

Research Article

Self-Polymerization Reaction of Epoxidized Oleic Acid: Kinetic and Product Characterization

Dyah Retno Sawitri¹, Panut Mulyono², Rochmadi Rochmadi², Arief Budiman^{2,*}¹Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Islam Indonesia, Jalan Kaliurang KM 14.5, Yogyakarta, Indonesia.²Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika 2, Yogyakarta, Indonesia.Received: 7th July 2023; Revised: 24th August 2023; Accepted: 24th August 2023Available online: 5th September 2023; Published regularly: October 2023

Abstract

Epoxidized oleic acid can be transformed into vegetable oil-based polyesters through a self-polymerization reaction. This study aims to develop the kinetic model for the polymerization reaction between epoxide and carboxyl groups and the product characterization regarding its functional groups, molecular weight, and thermal stability. The polymerization reaction was carried out at the temperature of 120–180 °C for 2–6 h with the highest conversion of oxirane number up to 97%. Kinetic study showed one-step reaction model between oxirane and carboxylic group gives the activation energy value of 34.71 kJ/mol. Furthermore, the two simultaneous reaction model with further reaction between oxirane group and hydroxyl group also taken into account. The later provides a better agreement between the experimental data and the calculated conversion value. The activation energy values in the first and second steps are 38.61 and 26.00 kJ/mol, respectively. The product characterization showed that adding adipic acid did not significantly affect the polymer's molecular weight and thermal stability. The polydisperse characteristics of the poly(oleic acid) produced in this study enable poly(oleic acid) to be used as a lubricant, a polymer additive, or a precursor to produce polymers with higher molecular weights by taking advantage of the accessibility of OH groups.

Copyright © 2023 by Authors, Published by BCREC Group. This is an open access article under the CC BY-SA License (<https://creativecommons.org/licenses/by-sa/4.0>).

Keywords: Poly(oleic acid); Step-growth Polymerization Kinetic; Ring-opening polymerization; Vegetable Oil-based Polyester

How to Cite: D.R. Sawitri, P. Mulyono, R. Rochmadi, A. Budiman (2023). Self-Polymerization Reaction of Epoxidized Oleic Acid: Kinetic and Product Characterization. *Bulletin of Chemical Reaction Engineering & Catalysis*, 18(3), 386-397 (doi: 10.9767/bcrec.19251)

Permalink/DOI: <https://doi.org/10.9767/bcrec.19251>

1. Introduction

Vegetable oil-based polymers have received much attention in recent years. Through a series of transformations, vegetable oils can be transformed into various polymers such as polyester [1], polyether [2], and polyurethane [3]. This transformation can be carried out chemically on triglycerides, fatty acids, or fatty esters [4,5]. Oleic acid is one of the unsaturated fatty acids easily found in various types of vegetable

oil. It can be used as a raw material for bio-based polymer synthesis with diverse reaction routes, chemical structures, and applications [6–11]. Among those possible reaction routes, one promising is the synthesis of poly(oleic acid) (POA). Oleic acid can be first converted into epoxidized oleic acid (EOA), followed by a polymerization reaction to produce polyester.

The polymerization reaction to form polyester is categorized as step-growth polymerization and generally involves two types of bifunctional monomers. Bifunctional monomers are monomers that have the same functional group at

* Corresponding Author.
Email: abudiman@ugm.ac.id (A. Budiman)

both ends. Two types of monomers commonly used for polyesterification are dicarboxylic acids and diols. One of the most widely known reactions is the condensation reaction of dimethyl terephthalate or terephthalic acid with ethylene glycol to produce poly(ethylene terephthalate) or PET [12]. However, the polymerization reaction to form a polyester can also be carried out by a different route with a single monomer. Two well-known routes are the self-condensation reaction of ω -hydroxy acids and the ring-opening polymerization reaction of lactone [13]. The synthesis of poly(oleic acid) from oleic acid also involves only a single monomer with two functional groups (AB monomer) but without producing a simple compound as a by-product and does not involve a condensation process. Several types of polymers made from AB monomers include vegetable oil-based hyperbranched polyester [14,15], poly(silyl ether) [16], poly(ether sulfone) [17], perfluoro cyclo alkene aryl ether polymers [18], and carbazol-based copolymers [19].

Although not well studied, poly(oleic acid) can be developed as a new material with unique characteristics. As far as literature studies have been conducted, in-depth research on the synthesis of poly(oleic acid) has not been widely discussed. Miao *et al.* [6] explained that epoxidized oleic acid produced through enzymatic epoxidation could be converted into polyester. Furthermore, our preliminary research shows that the same type of polymer can also be synthesized via the chemical epoxidation route [20]. Using oleic acid from crude palm oil, Bahadi *et al.* [21] synthesized epoxidized oleic acid via a chemical epoxidation route to produce palm oil-based polyester. However, the discussion on the kinetics of the polymerization reaction of epoxidized oleic acid has not been studied. The kinetic study of AB-type monomers self polymerization has been carried out using thermal analysis [22,23], the role of molar mass of macromonomers [24], and multi-parameter optimization [25]. In this study, self-polymerization kinetic uses a step-growth mechanism approach with two models to understand the reaction progress better. The effect of temperature on the kinetics of the polymerization reaction has been studied. In addition, the effect of adipic acid on the characteristics of the resulting polymer is also discussed. Adipic acid is a dicarboxylic acid that has been widely used as a monomer for various types of polymer [26,27], plasticizer [28], and reinforcing additive [29] in polymer synthesis. In this study, adipic acid can be utilized as a spacing agent to overcome the steric hindrance

in monomer using the carboxylic group to react with the resulting hydroxyl group.

2. Materials and Methods

2.1 Materials

Oleic acid 90% and adipic acid were purchased from Sigma-Aldrich Singapore. Formic acid 98%, hydrogen peroxide 30% (stabilized for synthesis), n-hexane, and all reagents for analysis were purchased from Merck.

2.2 Oleic Acid Epoxidation

EOA was prepared from oleic acid via in-situ chemical epoxidation using formic acid as an oxygen carrier and n-hexane as a solvent under optimized reaction conditions [20]. First, oleic acid (50 g), formic acid (20 mL), and solvent (50 g) were transferred to a three-neck flask equipped with a stirrer, heater, thermometer, and reflux system. The mixture was heated to the reaction temperature, and then hydrogen peroxide (71 mL) was slowly dripped into the flask for 20 min. The reaction was carried out for 2 h at a constant temperature of 55 °C. After completion, the reaction product was put into a separatory funnel to separate the organic and aqueous phases. The organic phase was washed with warm distilled water three times and centrifuged. After centrifugation, the wet sample was dried at a temperature of 3–5 °C overnight to obtain dry powders of EOA.

2.3 Polymerization Reaction

The epoxidized oleic acid was put into a three-neck flask with a heater, stirrer, thermometer, and reflux system. The mixture was heated to the reaction temperature, and several samples were taken periodically for analysis. The total reaction time was 6 h. The polymerization reaction was studied by varying the reaction temperature (120, 135, 150, 165, and 180 °C) and adding adipic acid. The epoxide concentration was analyzed by titration using hydrogen bromide solution in acetic acid and crystal violet indicator. The carboxylate concentration was calculated from acid value and analyzed by titration using potassium hydroxide solution and phenolphthalein indicator [30].

