfonic acid¹², aluminum complex¹³, zinc complex¹⁴, and distannoxane.¹⁵ But, some of their catalysts performed have some weaknesses. For example, they suffered from moisture and air. Then, they can also exposure to corrosive. In addition, they were difficult to control the Lewis acidity at the metal center.

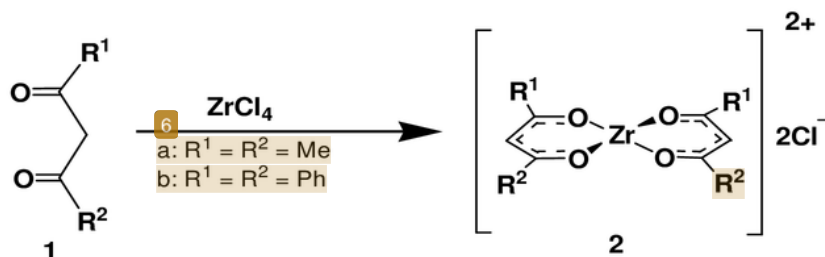
Moreover, the ROP of ϵ -CL has been performed by using the tetrakis(acetylacetonato)zirconium (IV) complex as a catalyst by another group research. Their catalysts have a similar β -diketonate ligand. But, they have a different coordination number (CN=4). PCL that they produced only resulted in a low degree of polymerization (DP) degree (DP = 8).¹¹ It is expected that, this research can produce PCL which has a

Rasayan J. Chem., 12(4), 2132-2140(2019)
<http://dx.doi.org/10.31788/RJC.2019.1245463>



high degree of polymerization ($DP > 8$) by using bis(β -diketonato)zirconium (IV) chloride catalysts. The PCL which high DP will produce good mechanical properties such as high crystalline, high decomposition temperature, and biocompatible.⁵⁻⁹

In this research, ROP of ϵ -CL will have been performed by using two series of bis(β -diketonato)zirconium (IV) chloride complex catalyst (CN=2) as a modified Lewis acid catalyst. This complex is not corrosive, and also not moisture and air-sensitive based on the results of characterization (FT-IR, ^1H NMR, elemental analysis) and its reaction as depicted in scheme-1.¹⁶⁻¹⁷ Moreover, the zirconium complex is easy to control the Lewis acidity at the metal center by changing the withdrawing (phenyl) or donor electron character on the ligand (methyl).



Scheme-1: Synthesis of bis(β -diketonates)zirconium (IV) chloride.¹⁶⁻¹⁷

EXPERIMENTAL

Material and Methods

This research was carried out at the Inorganic Laboratory, Universitas Negeri Medan. Zirconium tetrachloride, β -diketonate ligands, and ϵ -CL were obtained from Merck. Perkin Elmer 133e spectrometer displayed the IR spectra while KBR pellets were used for the solid form in samples. ^1H NMR and ^{13}C NMR (500 MHz) spectra were recorded on Agilent 500 spectrometer in CDCl_3 . X-ray powder diffractions (XRD) were performed on an XRD-6100 Shimadzu diffractometer using $\text{Cu-K}\alpha$ radiation. The melting temperature and enthalpy melting were analyzed by differential scanning calorimetry (DSC-60 Plus Series: SHIMADZU) at $10\text{ }^\circ\text{C}/\text{min}$ which the heating is ranged between $40\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$. The decomposition temperature was analyzed by thermogravimetry analysis (NETZSCH STA 449 F1 Jupiter) at $10\text{ }^\circ\text{C}/\text{min}$ which the heating is ranged between $40\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$.

Synthesis of Bis(β -diketonates)Zirconium (IV) Chloride

A mixture of zirconium tetrachloride (1 mmol), acetylacetonone ligand (1a) (2.4 mmol), and benzene solvent was stirred under an inert atmosphere at room temperature for 3 hours. After that, the mixture which had been reacted was refluxed for 14 hours. Furthermore, the resulting mixture was cooled and then left until the product precipitate forms whereas the filtrate are removed. Finally, the product was washed using n-hexane and dried *in vacuo* to produce bis(acetylacetonone)zirconium (IV) chloride (2a). The same treatment was also done for the reaction using dibenzoylmethane (1b) ligand to produce bis(dibenzoylmethane)zirconium (IV) chloride (2b).¹⁶⁻¹⁷

Ring-Opening Polymerization of ϵ -Caprolactone

Bis(β -diketonates)zirconium (IV) chloride (0.21 mmol) catalyst was dissolved in 5 mL methanol and put into a schlenk flask. Then, methanol was evaporated by heating at $80\text{ }^\circ\text{C}$ and drying in *vacuo* for 4 hours. Furthermore, ϵ -CL monomer (44 mmol) and zirconium β -diketonate catalyst were mixed at room temperature in the schlenk flask.

