

Synthesis, Properties, and Function of Self-Healing Polymer-Based on Eugenol

Erwin Abdul Rahim*

Department of Chemistry, Tadulako University, Jl. Sukarno-Hatta Km 9, Palu 94148, Central Sulawesi, Indonesia

* Corresponding author:

email: Erwin_abdulrahim@yahoo.com

Received: December 23, 2021

Accepted: April 4, 2022

DOI: 10.22146/ijc.71486

Abstract: Eugenol-based self-healing polymers were synthesized in a very short time of 94–159 s. Polymerization of eugenol catalyzed by H_2SO_4 - CH_3COOH yielded the corresponding self-healing polymers in quantitative yields in the range of molecular weight $(5.18-15.10) \times 10^5$ g/mol. The polymer exhibited self-healing behavior at room temperature due to hydrogen bonds between the hydroxyl groups of polyeugenol and the hydroxyl groups of sulfuric acid. This material can function as a polyelectrolyte and a novel self-healing catalyst for biodiesel production.

Keywords: self-healing polymer; eugenol; catalyst; biodiesel production

■ INTRODUCTION

Smart polymers are polymers that can only respond to small external stimuli. These small external stimuli include UV radiation, pH, temperature, magnetic field, etc. Self-healing smart polymers are a new class of smart materials that can repair themselves in the event of damage without the need for detection or repair by any kind of manual intervention. The increasing demand for fuel oil stocks used in the production of polymers and the need for polymer materials with improved performance in demanding applications further increases the need for durable materials. These challenges enable the synthesis of self-healing materials [1-5]. Compared to liquid electrolytes, solid electrolytes have higher safety and better thermal stability. In particular, the application of self-healing materials has led to intensive research on electronics, batteries, supercapacitors, solar cells, etc. Therefore, the practical demand for polyelectrolytes with self-healing properties will lead researchers to develop new self-healing materials [6-11].

In conjunction with world petroleum exhaustion, one improvement of renewable vitro sources is unique to selective fuel, especially vegetable oil as biodiesel. Biodiesel possess characteristics that matches diesel engine. These characteristics include being biodegradable, ecologically friendly, renewable, non-toxic and having high-thickness, high cetane number, and suitable sulphur content. The main disadvantage of commercialization of

biodiesel is that it requires relatively expensive ingredients, i.e. beef oil with high quality and low free fatty acids, resulting in high manufacturing costs. One way to reduce the cost of biodiesel production is to use an inexpensive material with high free fatty acid content, for example, waste cooking oil (WCO). The preparation of waste cooking oil and methanol biodiesel involves an ester exchange reaction with a base catalyst and the formation of methyl ester and by-products in glycerol. However, the use of edible oils in this transesterification reaction resulted in very small transformation of biodiesel. This is because edible oil contains free fatty acids between 3–40%. Many researchers have developed a catalyst for the production of biodiesel made of skilled edible oil. One of them is a solid acid catalyst that replaces the liquid acid to eliminate corrosive and ecological problems [12]. An interesting topic regarding solid acid catalysts is green organic synthesis. Soluble polymer catalyst is one of the catalysts used for green organic synthesis. Some catalysts dissolved between them are polymeric based stimulation weakening catalysts. For instance, Sun et al. used polymer-based stimuli-responsive recyclable catalytic systems for organic synthesis [13], while Bergbreiter used soluble polymer as a tool in catalysis and also to recover catalysts and ligands [14]. However, until now, the use of self-healing polymer-based catalysts to produce biodiesel from waste used cooking oil has never been reported.

Indonesia is one of the world's major oil producers. In addition, Indonesia accounts for about half of the world's clove leaf oil consumption. The level of eugenol, also known as 3-(4-hydroxy-3-methoxyphenyl) propene, in oil is set at 80–90% by weight [15-18]. Furthermore, eugenol has the potential to be an excellent raw material for the creation of more valuable chemicals. To increase the price of eugenol, a number of tests were carried out. Eugenol-based optically active helical polyacetylene catalysts as a new smart material have been produced, according to a recent breakthrough. The intelligent material became motion-responsive, and gave birth to a new smart material [19].