2.4 Polymerization Kinetic

The polymerization reaction in this study occurs between two functional groups (the epoxide and the carboxylate group) on the same molecule without forming side products.

Thus, this reaction can be categorized as self-polymerization. This study assumes the reaction kinetics following the step-growth polymerization reaction kinetics model with two reaction scenarios (Figure 1). In the first scenario, referred to as Model 1, the polymerization reaction occurs only between the oxirane functional group (EP) and the carboxylic acid functional group (COOH) to produce the polymer product of P_1 . In comparison, the second scenario (Model 2) assumes that a side reaction occurs between the OH group of the polymer chain formed (P_1) and the oxirane functional group to produce the polymer product of P_2 .

2.4.1 Model 1

The rate of reaction:

$$-\frac{d[EP]}{dt} = k[EP][COOH] \quad (1)$$

Both groups are in the same molecule, but their concentrations are different ($[EP] \neq [COOH]$). This difference is caused by the incomplete

yield of the epoxidation reaction, so the oleic epoxide produced is a mixture of the remaining raw materials and reaction by-products.

The integration result of Equation (1) can be written as follows :

$$\frac{1}{[EP]_0 - [COOH]_0} \ln \frac{[EP][COOH]_0}{[EP]_0[COOH]} = kt \quad (2)$$

If expressed in conversion:

$$\ln \frac{1 - x_{EP}}{1 - \alpha x_{EP}} = k[EP]_0 \left(1 - \frac{1}{\alpha}\right) t \quad (3)$$

with

$$\alpha = \frac{[EP]_0}{[COOH]_0}$$

2.4.2 Model 2

From mass balance:

$$\frac{d[EP]}{dt} = -k_1[EP][COOH] - k_2[P_1][EP] \quad (4)$$

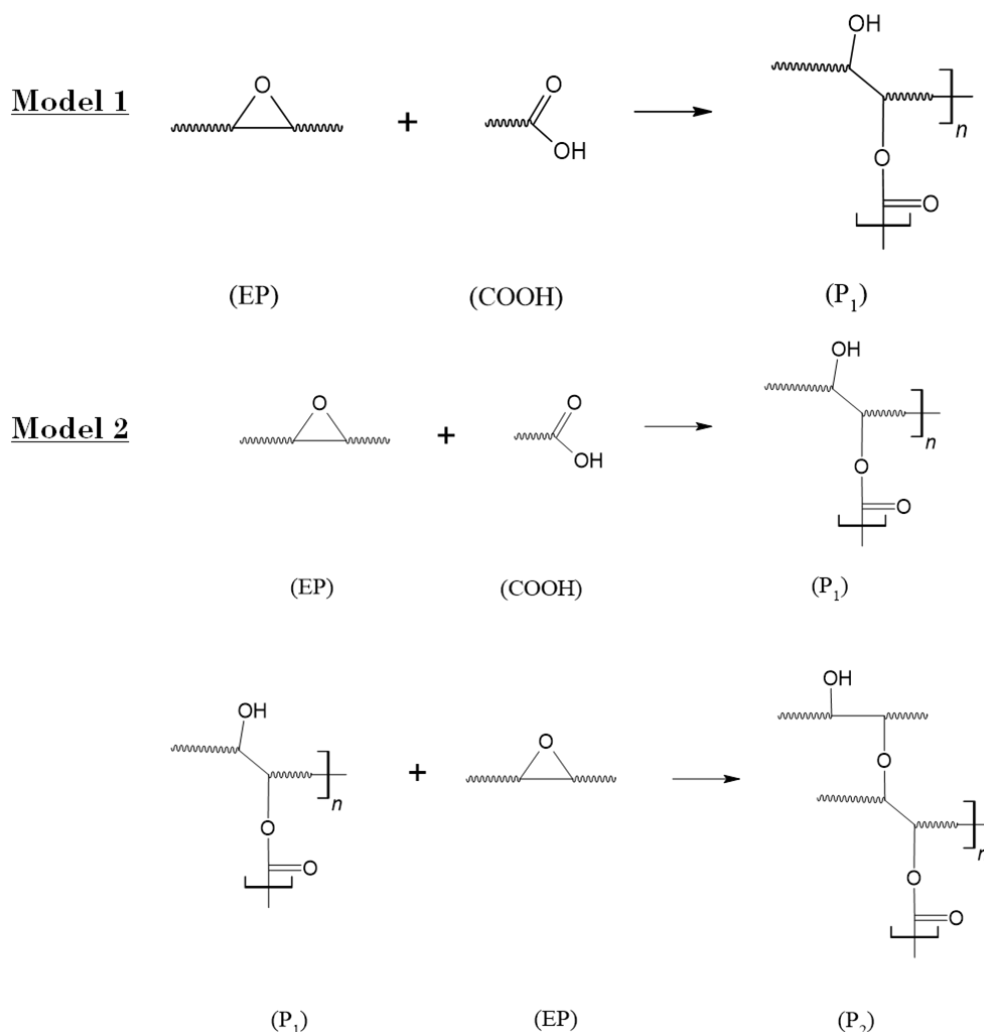


Figure 1. The reaction scenario for Models 1 and 2.

$$\frac{d[COOH]}{dt} = -k_1[EP][COOH] \quad (5)$$

$$\frac{d[P_1]}{dt} = k_1[EP][COOH] - k_2[P_1][EP] \quad (6)$$

$$\frac{d[P_2]}{dt} = k_2[P_1][EP] \quad (7)$$

Initial conditions:

At $t = 0$, $[EP] = [EP]_0$; $[COOH] = [COOH]_0$; $[P_1] = 0$; $[P_2] = 0$;

where, k , k_1 , and k_2 represent the kinetic constant for Model 1, the first, and the second reaction in Model 2, respectively. The square bracket $[]$ is the symbol for each species concentration, x for the epoxide conversion, and t represents the reaction time. The values of k_1 and k_2 were optimized using the minimization of the Sum of Square of Errors (SSE) between experimental data and calculated concentration for each component using the following equation:

$$SSE = \sum \{ [EP]_{calc} - [EP]_{data} \}^2 + \sum \{ [COOH]_{calc} - [COOH]_{data} \}^2 \quad (8)$$

2.5 Product Characterizations

Fourier Transform Infrared Spectrometer (FTIR Nicolet Avatar 360 IR) was used to analyze functional groups. The wavelength used is in the range of $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . Gel Permeation Chromatography (GPC Tosoh 20) was used to determine the molecular weight of the polymer. The analysis was carried out at a temperature of 40°C . Polystyrene was used as the standard polymer compound, and 1 mL/min tetrahydrofuran (THF) as eluent.

Simultaneous Thermal Analysis (STA Mettler Toledo) was used to determine the thermal stability of the resulting polymer products, which include Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry

(DSC). The analysis was conducted at $30\text{--}500^\circ\text{C}$ with nitrogen gas flow and a heating rate of 20°C/min .