Polymerizations were heated at $100\text{ }^\circ\text{C}$ for 4 h in the oil bath. The product was then slowly dissolved using 30 mL chloroform and stirred using the sonication method for 30 minutes. After that, the product was stirred for 2 hours until dissolved and then refluxed to produce a clear solution. Next, that solution was precipitated using diethyl ether. Last, it is filtrated and dried in a vacuum pump to produce a white polymeric solid. The resulting PCL was measured by using FT-IR, ^1H NMR, XRD, TGA, and DSC.¹⁵

Computational Method

PM3 semi-empirical method was carried out to optimize the complex and reactant structure which is proved more accurate to calculate the geometries of zirconium complexes. Then, the geometry structure was calculated and visualized using the HyperChem 8.0 program package which runs by a personal computer with Windows 07 operating system.¹⁸⁻²⁰ Furthermore, all energies were applied to the Polak-Ribiere minimization algorithm and were minimized to the RMS gradient of less than 0.1 kcal/ (Å° mol).¹¹

RESULTS AND DISCUSSION

IR and ¹H NMR Spectroscopies

The FT-IR spectra of two PCL obtained by using catalyst 2a – 2b as founded by other research groups are shown in Figure-1.²¹ All FT-IR spectra showed CH₂- asymmetric absorption and CH₂- symmetrical absorption group at 2949 cm⁻¹ and at 2865 cm⁻¹. Then, the absorption band at 1470 cm⁻¹ is related to asymmetric CH- from CH₂- scissoring. While the absorption band at 732 cm⁻¹ is related to the rocking movements of methylene (CH-).

Furthermore, the characteristic absorption band at 1724 cm⁻¹ is related to an ester group of PCL (C=O) while the absorption band at 1248 cm⁻¹ is related to a strain of C-O ester. Based on these FTIR spectra, PCLs have been formed and the reaction is depicted in Scheme-2.

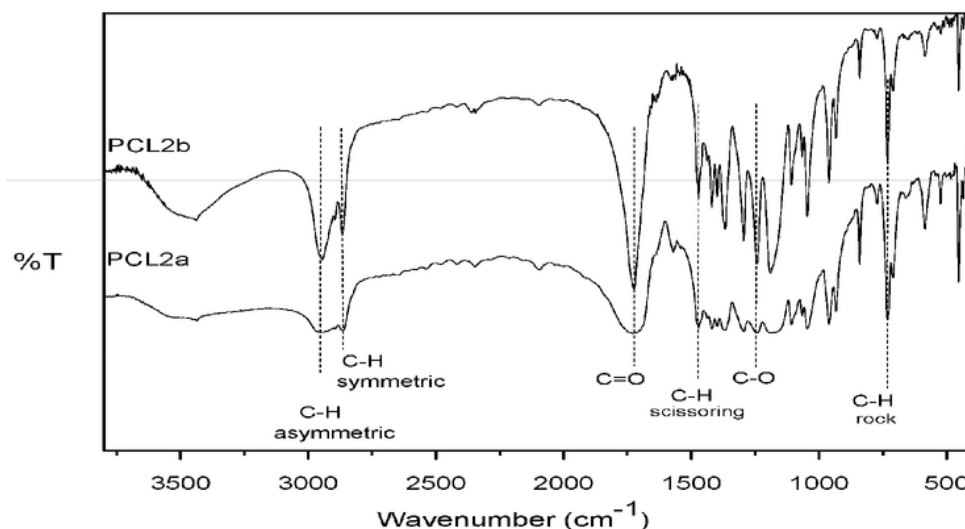
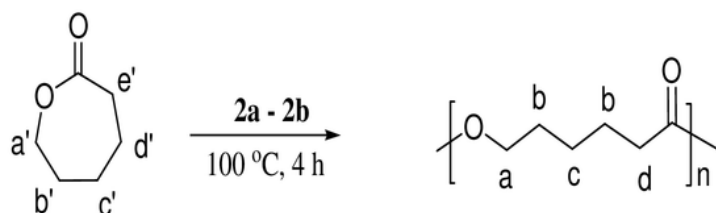


Fig-1: FTIR Spectra of PCL Generated by Catalyst 2a (PCL2a); PCL Generated by Catalyst 2b (PCL2b).



Scheme-2: ROP of ϵ -CL using 2a – 2b Catalyst

¹H NMR spectra of PCL generated by catalyst 2a – 2b in CDCl₃ solvent showed a similar ¹H NMR pattern as depicted in Fig.-2.

Based on the ¹H NMR analysis as reported in the previous research²²⁻²³, the chemical shifts in the range of 3.95 - 4.12 ppm are related to -CH₂ protons close to oxygen in ester bonds (H_a). While the chemical shifts in the range of 2.23 - 2.37 ppm is related to -CH₂ protons close to the carbonyl group (H_d). Last, the chemical shifts in the range 1.61 - 1.73 ppm and around 1.30 - 1.47 ppm is related to -CH₂ protons in the

polymer center (H_b and H_c). Based on this 1H NMR result, ε -CL has been successfully polymerized in the existence of catalyst 2a – 2b.