This paper reports the synthesis, properties and function of eugenol-based self-healing polymers. The effects of catalyst concentration, reaction time, amount of methanol, and reaction temperature on the yield of biodiesel are investigated, as well.

■ EXPERIMENTAL SECTION

Materials

The materials used were eugenol (99.99% purity; obtained from Happy Green Co.), concentrated sulfuric acid, glacial acetic acid, methanol (p.a), ethanol 98%, chloroform, ethyl acetate, diethyl ether, *n*-hexane, benzene, anhydrous sodium sulfate (all were obtained from Sigma-Aldrich), and distilled water (obtained from Organic Laboratory, Palu, Central Sulawesi), WCO were collected from author's university canteen.

Instrumentation

¹H spectra were recorded in chloroform-d (CDCl₃) on a JEOL EX-400 spectrometer. IR spectra were measured on a Bruker spectrophotometer. The tools used in this study were the melting point apparatus, pH meter, Ostwald viscometer, multimeter, analytical balance, stopwatch, separating funnel, hot plate, magnetic stirrer, aluminium foil, filter paper, and laboratory glassware.

Procedure

Synthesis of self-healing polymer-based on eugenol (SHPBE)

A 250 mL measuring cup was filled with up to 10 g of eugenol. Then, using a magnetic stirrer, 2.5 mL of

catalyst (H₂SO₄-CH₃COOH; with a CH₃COOH percentage of 2, 4, 6%) was progressively added to the cup while being continually mixed (room temperature). The appearance of formed polymer and the release of concentrated white smoke indicated polymer formation. To stop the polymerization, 1 mL of methanol was introduced to the cup. After that, the polymer was allowed to settle for 24 h at room temperature before being identified. By dissolving SHPBE in ether and rinsing the catalyst away from the polymer with water, pure polyeugenol can be produced.

Determination of the molecular weight of SHPBE

One gram of SHPBE was dissolved in ethanol to 0.02 g/mL in a 50 mL volumetric flask. The polymer concentration was changed to 0.01500, 0.01000, 0.00500, 0.00250, and 0.00125 g/mL using ethanol dilution. The flow time of pure solvent, ethanol, and each concentration of polymer solution was measured using an Ostwald viscometer to give t₀, t₁, t₂, t₃, t₄, t₅, and t₆. Using the Poiseuille equation, we get η_{sp}/C vs *C*. By projecting the curve to a concentration (*C*) of zero, we get $[\eta]$. The Mark-Houwink equation and the right parameters for *K* and *a* were used to calculate the polymer's molecular weight.

Self-healing properties

The support catalyst polymer was cut into small pieces and separated from the other parts. Then the polymer was left at room temperature for 24 h and observed for the process of self-healing.

Determination of ionic conductivity

Using ethanol as the solvent, the polymer was made into a solution with a thickness of 1 cm and a diameter of 6 cm for the electrodes. This investigation employed a frequency of 1–100 kHz and a voltage of 20 mV. To test the polymer's impedance, the material was clamped between two electrodes linked to the positive and negative poles of the LCR meter. Eq. (1) can be used to compute ionic conductivity.

$$\rho = RA/i; \sigma = 1/\rho \quad (1)$$

Biodiesel synthesis

A circular bottom flask with a magnetic stirrer was filled with 25 g of waste cooking oil. The catalyst was