3. Results and Discussion

The synthesis of poly(oleic acid) was carried out by Miao *et al.* [6] through the enzymatic epoxidation route. In this research, poly(oleic acid) has been successfully synthesized by a chemical epoxidation route. The results of the functional group analysis can be seen in Figure 2. The Figure 2 shows that the typical absorption spectrum for the carboxyl group (C=O) of EOA at 1702.03 cm^{-1} was significantly shifted to form new peaks indicated as C=O and CO bonds in the ester functional group ($-\text{COOR}$) at 1731.98 and 1175.34 cm^{-1} , respectively. The emergence of a new peak also strengthened the successfulness of the polymerization reaction at a wavelength of 3454.98 cm^{-1} , which is a typical absorption for the hydroxyl group ($-\text{OH}$). From the raw material point of view, the disappearance of the peak at wavelength 844.49 cm^{-1} indicates that the epoxide group has been completely converted during the reaction.

3.1 Effect of Polymerization Temperature

The effect of temperature on the polymerization reaction was studied with EOA as raw material with an average initial oxirane number of 4.5% and an average acid number of 189 mg KOH/g. In addition, the final product of each temperature variation was analyzed using FTIR to obtain a qualitative description of the functional group changes that occurred during the reaction.

Figure 3 shows that the FTIR spectra for all temperatures have almost the same pattern. The observed characteristics of the spectra are mainly related to the ester and hydroxy groups. The shift in the absorption spectrum

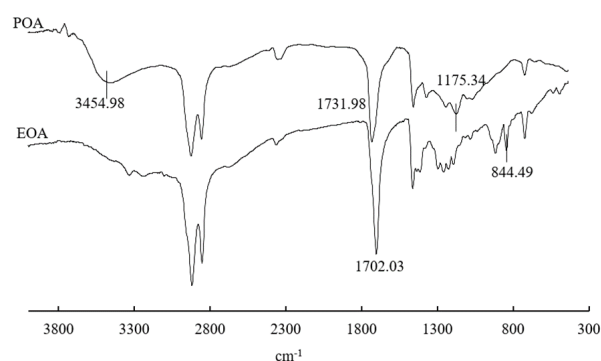


Figure 2. FTIR Spectra of EOA and POA.

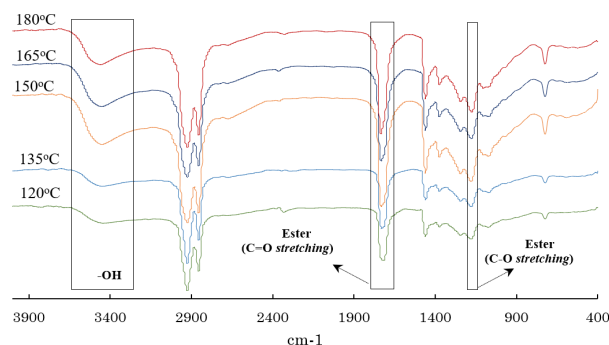


Figure 3. FTIR Spectra of POA at the various polymerization temperatures.

from position 1718 to 1734 cm^{-1} ($\text{C}=\text{O}$ stretching) and more visible peak at position 1176-1180 cm^{-1} (CO stretching) indicates that the higher the temperature, the more dominant the typical absorption for the ester group. From the hydroxy group's point of view, the higher the temperature, the more intense the peak observed in the wavelength range of 3443-3459 cm^{-1} .

Preliminary experiments show that the resulting product was only solidified when running over a specific temperature range (150-180 $^{\circ}\text{C}$) depending on the oxirane number of EOA. The higher the raw material's oxirane number, the lower the temperature needed for solidifying. The temperature range used in this study was 120-180 $^{\circ}\text{C}$ with increments of 15 $^{\circ}\text{C}$. The goal of the polymerization reaction is to obtain a solid polymer product. However, the oxirane and acid number measurements can only be conducted while the reaction product is still in the liquid phase. As soon as the reaction product solidifies, sampling and analysis become difficult. The experiment at 180 $^{\circ}\text{C}$, therefore, was ended after three hours due to this reason. The complete profile of the oxirane and acid numbers can be seen in Figure 4.

Considering that EOA obtained from the epoxidation reaction does not reach 100% yield [20], it can be said that more carboxylate groups are available for the polymerization reaction than the oxirane groups. Figures 4 show the differences between the initial values for the acid number and the oxirane for each temperature. The 0th minute of the reaction is when the reaction temperature is reached. The heating procedure needs time, and it is challenging to prevent an early reaction. The two figures also show that the decrease in the oxirane number is faster than the decrease in the acid number. This tendency indicates that

the reactivity of the oxirane or epoxide groups dominates compared to the reactivity of the carboxylate groups. The overall data shows the highest conversion from the oxirane and acid numbers is 97% and 84%, respectively. When viewed from the reaction mechanism, the conversion of the higher oxirane number may be due to side reactions between the oxirane group and the hydroxyl group formed from the primary reaction. Side reactions are common for polymerization reactions involving monomers with two different functional groups [31].

3.2 Polymerization Kinetics

3.2.1 Model 1

Acid and oxirane numbers at various times are used to obtain the value of the reaction rate constant (k). The reaction rate constant is defined as the slope of the plot between $\{1/([EP]_0 - [COOH]_0)\} \ln\{([EP][COOH]_0)/([EP]_0[COOH])\}$ vs. reaction time (t). The plot for each temperature and the value of k can be seen in Figure 5 and Table 1, respectively. Figure 5 shows a reasonable degree of linearity. A deviation from linearity was observed as the R^2 value was not in unity. Particularly at 120 $^{\circ}\text{C}$, the R^2 value was also lower than the other temperatures. The experimental data plot for Model 1 shows that the mean R^2 value is 0.9641.

The reaction rate constants at temperatures 120, 135, 150, and 165 $^{\circ}\text{C}$ are 3.84; 7.16; 10.17; and $11.38 \times 10^{-3} \text{ g.mmol}^{-1}.\text{min}^{-1}$, respectively. The increasing trend shows that the higher the temperature, the smaller the increase in the value of k . The possible cause is the increase in viscosity. The activation energy and pre-exponential factor can be calculated based on the Arrhenius equation from the four data. The activation energy value is 34.710 kJ/mol, and the pre-exponential factor is 179.414