The degree of polymerization (DP) of PCL had also been calculated by using a comparison method between the integration ratio of naphthalene (proton signal H_e and H_f) with PCL (H_a , H_b , H_c , H_d) in the 1H NMR spectrum. According to this calculation, it can be seen that the DP of PCL obtained using catalyst 2b is 20.

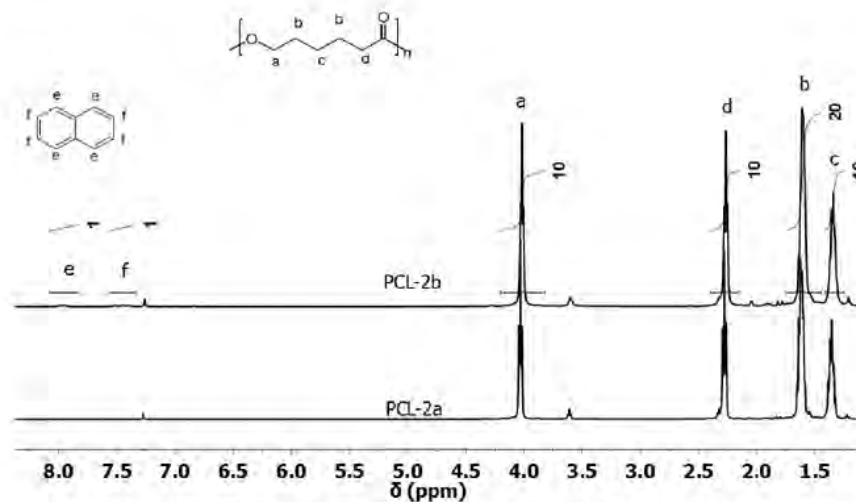


Fig-2. 1H NMR Spectra of the PCLs Obtained Using Catalyst 2a – 2b.

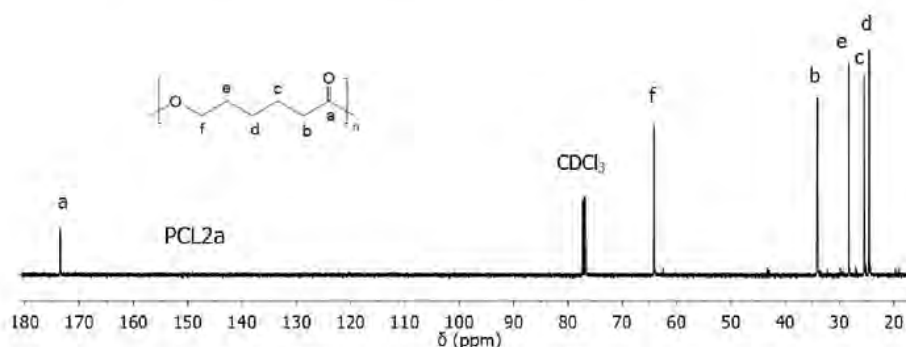


Fig-3: ^{13}C NMR Spectra of the Obtained PCLs Using Catalyst 2a.

According to the ^{13}C NMR analysis, as shown in Fig.-3, it can be seen that the chemical shift at 173.5 ppm is related to the carbon that is in the carbonyl group ($-C^d$), while the chemical shift in the range of 64.1 ppm is related to $-CH_2^f$ close to oxygen in the bond ester. Subsequently, chemical shifts at 34.06 ppm are related to $-CH_2^b$ close to the carbonyl group. Last, chemical shifts at 28.29 ppm, 25.46 ppm, and around 24.55 ppm are related to $-CH_2^{c,d,e}$ at the polymer center. This result is in the almost similar chemical shifts range as explained by previous work.²¹ Based on this ^{13}C NMR result, ε -CL has been successfully polymerized in the existence of catalyst 2a.

X-Ray Diffraction (XRD) Analysis

The characterization of the crystal and amorphous structure of PCL was conducted by using XRD analysis. XRD analysis can also be done to determine the crystal size and the level of PCL crystallinity. Crystalline polymers will produce sharp peaks, while amorphous polymers will produce wide peaks. In

general, polymers consist of crystalline and amorphous phases so that most of the polymers tend to be semicrystalline.

The XRD pattern of PCL obtained using catalyst 2a – 2b as reported in the previous research which is shown in Fig.-4.²⁴ The PCL crystal peak is overlapping at a wide peak (2θ) from 15° to 50° which indicates an amorphous and crystalline contribution to PCL. Meanwhile, the sharp crystalline peak is located at around $2\theta = 21^\circ$; 22° ; and 23° in corresponding with reflection planes (110), (111) and (200).²⁴ Based on the degree of crystallinity (X_c) calculation as depicted in Table 1, the X_c of PCL obtained using catalyst 2a – 2b is in the range of 80 - 83%.²⁴ These results indicate that the PCL obtained using 2a – 2b catalyst is semicrystalline polymer so that the polymer repeat unit in its chain is well organized. Meanwhile, the structure of the PCL is orthorhombic.