then added in various concentrations of 1, 2, 3, 4, and 5%, and added with methanol at a 1:15 ratio (sample:methanol). To see the influence of reflux time on the yield of biodiesel produced, the catalyst concentration that provides the maximum biodiesel production was varied at 1, 2, 3, and 4 h at 60 °C. In the third step, the effect of raw material to methanol ratios of 1:11, 1:13, 1:15, 1:17, and 1:19 was examined (w:w). The experiment on the influence of temperature (40, 60, 80, 100, and 120 °C) was undertaken at the fourth stage. A Buchner funnel was used to filter the products. After that, 30 mL distilled water and 120 mL *n*-hexane were added to the filtrate. The mixture was placed in a separating funnel and left for 24 h to separate into two layers. Esters and *n*-hexane make up the top layer, while distilled water and the catalyst make up the bottom layer. Anhydrous Na₂SO₄ was transmitted through the top layer (esters and *n*-hexane). Then, using *n*-hexane, the esters were separated by rotating and measuring the volume. GC-MS was used to perform a quantitative analysis of FAME. The results were weighed and the biodiesel yield was calculated using Eq. (2).

$$\text{FAME yield} = \frac{m \text{ actual}}{m \text{ theoretical}} \times 100\% \quad (2)$$

The actual and theoretical masses of FAME in grams are denoted by *m* actual and *m* theoretical.

RESULTS AND DISCUSSION

Synthesis of SHPBE

The synthesis route for SHPBE is shown in Fig. 1. Eugenol was quantitatively converted into polymer electrolyte. ¹H-NMR (Fig. 3) and IR spectroscopy were used to identify the polymer electrolyte. The

polymerization of eugenol using the H₂SO₄-CH₃COOH catalyst, which was found to be particularly effective for the polymerization of eugenol [12-19], produced excellent yields of the appropriate polymer (Table 1). According to FTIR analysis, the disappearance of absorption at wavenumbers 1637 and 995 cm⁻¹, which is indicative of vinyl group absorption, appeared in the IR spectrum of eugenol (Fig. 2(a)), but not in the spectrum of SHPBE (Fig. 2(b-d)). As a result, it pointed to the formation of SHPBE. SHPBE spectra in different concentrations of CH₃COOH were similar. The broad spectrum from -OH at wavenumber 3500 cm⁻¹ suggested the establishment of hydrogen bonding in Fig. 2(b-d). Furthermore, ¹H-NMR research reveals that the vinyl group's proton resonance at 5 ppm was not detectable, indicating that polymerization had occurred (Fig. 3).

Self-healing and Motion Responsive Properties

Fig. 4 shows that the resulting polymer can undergo self-healing at room temperature. It was seen that the separate parts of the polymer coalesced after 24 h.

Ionic Conductivity of SHPBE

This SHPBE has an ionic conductivity of 3.6 × 10⁻¹ S.cm⁻¹ and a semiconductor conductivity of 100-10⁻⁶ S.cm⁻¹. This SHPBE is a semiconductor polymer with