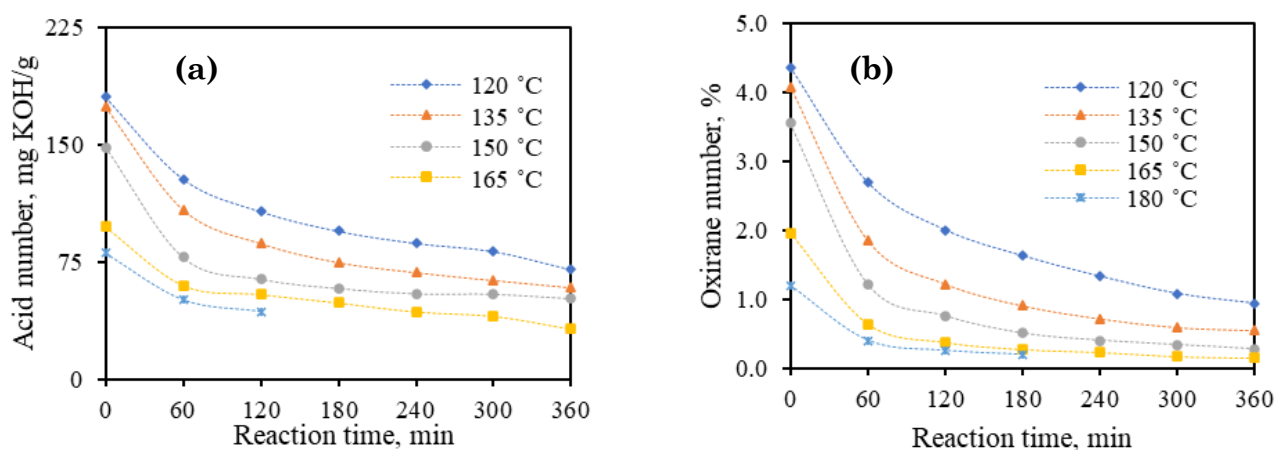


Figure 4. The profile of (a) acid number and (b) oxirane number.

g.mmol⁻¹.min⁻¹. Therefore, the Arrhenius equation for Model 1 can be expressed as follows:

$$k = 179.414 \exp\left(-\frac{34.710}{RT}\right) \quad (9)$$

3.2.2 Model 2

Model 2 was developed by considering the possibility of side reactions. This tendency can be seen from the rate of decrease in the oxirane number, which is faster when compared to the rate of decline in the acid number. Likewise, there are two kinetic constants in this case since there are two reactions. The values of k_1

and k_2 are determined by optimization at various temperatures. The comparison between the concentration data and the calculation results can be seen in Figure 6.

The graph shown in Figure 6 shows a good fit between the experimental data and the calculation results. The average R^2 value for Model 2 is 0.98986. This value is greater than the average R^2 for Model 1. It indicates that the reaction mechanism proposed in Model 2 is more representative than in Model 1. The fundamental difference between Model 1 and Model 2 lies in the side reaction (Reaction 2) that produces branched polymer chains.

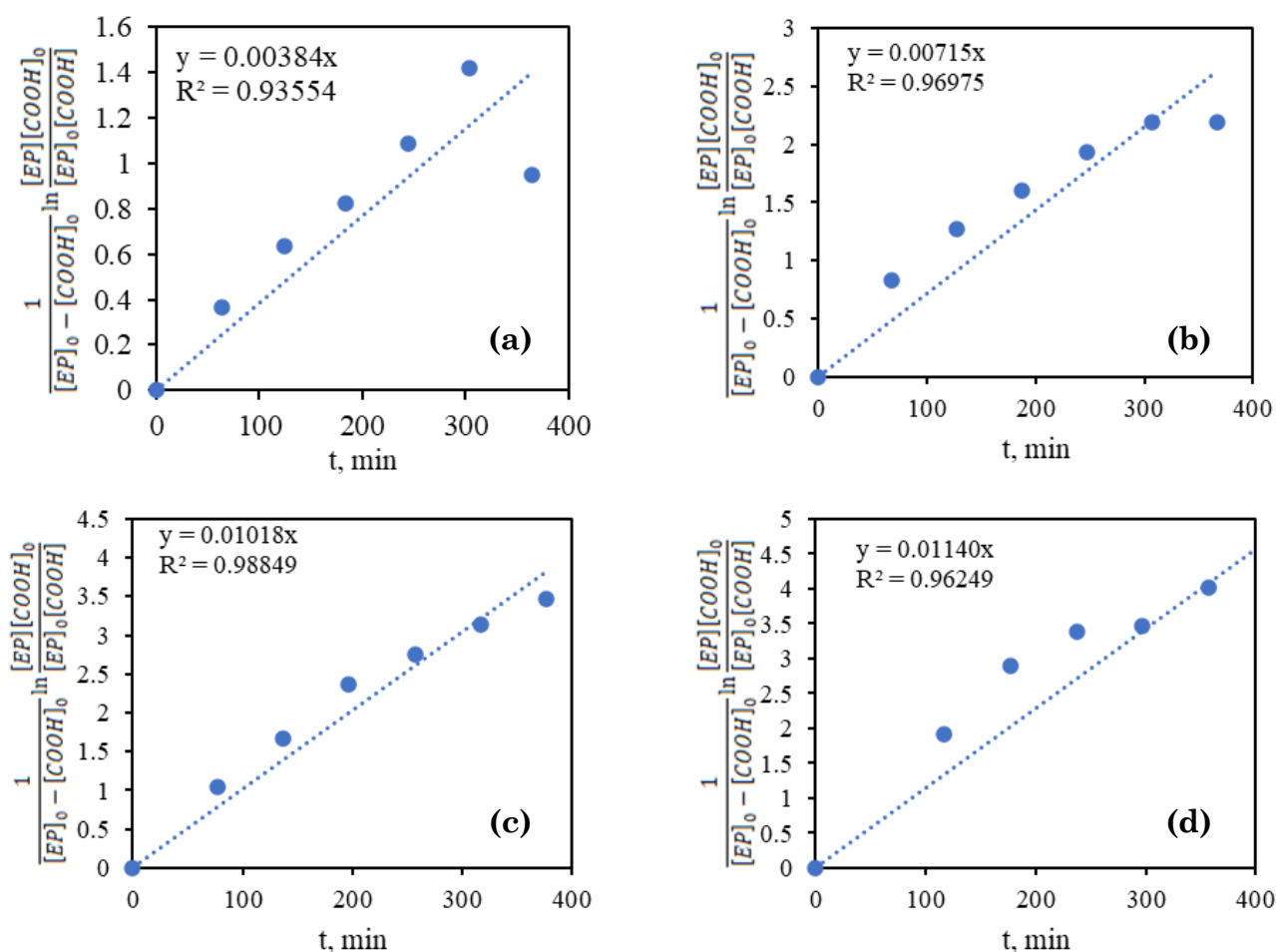


Figure 5. Plot of $1/([EP]_0 - [COOH]_0) \ln\{[EP][COOH]_0/[EP]_0[COOH]\}$ vs. time for the reaction temperature of (a) 120; (b) 135; (c) 150; (d) 165 °C.

Table 1. Polymerization reaction kinetic parameters for Model 2.