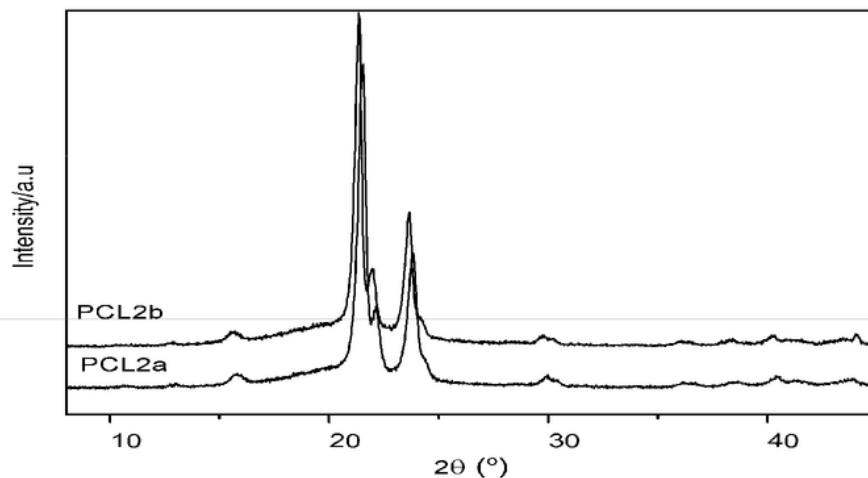


Fig.-4: XRD Pattern of PCL Obtained Using Catalyst 2a – 2b (PCL 2a – PCL 2b)

The Scherrer equation as shown below (equation-1) is used to determine the crystallite size (D) of the PCL crystal. It is derived from calculating the amount of FWHM (Full Width at Half Maximum) from the peak of the XRD field. Whereas, the Origin software is used to make the Bragg angle.

$$D = \frac{k\lambda}{FWHM \cos \theta} \quad (1)$$

The meanings are, the value of Scherrer constant (k) = 0.94, the value of X-ray wavelength (λ) = 0.15406. FWHM is the crystal grain size, θ is the diffraction angle.²⁵ The results of calculating the crystalline size of PCL are presented in Table-1.

Table-1. Crystallite Size (nm) for PCL (110), (111), and (200) Orientation Planes

Crystallite size	2θ	PCL-2a		PCL-2b	
		nm	X_c (%)	nm	X_c (%)
D110	21	20.03	83	22.65	80
D 111	22	16.89		16.43	
D 200	23	16.56		19.38	

$$X_c = \left[\frac{\text{the area inside the crystalline peaks}}{\text{the total area inside all the peaks}} \right] \times 100\%$$

According to the results from calculating, the crystal size in the orientation plane 110 (D110), it was found that the D110 of PCL obtained using 2a – 2b catalysts were in the range 20.03-22.65 nm. Whereas, the crystal size of PCL obtained using 2a – 2b catalysts in the orientation plane 111 (D111) were in the range 16.43-16.89 nm. Furthermore, the crystal size of PCL obtained using 2a – 2b catalysts in the

orientation plane 200 (D200) were in the range 16.56-19.38 nm. These results show that the grains of nanocrystalline embedded in the amorphous matrix.

Thermal Analysis

The thermal properties of PCL analyzed using DSC as shown in Fig.-5. In particular, the DSC was used to investigate the melting temperature (T_m) and melting enthalpy (ΔH_m) of PCL. The melting enthalpy (ΔH_m) shows some energy needed to reform the solid to the liquid.

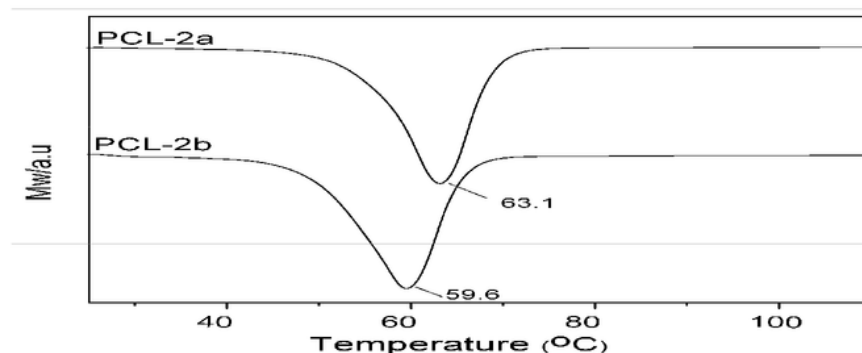


Fig.-5: DSC Thermograms of the Obtained PCL Using Catalyst 2a (PCL-2a), obtained PCL Using Catalyst 2b (PCL-2b).

The T_m of PCL obtained using catalyst 2a-2b were observed between 59.6 °C and 63.1 °C. The T_m of PCL is in the almost similar temperature range as previously have reported²⁶⁻²⁷ as shown in Table-2. Meanwhile, the melting enthalpy (ΔH_m) of PCL obtained using catalyst 2b shows higher ΔH_m compared to those catalyzed by 2a as shown in Table-2.