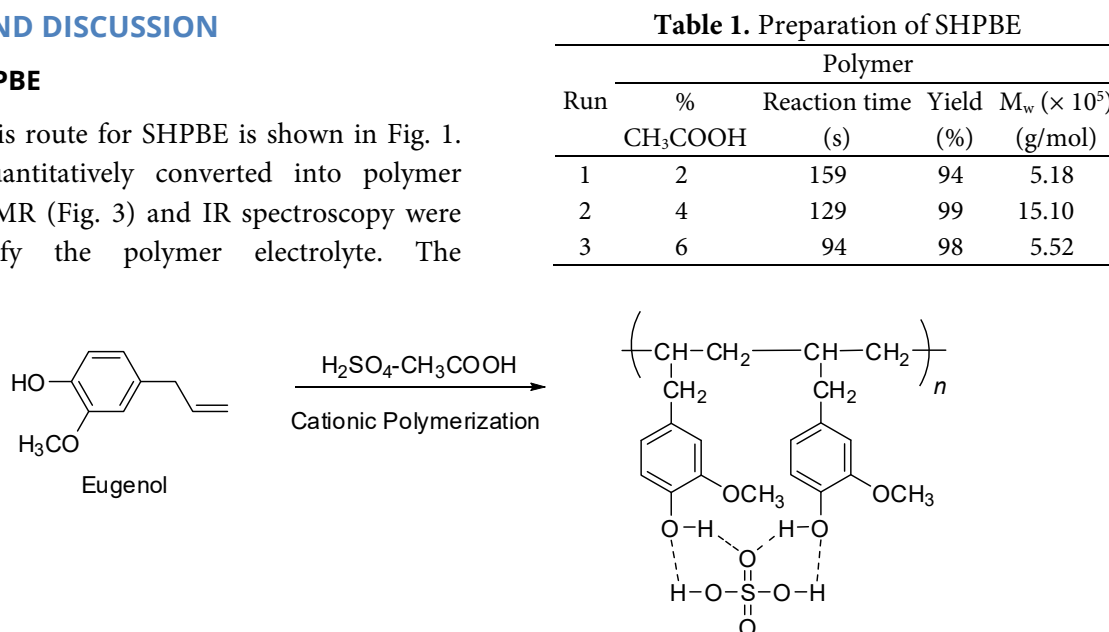


Fig 1. Schematic synthesis of SHPBE

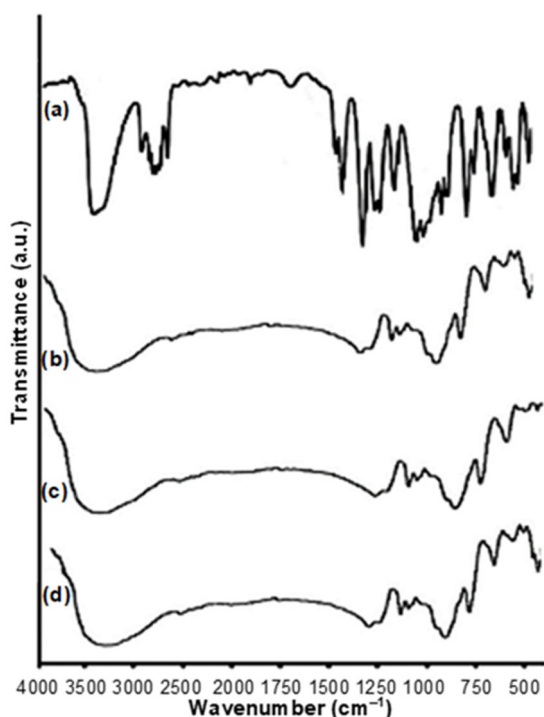


Fig 2. IR of SHPBE

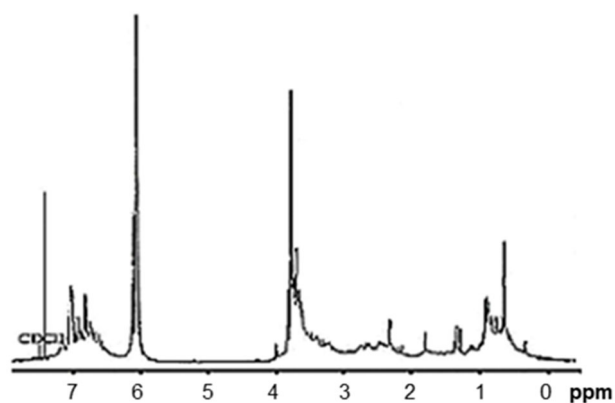
Fig 3. ¹H-NMR of SHPBE (Table 1, Run 2)

Fig 4. SHPBE at room temperature

Table 2. Comparison of the polymer properties with previous work

Sample	Properties	Ionic conductivity (S.cm ⁻¹)
This work	Self-Healing	3.6×10^{-1}
Xie et al. [2]	Self-Healing	$1.1 \times 10^{-4} - 1.78 \times 10^{-4}$
Evans et al. [7]	Self-Healing	3.5×10^{-4}
Nakamura et al. [20]	Not Self-Healing	$> 10^{-1}$

electrolytic characteristics. It can be utilized as a polymer electrolyte for Lithium-ion batteries because its conductivity is better than 10^{-5} S.cm⁻¹ [8]. Table 2 compares the ionic conductivity achieved in this work to the ionic conductivity of the polymer electrolyte that was previously investigated. When compared to earlier studies, the sample size in this study is quite substantial. Membranes created by adding sulfuric acid (H₂SO₄) to cross-linked poly (4-vinyl pyridine) demonstrated ionic conductivity larger than 10^{-1} but no self-healing characteristics, according to Nakamura et al. [20]. This study's conductivity is the same as the previous one using the polymer/H₂SO₄ system.