Temperature (°C)	k_1 (g.mmol ⁻¹ .min ⁻¹)	k_2 (g.mmol ⁻¹ .min ⁻¹)
120	0.002260	0.000515
135	0.003879	0.001215
150	0.006157	0.001383
165	0.007430	0.001197
A (g.mmol ⁻¹ .min ⁻¹)	332.14	1.92
Ea (kJ/mol)	38.61	26.00

Table 1 shows that both k_1 and k_2 values positively correlate with increasing temperature. However, k_2 deviations are observed at a temperature of 165 °C, where the reaction rate constant is smaller than the reaction rate at 150 °C. It is probably due to the drastic increase in viscosity, which microscopically affects the movement of molecules. Table 1 also shows that the activation energy for reaction 1 is similar to the activation energy of Model 1. The activation energy value for reaction 2, which is lower than reaction 1, is a consequence of the decrease in the value of the reaction constant at a temperature of 165 °C. The Arrhenius equation for Model 2 can be expressed as follows:

$$k_1 = 332.14 \exp\left(-\frac{38.61}{RT}\right) \quad (10)$$

$$k_2 = 1.92 \exp\left(-\frac{26.00}{RT}\right) \quad (11)$$

The activation energies for most polymerization reactions with the chain-growth mecha-

nism are about 84 kJ/mol. Furthermore, the chain-growth mechanism is divided into three stages (initiation, propagation, and termination). Typical activation energy values for the thermal decomposition reaction of the initiator at the initiation stage are 126-165 kJ/mol, the propagation is 20-40 kJ/mol, and the termination is 8-20 kJ/mol [31]. By looking at these values, although the mechanisms that occur are different, it can be said that the activation energy values obtained from this study are still within a reasonable range. When viewed from a similar reaction mechanism as this study, a kinetic analysis of the self-polymerization of gadolinium methacrylate has the activation energy values calculated at 58.85-103.35 kJ/mol [23].

3.3 Effect of Adipic Acid

Adipic acid was added to the epoxidized oleic acid before the polymerization reaction. Adipic acid is in the solid phase at room temperature with a melting point of 152.1 °C.

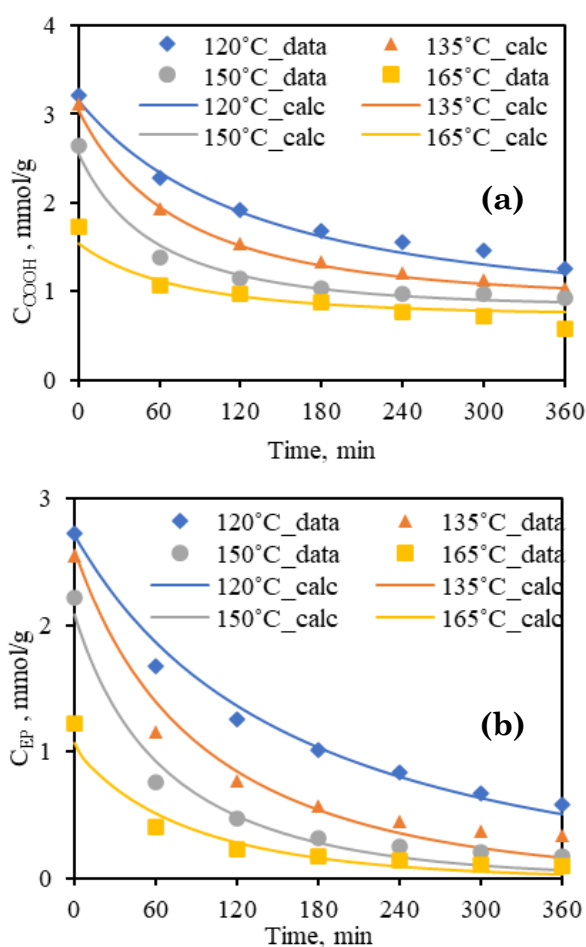


Figure 6. Experimental concentration data vs. calculated concentration of (a) carboxyl group and (b) epoxide group.

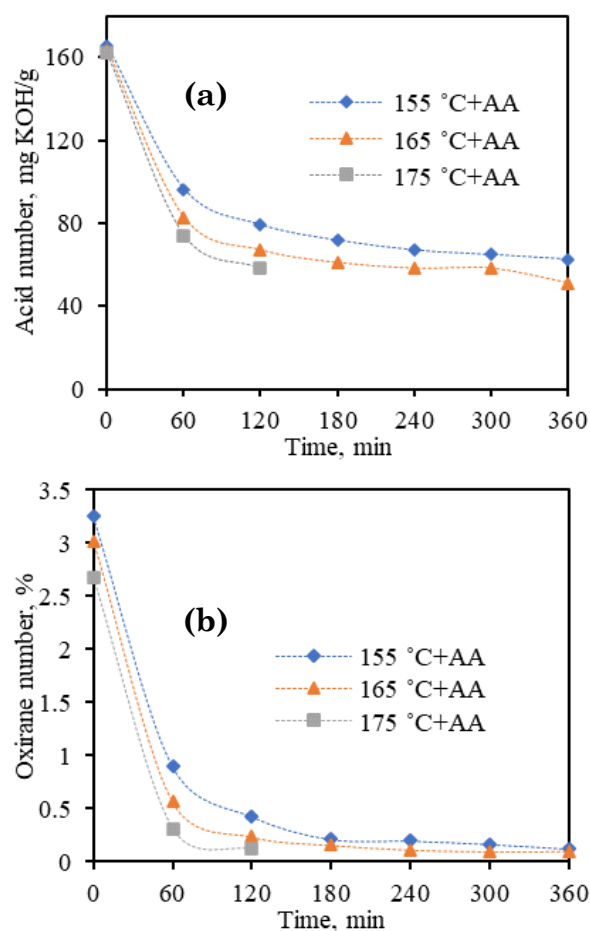


Figure 7. The profile of (a) acid number and (b) oxirane number on the polymerization reaction with adipic acid.

Therefore, the polymerization reaction by adding adipic acid was carried out at the lowest temperature of 155 °C. The polymerization reaction was only carried out up to a temperature of 175 °C because the reaction product solidified after two hours. Thus, for adding adipic acid, the profile of the oxirane acid number as a function of time up to the 6th hour is only shown for two temperatures. In addition to quantitative analysis of the oxirane number and acid number, a qualitative study using FTIR was also carried out for the reaction results to compare the spectra between the polymerization results with and without adipic acid. Comparisons were made for the polymerization results only at the same temperature (165 °C). The complete oxirane number analysis results for each temperature and time can be seen in Figure 7. Meanwhile, the spectra can be seen in Figure 8 for the qualitative analysis using FTIR.

Figure 7 shows that the decrease in acid and oxirane numbers has the same trend as the previous polymerization without adipic acid. The difference in concentration versus time profile in this variation shows that the distance is not as wide as the distance seen in the polymerization reaction without adipic acid because this variation's temperature increment is lower than the previous variation. The decrease

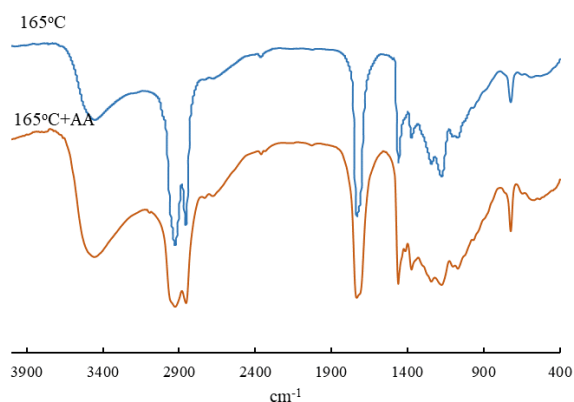


Figure 8. FTIR spectra of the resulting polymer on the polymerization reaction with and without adipic acid.

in the oxirane number is more dominant when compared to the decline in the acid number. The highest conversions for oxirane and acid numbers were 98% and 72%, respectively. Thus, it can be concluded that the conversion value of the oxirane number with or without the addition of adipic acid can be said to be not much different. As for the conversion of acid numbers, the conversion value indicated by adding adipic acid was 12% lower than the polymerization without adipic acid. The lower conversion is probably caused by the remaining unreacted adipic acid, causing the measured acid number at the end of the reaction to be higher. It is also confirmed by the results of qualitative analysis using FTIR in Figure 8.