The thermal properties of PCL are also characterized by using TGA which is shown in Fig.-6. TGA is an instrument that can measure the mass changes and the decomposition temperature (T_d) of PCL. The TGA curve for all PCL obtained using catalyst 2a-2b only shows one mass decrease curve, which is started from 272 °C to 438 °C. Subsequently, the thermal decomposition of PCL occurs at the above temperatures 438 °C and no again change occurs (plateau). Based on the TGA curve, the T_d of all PCLs obtained using catalyst 2a – 2b had the same results with the previous work, so the thermal stability of it is also almost the same.^{21,24}

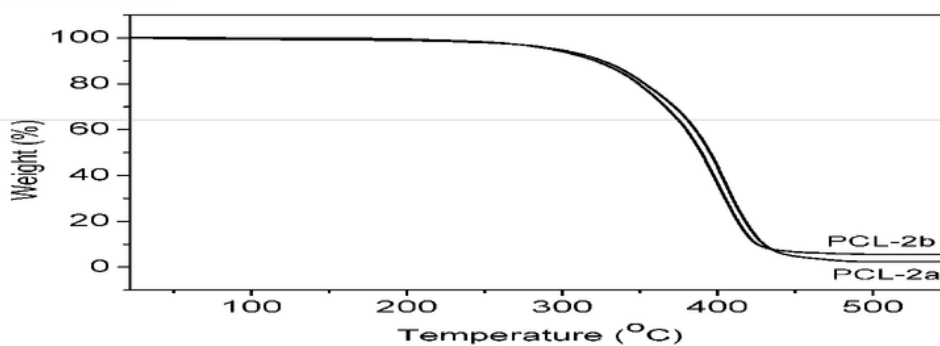


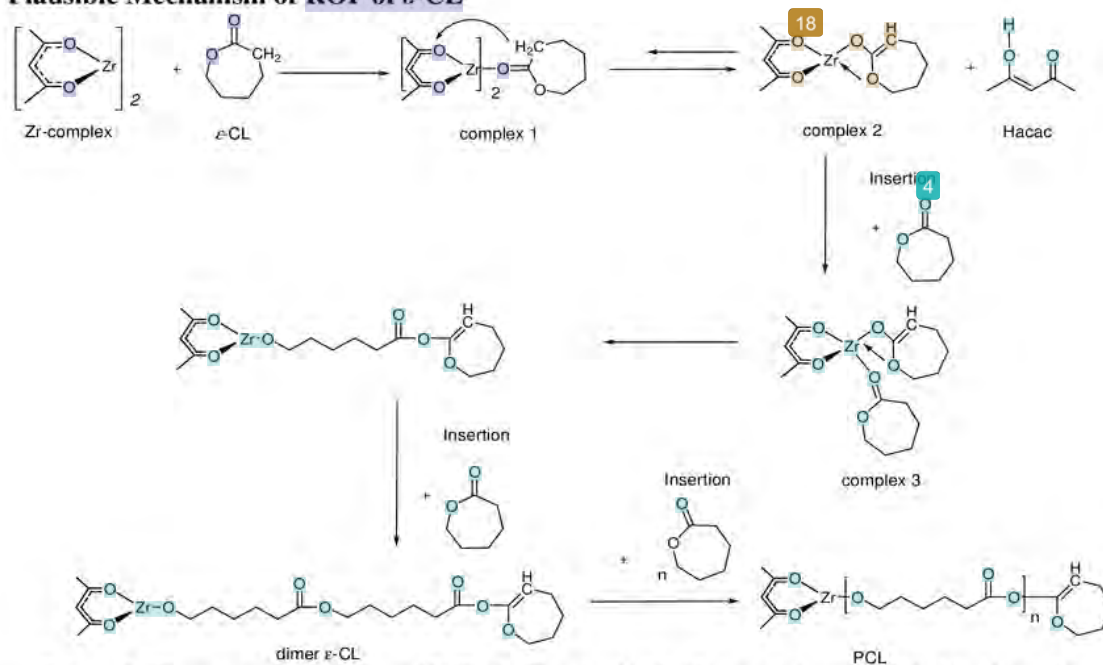
Fig.-6: TGA Thermogram of the PCL Obtained Using Catalyst 2a (PCL2a) and 2b (PCL2b).