Solubility of SHPBE

The solubility of this SHPBE was excellent. THF, benzene, toluene, CH₂Cl₂, CHCl₃, acetone, DMF, DMSO,

can totally dissolve SHPBE in common solvents. The widespread use of homogeneous catalysts in synthesis, interest in green chemistry and sustainability, and the capacity to synthesize polymers with tailored specific features are all driving causes behind the growing interest in soluble polymers as catalysis tools [12].

SHPBE for Biodiesel Production from Waste Used Cooking Oil

From Fig. 5, it can be seen that at a catalyst concentration of 4%, the highest biodiesel yield was 56.98%, but the addition of 5% catalyst decreased the yield to 55.03%. At present, the reason for this finding is not clear. In this treatment, reflux time is carried out, which aims to see the highest yield. In Fig. 6, it can be seen that the higher the reflux time, the higher the yield of biodiesel produced, in which the highest yield was 57.79%.

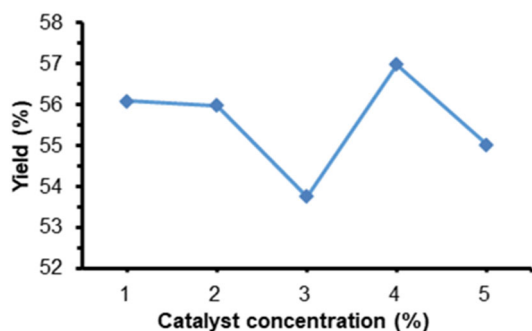


Fig 5. Effect of catalyst amount

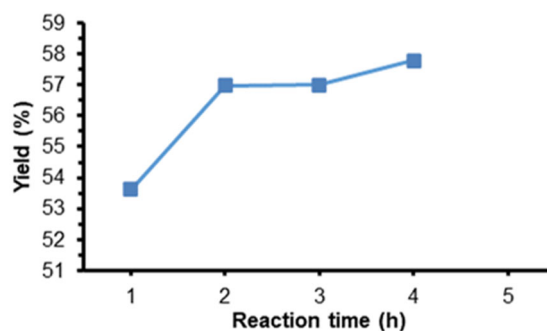


Fig 6. Effect of reaction time

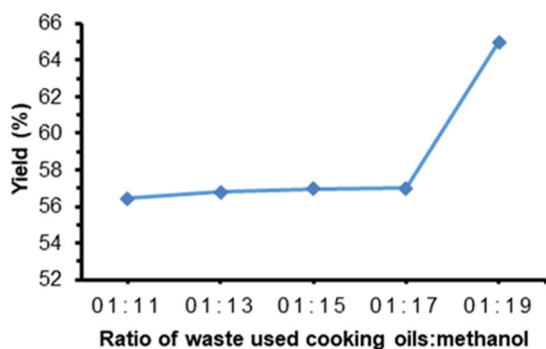


Fig 7. Effect of methanol amount

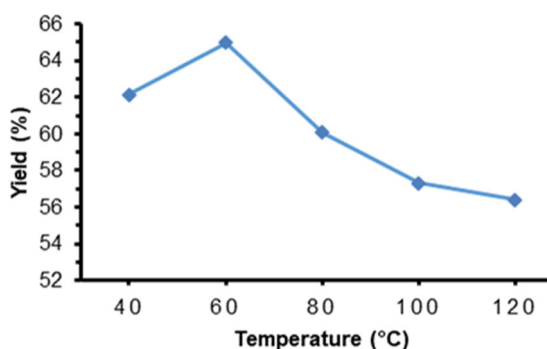


Fig 8. Effect of reaction temperature

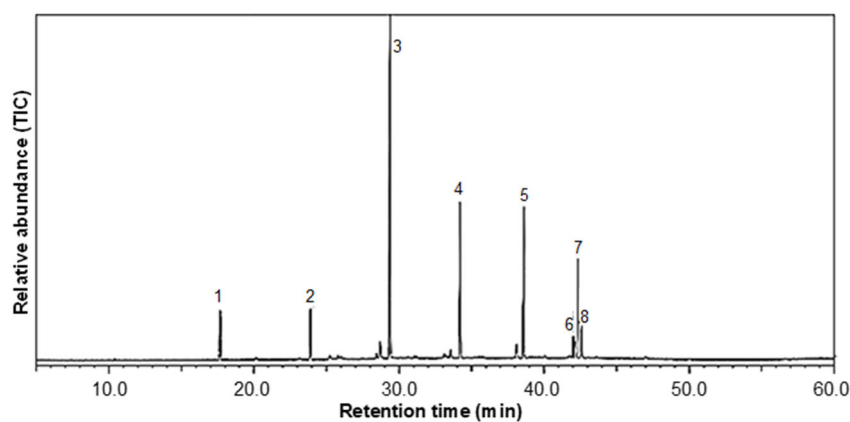


Fig 9. GC chromatogram of biodiesel using SHPBE

Table 3. Methyl ester compounds found in WCO

Peak	Retention peak (min)	Area (%)	Fatty acid methyl ester (FAME)
1	17.680	4.62	Methyl caprylate