The FTIR spectra for the polymerization results with or without adipic acid at a reaction temperature of 165 °C, as shown in Figure 8, show that adding adipic acid did not significantly change the profile of the functional groups of the reaction products. The absorption for the OH group on the addition of adipic acid looks more intense at a wavelength of 3455 cm⁻¹, while without adipic acid at 3451 cm⁻¹. Meanwhile, the typical absorption for long-chain linear aliphatic compounds at 2930 and 2850 cm⁻¹ was more clearly observed in the polymerization results without adding adipic acid. It indicates the possibility that there is still unreacted adipic acid residue. The two spectra show approximately the same trend when viewed from the ester functional group.

3.4 Product Characterization Results

3.4.1 GPC analysis

Poly(oleic acid) produced from the temperature variation of the polymerization reaction mostly has a high viscosity and shows very low solubility in THF. Samples for molecular weight analysis were specially made, considering that the resulting polymer still has sufficient solubility in the solvent. Three types of samples are coded A, B, and B+AA. The difference between code samples A and B is in the initial oxirane value of the oleic epoxide used.

Table 2. GPC analysis result.

Code	Mn (Da)	Mw (Da)	Mw/Mn
A	309	2527	8.19
B	479	2536	5.29
B+AA	331	2540	7.67

A: sample with oxirane value of 4%

B: sample with oxirane value of 4.5%

B+AA: sample with oxirane value of 4.5% and with the addition of adipic acid

Sample A has an oxirane value of 4%, while sample B has a value of 4.5%. Code AA indicates the addition of adipic acid. The three samples were reacted at 155 °C for 2 h. The results of the analysis of the molecular weight of the polymer using GPC can be seen in Table 2.

Table 2 shows a relatively significant difference in values between M_n and M_w . The M_w/M_n ratio is called the polydispersity index (PDI). PDI describes the molecular weight distribution range of a polymer. The higher the PDI value, the wider the range of molecular weight distribution of a polymer, which means the polymer has a non-uniform chain length. The ideal PDI is 1, where all the polymer chains have the same size. The step-growth polymerization reaction generally has a PDI value of around 2, while the chain-growth polymerization reaction has a PDI range of 1.5-20 [32]. In this study, the reaction between the oxirane and carboxylate groups can be categorized as a step-growth polymerization reaction when viewed from the functional groups involved. However, the PDI shown by the three

samples has a wide range of PDI (5-8). It is probably due to side reactions, as discussed in the section on reaction kinetics. The presence of side reactions produces polymers with branched chains and with various chain lengths. In addition, the purity of raw materials can also cause a wide range of molecular weight distribution. Bahadi *et al.* have synthesized palm oleic acid based polyester from epoxidized oleic acid with higher oxirane number (5.3%) and the result shows the range of PDI is 1.1-2.1 [21].

Table 2 also shows that although the M_n for the three samples has a reasonably significant difference, the M_w for the three samples has approximately the same range. Oleic epoxide as a monomer has a molecular weight of 298.5 gram.mol⁻¹. When viewed from M_n , the calculated degree of polymerization is only 1-1.6. Meanwhile, from the M_w point of view, the degree of polymerization reached 8.5 for all samples. Thus, it can be concluded that under the same operating conditions, the degree of polymerization between the raw materials with different initial oxidant numbers did not give a significant difference in the molecular weight of the resulting polymer. The same applies to the addition of adipic acid. In addition, it can also be concluded that with the process used in the laboratory, the resulting polymer still does not produce a large enough molecular weight. Compared with the polymerization reaction results with a similar mechanism, the polymer produced in this study can still be relatively low. Poly(ether sulfone) produced through self-polymerization of AB monomer has an average molecular weight range of 8000-111000 Da and PDI of 1.3-1.7 [17].

3.4.2 STA analysis

Simultaneous Thermal analysis was carried out using TGA-DSC simultaneously. Samples

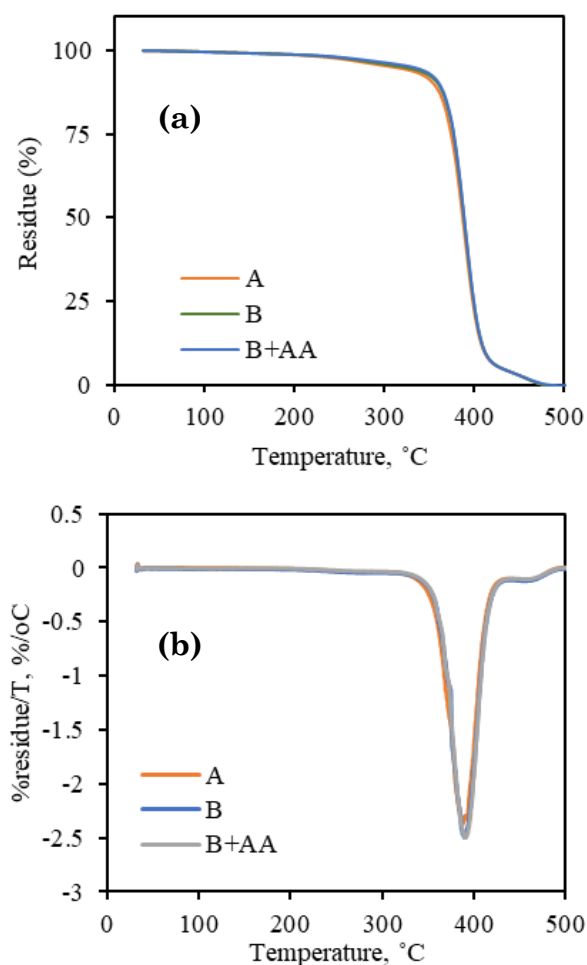


Figure 9. (a) TGA and (b) DTG of poly(oleic acid).

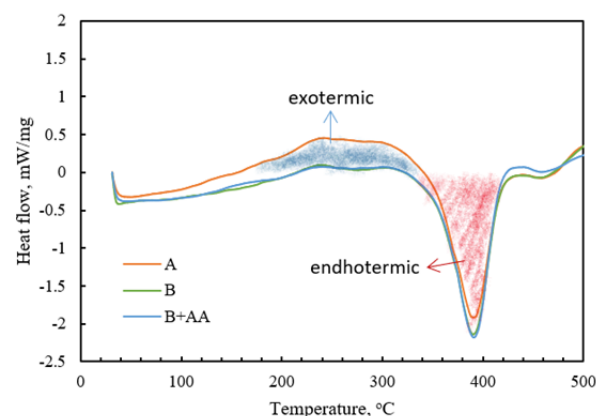


Figure 10. DSC result of poly(oleic acid).

analyzed in the thermal study have the same codes as samples for molecular weight analysis—the difference in temperature and reaction time. In the thermal analysis, the sample was reacted at 185 °C for 3 h to obtain a gel-like polymer sample. The results of the TGA and Differential Thermogravimetric (DTG) analysis can be seen in Figure 9, and The DSC curves for the three samples can be seen in Figure 10. From the three samples analyzed, it can be seen that there are no significant differences in the TGA and DTG charts. It is in line with the results of the molecular weight analysis. It strengthens the previous conclusion that the value of the initial oxirane number and the addition of adipic acid did not make any difference to the resulting product in terms of molecular weight and thermal properties.