Table-2: Thermal Analysis of PCL Obtained Using Catalyst 2a – 2b

Catal	T_d (°C)	T_m (°C)	Enthalpy (J/g)	Polymer Phase
2a	274-438	63.18	111.2	White solid
2b	295-435	59.62	109.0	White solid

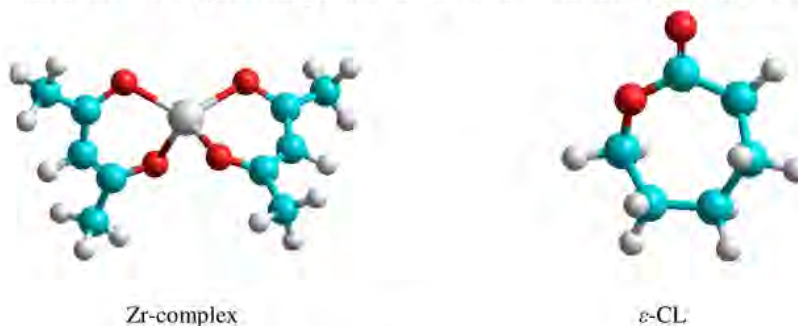
After analyzing PCL by using FTIR, ^1H NMR, ^{13}C NMR, XRD, DSC, and TGA, it is shown that the PCL obtained in this research have the same result as the previous work.²¹⁻²⁷ But the catalyst carried out in this work was 2a-2b catalysts.

Plausible Mechanism of ROP of ϵ -CL ¹¹



Scheme-3: The proposed mechanism of ROP of ϵ -CL using bis(β -diketonato)zirconium(IV) chloride catalyst

There are several reaction steps to obtain PCL using bis(β -diketonato)zirconium (IV) chloride catalyst, i.e. coordination, deprotonation, insertion, and the chain propagation step as shown in Scheme-3.¹¹ The first step was the formation of an unstable five-coordinate compound (Complex 1) via coordination of the carbonyl oxygen from ϵ -CL on the zirconium central atom. The second step was deprotonation of ϵ -CL, followed by the proton transfer on the acac ligands, which causes ligand exchange reactions that produce a stable four-coordinate compound (Complex 2). At this step, Hacac ligand dissociation also occurred. The third step was the coordination of the second ϵ -CL molecule to the zirconium central atom via the carbonyl oxygen-free electron pair (ϵ -CL) to form an intermediate five-coordinate compound (Complex 3). As a result, an acyl oxygen-zirconium bond was formed. The fourth step was the chain propagation through the insertion of the ϵ -CL molecule that corresponds with the coordination mechanism (dimer ϵ -CL). The insertion process can be continued to form a longer PCL after the next ϵ -CL molecule was coordinated at the zirconium central atom. The optimized geometries of the reactant and complex are shown in Fig.-7.



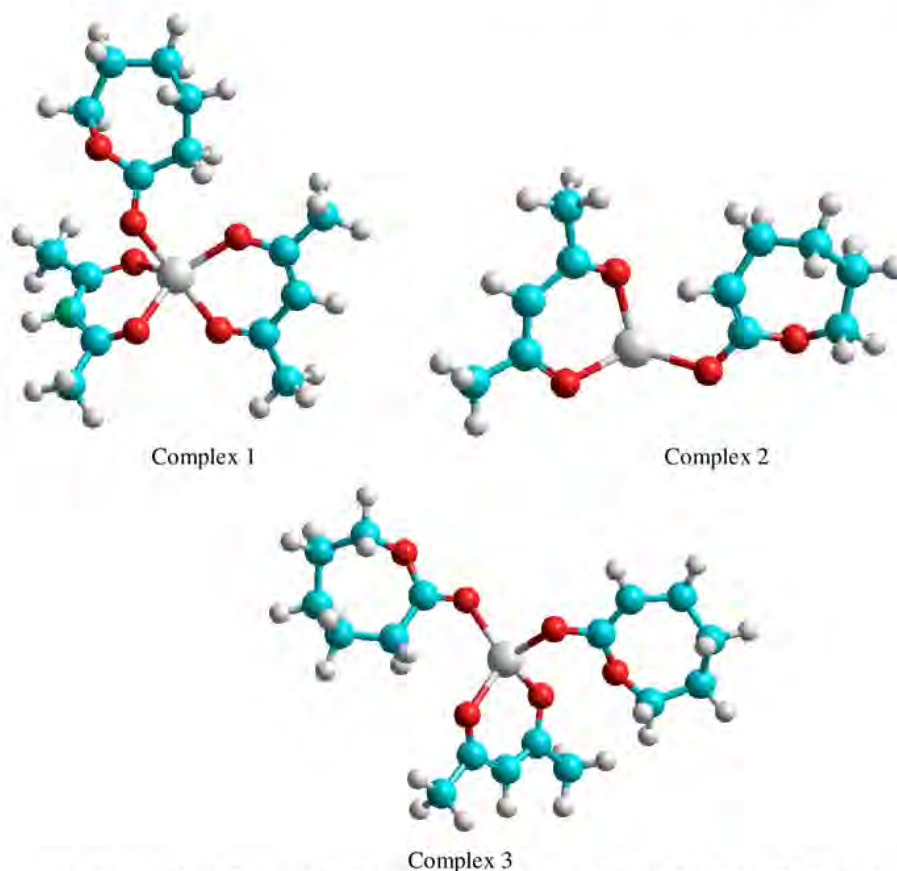


Fig.-7: Optimized Geometries of the Intermediates States During ROP of ϵ -CL using bis(β -diketonato)Zirconium (IV) Chloride Catalyst