2	23.913	5.02	Methyl caprate
3	29.407	38.59	Methyl laurate
4	34.234	17.40	Methyl myristate
5	38.616	16.62	Methyl stearate
6	42.025	3.01	Methyl linoleate
7	42.138	11.53	Methyl oleate
8	42.582	3.21	Methyl lignoserate

From Fig. 7, it can be seen the higher the oil: methanol ratio, the higher the yield of biodiesel. These results are in accordance with the research of Chuepeng [10], which states that an excessive amount of methanol must be added so that the reaction moves towards the product. From Fig. 8, it can be seen that the increase in biodiesel yield occurred from a temperature of 40 °C, namely 62.13, to 64.97% at 60 °C, and there was a significant decrease when the temperature was above 60 °C. At present, the reason for this finding is not clear. Fig. 9 shows the chromatogram of biodiesel, and Table 3 shows that methyl ester was found in WCO.

■ CONCLUSION

SHPBE with molecular weights ranging from $(5.18-15.10) \times 10^5$ g/mol has been successfully synthesized. At room temperature, SHPBE has self-healing properties. This material also has a 3.6×10^{-1} S.cm⁻¹ ion conductivity and is soluble in common organic solvents. The effects of operating factors such as catalyst amount, reaction time, methanol to WCO weight ratio, and temperature on FAME yields were examined and the maximum FAME yield obtained was 64.97%.

■ ACKNOWLEDGMENTS

EAR acknowledges the support of the Department of Chemistry, Faculty of Mathematics and Natural Science, Tadulako University.