The TGA graph of the three samples generally shows a one-stage decomposition process. It is also confirmed by the DTG graph, which only shows one dominant peak. From these two graphs, information can be obtained regarding the temperature of the initial decomposition reaction recorded at 5% weight loss ($T_{5\%loss}$) and the temperature when the decomposition speed reached its maximum (T_{peak}). The value of each parameter for the three samples can be seen in Table 3.

Table 3 shows that the initial temperature of decomposition and the temperature at which the decomposition speed reaches its maximum tend to increase with the increase in the initial oxirane number and adipic acid addition. However, the difference between the three samples can be insignificant. By seeing that there is only one step of the decomposition reaction, it is most likely that the ester bond decomposition reaction is dominant, which generally occurs at a temperature of 350-395 °C [6]. The initial decomposition temperature of the product resulting from this research is still low, indicating that the product has low thermal stability. Poly(ether sulfone) from a similar reaction mechanism shows an initial decomposition value of 440-494 °C [17].

In line with the TGA/DTG curve, Figure 10 shows that one dominant peak for the three samples indicates an endothermic process in

the same temperature range as the maximum decomposition reaction. However, specifically for sample A, there is a tendency for different peaks in the temperature range of 160-300 °C. The process indicated by the peak is exothermic. When viewed from the typical sloping and widening peak shape, there is a possibility that a further polymerization reaction occurs. It can also be attributed to preliminary experiments showing that the higher the initial oxirane number, the lower the temperature required to achieve the same conversion. The curves corroborate this possibility for samples B and B+AA, which have the same oxirane number. The two curves coincide and do not show an exothermic peak. A common trend is exothermic peaks in DSC analysis for compounds that undergo self-polymerization. Bis-benzoxazine has a similar tendency, which undergoes self-polymerization to poly(bis-benzoxazine) [33].

Based on the overall characterization results, it can be concluded that the poly(oleic acid) produced in this study has polydisperse characteristics (a wide range of molecular weights) and a decomposition temperature of 388-390 °C. Based on these characteristics, poly(oleic acid) can be used as a lubricant, an additive for polymers, or a precursor to produce polymers with higher molecular weights by utilizing the availability of OH groups.

4. Conclusions

Poly(oleic acid) has been successfully synthesized from oleic acid through a chemical epoxidation reaction-polymerization process. The resulting polymer has a low molecular weight with an average molecular weight (M_n) of 309-479 Da and an average molecular weight (M_w) of 2527-2540 Da. The addition of adipic acid did not affect the molecular weight of the resulting polymer. The reaction kinetics model is well approached using a step-growth polymerization model where a side reaction occurs simultaneously between the hydroxyl and oxirane groups. The activation energy of the polymerization reaction was obtained in the range of 26-38 kJ/mol.

CRedit Author Statement

Author Contributions: D.R. Sawitri: Experiment, Methodology, Investigation, Data Analysis, Writing, Review, and Editing; P. Mulyono: Conceptualization, Methodology, Review, Supervision; R. Rochmadi: Validation, Data Curation, Review, Supervision; A. Budiman: Resources, Conceptualization, Methodology, Re-

Table 3. Decomposition temperature of poly(oleic acid).

Code	$T_{5\%loss}$ (°C)	T_{peak} (°C)
A	311.43	387.92
B	322.93	389.17
B+AA	332.88	390.43

view, Validation, Supervision. All authors have read and agreed to the published version of the manuscript.

Acknowledgments

The authors are grateful to LPDP (Indonesia Endowment Fund for Education, Ministry of Finance, Republic of Indonesia) for the financial support.

References

- [1] Gobin, M., Loulergue, P., Audic, J.L., Lemiègre, L. (2015). Synthesis and characterisation of bio-based polyester materials from vegetable oil and short to long chain dicarboxylic acids. *Industrial Crops and Products*, 70, 213–220. DOI: 10.1016/j.indcrop.2015.03.041.
- [2] Miao, S., Wang, P., Su, Z., Zhang, S. (2014). Vegetable-oil-based polymers as future polymeric biomaterials. *Acta Biomaterialia*, 10(4), 1692–1704. DOI: 10.1016/j.actbio.2013.08.040.
- [3] Rayung, M., Aung, M.M., Ahmad, A., Su'ait, M.S., Abdullah, L.C., Jamil, S.N.A.M. (2019). Characteristics of Ionically Conducting Jatropha Oil-based Polyurethane Acrylate Gel Electrolyte Doped with Potassium Iodide. *Materials Chemistry and Physics*, 222, 110–117. DOI: 10.1016/j.matchemphys.2018.10.009.
- [4] Espinosa, L.M. De, Meier, M.A.R. (2011). Plant oils: The perfect renewable resource for polymer science?! *European Polymer Journal*, 47(5), 837–852. DOI: 10.1016/j.eurpolymj.2010.11.020.
- [5] Uyama, H. (2018). Functional polymers from renewable plant oils. *Polymer Journal*, 50, 1003–1011. DOI: 10.1038/s41428-018-0097-8.
- [6] Miao, S., Zhang, S., Su, Z., Wang, P. (2008). Chemoenzymatic Synthesis of Oleic Acid-Based Polyesters for Use as Highly Stable Biomaterials. *Journal of Polymer Science: Part A: Polymer Chemistry*, 46(12), 4243–4248. DOI: 10.1002/pola.22721.
- [7] Nicolau, A., Mariath, R.M., Martini, E.A., dos Santos Martini, D., Samios, D. (2010). The polymerization products of epoxidized oleic acid and epoxidized methyl oleate with cis-1,2-cyclohexanedicarboxylic anhydride and triethylamine as the initiator: Chemical structures, thermal and electrical properties. *Materials Science and Engineering C*, 30(7), 951–962. DOI: 10.1016/j.msec.2010.04.014.
- [8] Sander, M.M., Nicolau, A., Guzzatto, R., Samios, D. (2012). Plasticiser effect of oleic acid polyester on polyethylene and polypropylene. *Polymer Testing*, 31(8), 1077–1082. DOI: 10.1016/j.polymertesting.2012.08.006.
- [9] Roumanet, P., Laflèche, F., Jarroux, N., Raoul, Y., Claude, S., Guégan, P. (2013). Novel aliphatic polyesters from an oleic acid based monomer. Synthesis, epoxidation, cross-linking and biodegradation. *European Polymer Journal*, 49(4), 813–822. DOI: 10.1016/j.eurpolymj.2012.08.002.
- [10] Wu, Y., Li, A., Li, K. (2014). Development and evaluation of pressure sensitive adhesives from a fatty ester. *Journal of Applied Polymer Science*, 131(23), 41143. DOI: 10.1002/app.41143.
- [11] Omrani, I., Ahmadi, A., Farhadian, A., Shendi, H.K., Babanejad, N., Nabid, M.R. (2016). Synthesis of a bio-based plasticizer from oleic acid and its evaluation in PVC formulations. *Polymer Testing*, 56, 237–244. DOI: 10.1016/j.polymertesting.2016.10.027.
- [12] Pang, K., Kotek, R.Ä., Tonelli, A. (2006). Review of conventional and novel polymerization processes for polyesters. *Progress in Polymer Science*, 31, 1009–1037. DOI: 10.1016/j.progpolymsci.2006.08.008.
- [13] Jérôme, C., Lecomte, P. (2008). Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization. *Advanced Drug Delivery Reviews*, 60, 1056–1076. DOI: 10.1016/j.addr.2008.02.008.
- [14] Shan, P., Chen, N., Hao, C., Liu, H., Zhang, X. (2020). Facile and solvent-free synthesis of a novel bio-based hyperbranched polyester with excellent low-temperature flexibility and thermal stability. *Industrial Crops and Products*, 148, 112302. DOI: 10.1016/j.indcrop.2020.112302.
- [15] Testud, B., Pintori, D., Grau, E., Taton, D., Cramail, H. (2017). Hyperbranched polyesters by polycondensation of fatty acid-based AB: N-type monomers. *Green Chemistry*, 19(1), 259–69. DOI: 10.1039/c6gc02294d
- [16] Zhai, X.Y., Hu, S.B., Shi, L., Zhou, Y.G. (2018). Synthesis of Poly(silyl ethers) via Iridium-Catalyzed Dehydrocoupling Polymerization. *Organometallics*, 37(14), 2342–2347. DOI: 10.1021/acs.organomet.8b00316.
- [17] Matsumoto, K., Komuro, H., Kai, T., Jikei, M., (2013). Synthesis of poly(ether sulfone)s by self-polycondensation of AB-type monomers. *Polymer Journal*, 45, 909–914. DOI: 10.1038/pj.2013.11.
- [18] Campos, R., Mansur, A.A., Cook, C.H., Batchelor, B., Iacono, S.T., Smith, D.W. (2014). AB-type monomers for the preparation of perfluorocycloalkene (PFCA) aryl ether polymers. *Journal of Fluorine Chemistry*, 166, 60–68. DOI: 10.1016/j.jfluchem.2014.07.013.