CONCLUSION

PCL has been successfully obtained in this research by using catalyst 2a-2b at 100 ° C for 4 h. PCL generated by using catalyst 2b has a DP of 20. Meanwhile, PCL generated by using 2a-2b catalysts has the degree crystallinity (X_c) around 83% (PCL-2a) and 80% (PCL-2b) so it's a semicrystalline polymer. The high X_c of PCL generated by using 2a-2b related to the high regularity of the PCL chain. Furthermore, PCL generated by using catalyst 2a-2b has a melting temperature of around 59.6 °C and 63.7 °C respectively. Whereas the thermal decomposition of PCL occurs starts from 272 °C to 438 °C. On the other hand, the reaction mechanism of PCL obtained using bis(β -diketonato)zirconium(IV) chloride catalyst occurs through four reaction steps, they are coordination, deprotonation, insertion, and chain propagation.

ACKNOWLEDGMENT

For the research, the authors express gratitude to the Dirjend Penguatan Riset dan Pengembangan, Republik Indonesia for financial support of this research via Hibah PDUPT 2018 (Nomor: 073/SP2H/LT/DRPM/2018), and 2019 (190/SP2H/LT/DRPM/2019). We also express gratitude to Universitas Negeri Medan for facility support of this research.

REFERENCES

1. B. Yamini, and R. Nanthini, *Rasayan Journal of Chemistry*, **11**(1), 413(2018), DOI: 10.7324/RJC.2018.1112002.
2. B. Yamini, and R. Nanthini, *Rasayan Journal of Chemistry*, **11**(2), 440(2018), DOI: 10.31788/RJC.2018.1121992.

3. T.O. Siyanbola, A. F. Akinsola, O. R. Obanla, A. A. Adebisi1, A. A. Akinsiku, I. O. Olanrewaju, K. O. Ogunniran, O. S. Taiwo, K. O. Ajanaku, and O. A. Bamgboye, *Rasayan Journal of Chemistry*, **10(3)**, 1003(2017), DOI: 10.7324/RJC.2017.1031811.
4. M. Arcana, B. Tanajaya, B. Anwar, C. L. Radiman, and M. A. Sulfikar, *Journal of Mathematical and Fundamental Sciences*, **37A(2)**, 93(2005), DOI: 10.5614%2Fitbj.sci.2005.37.2.1.
5. C. C. Eng, N. A. Ibrahim, N. Zainuddin, H. Ariffin, W. M. Z. W. Yunus, and Y. Y. Then, *International Journal of Polymer Science*, ID 715801, 1 (2014), DOI: 10.1155/2014/715801.
6. S. Gea, C.T. Reynolds, N. Roohpur, N. Soykeabkaew, B. Wirjosentono, E. Bilotti, and T. Peijs, *Journal of Biobased Materials and Bioenergy*, **4(4)**, 384 (2010), DOI:10.1166/jbmb.2010.1108.
7. M.Tarnačka, A. Dzienia, P. Maksym, A. Talik, A. Zięba, R. Bielas, K. Kaminski, M. Paluch, *Macromolecules*, **51(12)**, 4588 (2018), DOI: 10.1021/acs.macromol.8b00409.
8. Z. Grobelny1, S. Golba, J. J.-Suliga, *Polymer Bulletin*, **76**, 3501 (2019), DOI: 10.1007/s00289-018-2554-0.
9. R. M. Slattery, A. E. Stahl, K. R. Brereton, A. L. Rheingold, D. B. Green, J. M. Fritsch, *Journal of Polymer Science, Part A: Polymer Chemistry*, **57**, 48 (2019), DOI: 10.1002/pola.29280.
10. N. Wanna, T. Kraithong, T. Khamnaen, P. Phiriyawirut, S. Charoenchaidet, J. Tantirungrotechai, *Catalysis Communications*, **45**, 118 (2014), DOI: 10.1016/j.catcom.2013.11.009.
11. P. Dobrzynski, *Polymer*, **48**, 2263 (2007), DOI:10.1016/j.polymer.2007.02.005.
12. J. M. Campos, M. R. Ribeiro, M. F. Ribeiro, A. Deffieux, and F. Peruch, *European Polymer Journal*, **49**, 4025 (2013), DOI: 10.1016/j.eurpolymj.2013.09.008.
13. X. Liu, C. Jian, D. Yu, J. Zhang, N. Tang, C. Wang, J. Wu, *Inorganic Chemistry Communications*, **36**, 206(2013), DOI: 10.1016/j.inoche.2013.09.015.
14. H.-L.Chen, H.-J.Chuang, B.-H.Huang, and C.-C. Lin, *Inorganic Chemistry Communications*, **35**, 247(2013), DOI: 10.1016/j.inoche.2013.06.048.
15. I. M.Arcana, M. Hasan, S.D. Angraini, A.A. Febrianti, and A. Ardana, *ITB Journal of Science*, **41A(2)**, 78(2009), DOI: 10.5614%2Fitbj.sci.2009.41.2.2.
16. Y. Permana, S. Shimazu, N. Ichikuni, T. Uematsu, *Catalysis Communications*, **6**, 426(2005), DOI:10.1016/j.catcom.2005.03.012.
17. Y. Permana, N. Ichikuni, S. Shimazu, *ITB Journal of Science*, **44**, 263(2012), DOI: 10.5614/itbj.sci.2012.44.3.6.
18. M. Yusuf and D.E. Sitepu, *AIP Conference Proceeding*, **1803**, 020055-1(2017) DOI: 10.1063/1.4973182.
19. M. Yusuf, D. Roza and A.K. Nasution, *AIP Conference Proceeding*, **1904**, 020012-1 (2017), DOI: 10.1063/1.5011869.
20. M. Yusuf, Dahniar, D. Roza and M. Damanik, *Asian Journal of Chemistry*, **31(5)**, 982 (2019), DOI: 10.14233/ajchem.2019.21662.
21. A. Elzubair , C. N. Elias, J. C. M. Suarez , H. P. Lopes, M. V. B. Vieira, *Journal of Dentistry*, **34**, 784 (2006), DOI: 10.1016/j.jdent.2006.03.002.
22. T. K. Sen, A. Mukherjee, A. Modak, S. K. Mandal and D. Koley, *Dalton Trans*, **42**, 1893(2013), DOI: 10.1039/c2dt32152a.
23. T. Öztürk and E. Meyvacı, *Journal of Macromolecular Science, Part A, Pure and Applied Chemistry*, **54**, 9(2017), DOI: 10.1080/10601325.2017.1309251.
24. J. Han, L. Zhu, S. Zheng, *European Polymer Journal*, **48**, 730(2012), DOI: 10.1016/j.eurpolymj.2012.01.020.
25. M. Ravi, S. H. Song, K. M. Gu, J. N. Tang and Z. Y. Zhang, *Ionics*, **21(8)**, 2171(2015), DOI: 10.1007/s11581-015-1384-4.
26. Y. Liu, W. S. Dong, J.Y. Liu, and Y. S. Li, *Dalton Trans*, **43**, 2244(2014), DOI: 10.1039/c3dt52712c.
27. Y. Wang, M. A. Rodriguez-Perez, R. L. Reis, J. F. Mano, *Macromolecular Materials and Engineering*, **290**, 792 (2005), DOI: 10.1002/mame.200500003.