■ REFERENCES

- [1] Cheng, C., Li, J., Yang, F., Li, Y., Hu, Z., and Wang, J., 2018, Renewable eugenol-based functional polymers with self-healing and high temperature resistance properties, *J. Polym. Res.*, 25 (2), 67.
- [2] Wang, H., Wang, P., Feng, Y., Liu, J., Wang, J., Hu, M., Wei, J., and Huang, Y., 2019, Recent advances on self-healing materials and batteries, *ChemElectroChem*, 6, 1605–1622.
- [3] Liang, J.Y., Shin, S.R., Lee, S.H., and Lee, D.S., 2020, Self-healing and mechanical properties of thermoplastic polyurethane/eugenol-based phenoxy resin blends via exchange reactions, *Polymers*, 12 (5), 1011.
- [4] Sumerlin, B.S., 2018, Next-generation self-healing materials, *Science*, 362 (6411), 150–151.
- [5] Kumpfer, J.R., and Rowan, S.J., 2011, Thermo-, photo-, and chemo-responsive shape-memory properties from photo-cross linked metallo-supramolecular polymers, *J. Am. Chem. Soc.*, 133 (32), 12866–12874.
- [6] Terryn, S., Roels, E., Brancart, J., Van Assche, G., and Vanderborght, B., 2020, Self-healing and high interfacial strength in multi-material soft pneumatic robots via reversible Diels–Alder bonds, *Actuators*, 9 (2), 34.
- [7] Jing, B.B., and Evans, C.M., 2019, Catalyst-free dynamic networks for recyclable, self-healing solid polymer electrolytes, *J. Am. Chem. Soc.*, 141 (48), 18932–18937.
- [8] Yao, P., Yu, H., Ding, Z., Liu, Y., Lu, J., Lavorgna, M., Wu, J., and Liu, X., 2019, Review on polymer-based composite electrolytes for lithium batteries, *Front. Chem.*, 7, 522.
- [9] Jo, Y.H., Li, S., Zuo, C., Zhang, Y., Gan, H., Li, S., Yu, L., He, D., Xie, X., and Xue, Z., 2020, Self-healing solid polymer electrolyte facilitated by a dynamic cross-linked polymer matrix for lithium-ion batteries, *Macromolecules*, 53 (3), 1024–1032.
- [10] Ngai, K.S., Ramesh, S., Ramesh, K., and Juan, J.C., 2016, A review of polymer electrolyte: fundamental, approaches and application, *Ionics*, 22 (8), 1259–1279.
- [11] Choudhury, S., Stalin, S., Vu, D., Warren, A., Deng, Y., Biswal, P., and Archer, L.A., 2019, Solid state polymer electrolytes for high-performance lithium metal batteries, *Nat. Commun.*, 10 (1), 4398.
- [12] Komintarachet, C., and Chuepeng, S., 2009, Solid acid catalyst for biodiesel production from waste used cooking oils, *Ind. Eng. Chem. Res.*, 48 (20), 9350–9353.
- [13] Zhang, J., Zhang, M., Tang, K., Verpoort, F., and Sun, T., 2013, Polymer-based stimuli-responsive recyclable catalytic systems for organic synthesis, *Small*, 10 (1), 32–46.
- [14] Bergbreiter, D.E., 2014, Soluble polymers as tools in

- catalysis, *ACS Macro Lett.*, 3 (3), 260–265.
- [15] Rahim, E.A, 2020, Synthesis of soluble novel polyecetylenes containing carbamate and eugenol moieties, *Indones. J. Chem.*, 20 (4), 818–824.
- [16] Rahim, E.A., Sanda, F., and Masuda, T., 2004, Synthesis and properties of novel eugenol-based polymers, *Polym. Bull.*, 52 (2), 93–100.
- [17] Rahim, E.A., Istiqomah, N., Almilda, G., Ridhay, A., Sumarni, N.K., and Indriani, 2020, Antibacterial and antioxidant activities of polyeugenol with high molecular weight, *Indones. J. Chem.*, 20 (3), 722–728.
- [18] Rahim, E.A., Sanda, F., and Masuda, T., 2006, Synthesis and properties of optically active amino acid based polyacetylenes bearing eugenol and fluorene moieties, *J. Polym. Sci., Part A: Polym. Chem.*, 44 (2), 810–819.
- [19] Rahim, E.A., 2018, Unique polymerization and new smart material of eugenol-based helical polymers, *Int. J. Sci. Res.*, 7 (11), 990–996.
- [20] Kajita, T., Tanaka, H., Noro, A., Matsuhita, Y., and Nakamura, N., 2019, Acidic liquid-swollen polymer membranes exhibiting anhydrous proton conductivity higher than 100 mS cm⁻¹ at around 100 °C, *J. Mater. Chem. A*, 7 (26), 15585–15592.