- [19] Zhang, K., Tkachov, R., Ditte, K., Kiriya, N., Kiriya, A., Voit, B. (2020). AB- Versus AA+BB-Suzuki Polycondensation: A Palladium/Tris(tert-butyl)phosphine Catalyst Can Outperform Conventional Catalysts. *Macromolecular Rapid Communications*, 41(1), 1900521. DOI: 10.1002/marc.201900521.
- [20] Sawitri, D.R., Mulyono, P., Rochmadi, R., Budiman, A. (2021). Chemical Epoxidation of Oleic Acid to Produce AB Type Monomer for Fatty-Acid-Based Polyester Synthesis. *Jurnal Teknologi*, 83(6), 157–166. DOI: 10.11113/jurnalteknologi.v83.16912.
- [21] Bahadi, M., Salih, N., Salimon, J. (2021). Synthesis and characterization of biodegradable palm palmitic acid based bioplastic. *Biointerface Research in Applied Chemistry*, 11(6), 14359–14371. DOI: 10.33263/BRIAC116.1435914371
- [22] Hurre, S., Goldmann, A.S., Gliemann, H., Mutlu, H., Barner-Kowollik, C. (2018). Light-Induced Step-Growth Polymerization of AB-Type Photo-Monomers at Ambient Temperature. *ACS Macro Letters*, 7(2), 201–207. DOI: 10.1021/acsmacrolett.7b01001.
- [23] Wang, C., Wang, S., Zhang, Y., Wang, Z., Liu, J., Zhang, M. (2018). Self-polymerization and co-polymerization kinetics of gadolinium methacrylate. *Journal of Rare Earths*, 36(3), 298–303. DOI: 10.1016/j.jre.2017.09.015.
- [24] Chen, S.Q., He, C., Song, G., Li, L., Li, H.J., Haleem, A., He, W.D. (2020). Kinetically controlled cyclization in step-growth polymerization of AB₂ macromonomer: Role of molar mass of macromonomer. *Polymer*, 195, 122446. DOI: 10.1016/j.polymer.2020.122446.
- [25] Cheng, K.C., Su, Y.Y., Chuang, T.H., Guo, W., Su, W.F. (2010). Kinetic model of hyperbranched polymers formed by self-condensing vinyl or self-condensing ring-opening polymerization of AB monomers activated by stimuli with different reactivities. *Macromolecules*, 43(21), 8965–8970. DOI: 10.1021/ma101740r.
- [26] Sabahi, N., Roohani, I., Wang, C.H., Farajzadeh, E., Li, X. (2023). Thermoplastic polyurethane-based shape memory polymers with potential biomedical application: The effect of TPU soft-segment on shape memory effect and cytocompatibility. *Polymer*, 283, 126189. DOI: 10.1016/j.polymer.2023.126189.
- [27] Bueno, L., Toro, C., Martín, M. (2015). Techno-economic evaluation of the production of polyesters from glycerol and adipic acid. *Chemical Engineering Research and Design*, 93, 432–440. DOI: 10.1016/j.cherd.2014.05.010.
- [28] Vibha, K., Negi, S. (2020). Enzymatic plasticizing of lignin and styrene with adipic acid to synthesize a biopolymer with high antioxidant and thermostability. *Polymer Degradation and Stability*, 174, 109081. DOI: 10.1016/j.polymdegradstab.2020.109081.
- [29] Hosseini, A., Ramezani, S., Tabibiazar, M., Ghorbani, M., Samadi Kafil, H. (2021). Fabrication of cumin seed oil loaded gliadin-ethyl cellulose nanofibers reinforced with adipic acid for food packaging application. *Food Packaging and Shelf Life*, 30, 100754. DOI: 10.1016/j.fpsl.2021.100754.
- [30] Paquot, C. (1982). Standard methods for the analysis of oils, fats and derivatives. *Pure and Applied Chemistry*, 54(1), 233–246. DOI: 10.1351/pac198254010233.
- [31] Rudin, A., Choi, P. (2013). Polymer Reaction Engineering. *The Elements of Polymer Science & Engineering*, 495–520. DOI: 10.1016/b978-0-12-382178-2.00012-2.
- [32] Shrivastava, A. (2018). 2 - Polymerization. *Introduction to Plastics Engineering*, p. 17–48.
- [33] Hamerton, I., McNamara, L.T., Howlin, B.J., Smith, P.A., Cross, P., Ward, S., (2014). Examining the kinetics of the thermal polymerization of commercial aromatic bis-benzoxazines. *Journal of Polymer Science, Part A: Polymer Chemistry*, 52(14), 2068–2081. DOI: 10.1002/pola.27231.