[RJC-5463/2019]

Synthesis of Bis(β -diketonato)Zirconium (IV) Chloride As A Catalyst In The Ring Opening Polymerizations of ϵ -Caprolactone

ORIGINALITY REPORT

11%

SIMILARITY INDEX

5%

INTERNET SOURCES

8%

PUBLICATIONS

8%

STUDENT PAPERS

PRIMARY SOURCES

- 1** L. A. Tomachynski, V. Ya. Chernii, S. V. Volkov. "Synthesis and spectral characterization of bis(β -diketonato)zirconium(IV) and -hafnium(IV) phthalocyaninates", Journal of Porphyrins and Phthalocyanines, 2012
Publication 1%
- 2** Submitted to VIT University
Student Paper 1%
- 3** Submitted to Syiah Kuala University
Student Paper 1%
- 4** Submitted to University of Bath
Student Paper 1%
- 5** rasayanjournal.co.in
Internet Source 1%
- 6** Permana, Y.. "Studies on tris(β -diketonato)zirconium (IV); syntheses, characterization and catalytic activity for ring opening of oxiranes", Catalysis 1%

Communications, 200506

Publication

7	www.chemweb.com Internet Source	1%
8	Wenjuan Zhang, Shaofeng Liu, Wenhong Yang, Xiang Hao, Rainer Glaser, Wen-Hua Sun. "Chloroyttrium 2-(1-(Arylimino)alkyl)quinolin-8-olate Complexes: Synthesis, Characterization, and Catalysis of the Ring-Opening Polymerization of ϵ -Caprolactone", <i>Organometallics</i> , 2012 Publication	<1%
9	www.mdpi.com Internet Source	<1%
10	S L Manurung, Elfitra, S Frisniory. "Developing integrated creative problem solving (CPS) textbook for logic and set", <i>Journal of Physics: Conference Series</i> , 2019 Publication	<1%
11	Submitted to University of KwaZulu-Natal Student Paper	<1%
12	chinasciencejournal.com Internet Source	<1%
13	Submitted to Universiti Teknologi MARA Student Paper	<1%

14

Submitted to Middle East Technical University

Student Paper

<1%

15

Submitted to Samford University

Student Paper

<1%

16

ul.qucosa.de

Internet Source

<1%

17

pt.scribd.com

Internet Source

<1%

18

Submitted to Canakkale Onsekiz Mart University

Student Paper

<1%

Exclude quotes Off

Exclude matches Off

Exclude bibliography On