

Synthesis of Eugenol–Lauryl Methacrylate Copolymers via Cationic Polymerization

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Abstract. Eugenol is one of the most abundant natural resources in Indonesia. The recently bio-based polymer resin is created based on eugenol because eugenol is functionalized with the polymerizable group. In order to improve the functional properties of eugenol, in this research Eugenol–Lauryl Methacrylate copolymers (co-poly(Eg-LMA)) were synthesized by cationic polymerization using H₂SO₄ as an initiator under the nitrogen atmosphere. Structure identification of the copolymer showed the absorption of the vinyl group from the monomers disappear at the analysis through FTIR at the wave number 1637-1639 and 985-995 cm⁻¹ and also ¹H-NMR on the chemical shift 5,97 and 5,08 ppm. The resulting copolymers obtained brown powder in 32.03 % yields and melting point at 96 – 97 °C. Solubility test of the co-poly(Eg-LMA) showed that the polymer could not soluble in water but soluble in chloroform, diethyl ether, and benzene. Average molecular weight of co-poly(Eg-LMA) by Ostwald viscometry was obtained 42020 with the degree of polymerization by 200.

1 Introduction

Eugenol (4-allyl-2-methoxyphenol) is a major component of clove oil. It can be extracted from clove (*Syzygium aromaticum* syn. *Eugenia aromaticum*) [1]. These compounds are particularly widely used in various fields such as pharmaceutical industry, food, and beverage industry, as well in material synthesis [2]. The development of eugenol-based materials is now widely practiced because eugenol is a very useful compound with functional groups that can be polymerized. The eugenol structure has three functional groups, namely hydroxy groups, methoxy groups and allyl groups [3]. So that, eugenol can be used as starting material for the synthesis of new compounds [4].

Eugenol-based polymer modification has been widely used to improve the function, properties, and application of the material. Some modifications have been made by combining several other monomers such as Eugen oxy acetate acid [5] and methacryloyl chloride [1] or by the addition of cross-linking agents such as DVB [6]. However, to extend the utilization of eugenol, it is necessary to modify it with other monomers having specific functions, such as alkyl acrylates which are widely used for an oil absorbent [7].

The alkyl acrylate derivative compounds have many types with various functional properties. Recently, Jang & Kim [7] has modified various alkyl acrylates such as ethyl hexyl acrylate (EHA), lauryl acrylate (LA), lauryl methacrylate (LMA) and stearyl acrylate (SA) by copolymerization with styrene. Copolymer styrene with various alkyl acrylates is applied as an absorbent oil. Based on Jang & Kim [7] the best absorption activity is a copolymer styrene with LMA or SA. LMA is now widely developed by copolymerization with other monomers. The nature of poly-lauryl methacrylate has a



good absorption activity, but the nature of long chain acrylic acid polymers such as LMA tends to form crystalline phases. The high crystallinity of the polymer material causes its low swelling power [7]. Styrene is a petroleum derivative that structurally resembles eugenol. By copolymerization of eugenol with lauryl methacrylate compound is expected to form polymer stability with an amorphous phase.

The polymerization process can carry out in three ways: condensation polymerization, addition or radical polymerization. The most reactive polymerization process is radical polymerization [8]. However, in the polymerization process of phenolic compounds, these compounds have antioxidant activity which can inhibit the reaction of radical polymerization [9]. Several previous studies which carried out polymerization of eugenol with cationic addition polymerization with concentrated sulfuric acid catalyst [10], concentrated nitric acid [11], or with $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ [12].

This study was conducted to produce a new material that can extend the utilization of eugenol. Eugenol which structurally similar to styrene is expected to be copolymerized with LMA using cationic polymerization method with the concentrated sulfuric acid catalyst. It is expected that with this method can be produced a new material that can be utilized more widely and can improve the characteristic of the resulting polymer.

2 Materials and Methods

2.1. Materials

Eugenol(Eg) was obtained from PT. Indesso Aroma, Indonesia was used without further purification. Lauryl methacrylate (LMA, Aldrich) was shaken before polymerization with a 5% of sodiumhydroxide and then with distilled water, subsequent drying over Na_2SO_4 . Sulfuric acid (H_2SO_4 , Aldrich). Natrium Chloride, Chloroform, and Na_2SO_4 were obtained from Merck. Nitrogen gas also used.

2.2. Synthesis of co-poly(Eg-LMA)

Polymerization was carried out by a cationic mechanism, in a 100 mL three-neck flask equipped with magnetic stirrer and saturated with nitrogen gas, 1.970 g (0.012 mol) of the Eugenol and 2.035 g (0.008 mol) of the LMA were included. The mixture is stirred until the two solutions are mixed and then added 500 μL of sulfuric acid catalyst twice with an interval of 1 hour. Two hours after the last addition the copolymerization process was discontinued by the addition of 500 μL of methanol.

The resulting copolymer was then dissolved into water and extracted with chloroform to neutral pH. The organic phase extracted was added Na_2SO_4 then filtered and evaporated. The product was identified with FTIR and ^1H -NMR spectrophotometers.

2.3. Calculated average molecular weight of co-poly(Eg-LMA) using Ostwald viscometry

Determination of average molecular weight of co-poly(Eg-LMA) was performed by measuring the flow time using an Ostwald viscometer with a concentration of 0.01 g / mL; 0.005g / mL; 0.0025 g / mL and 0.00125 g/mL and the pure solvent time of chloroform. Flow time measurements are carried out at room temperature. The result of the measurement was obtained by the time flow data of co-poly(Eg-LMA) solution and pure chloroform solvent, then calculated relative viscosity (η_r) and specific viscosity (η_{sp}). The data obtained are then made in the graph η_{sp}/C versus C for obtaining an intrinsic viscosity $[\eta]$. The relative molecular period is calculated by the Mark-Houwink equation, with $k = 11 \times 10^{-3}$ and $a = 0.725$.

2.4. FTIR analysis

The spectra of the co-poly(Eg-LMA) were recorded at room temperature as KBr pellets on Shimadzu type FT-IR 8201 PC spectrophotometer. The light source of transmittance was in the range of 4000-500 cm^{-1} . The films were mounted directly in the sample holder.

2.5. $^1\text{H-NMR}$ analysis

$^1\text{H-NMR}$ spectra were taken in CDCl_3 at room temperature, on Angilent instrument 400 MHz. Chemical shift was reported in δ (ppm) using TMS as an internal standard, and coupling constants were expressed in hertz.

3 Result and discussion

3.1. Synthesis of co-poly(Eg-LMA)

The polymerization process of eugenol and LMA is carried out via a non-media cationic polymerization using H_2SO_4 as an initiator under the nitrogen atmosphere. The polymerization process appeared with a change of color from a clear solution to a thick purple gel then solidifies. In general, the cationic polymerization takes place through three stages of initiation, propagation, and termination [13], this process is a series of addition reaction of the vinyl group by the opening of the $\text{C}=\text{C}$ double bond to a single bond. The success of this process can be identified via FTIR and $^1\text{H-NMR}$ analysis.

The identification of co-poly(Eg-LMA) with both FTIR and $^1\text{H-NMR}$ spectrophotometers showed that the polymerization process has successfully combined the two monomers. Based on the results of the identification it was seen that the reacting process only via an opening of the vinyl group because the other groups such as $-\text{OH}$ group, methoxy ($-\text{OCH}_3$), or $-\text{C}=\text{O}$ carbonyl are not changed. Based on the results of the identification and analysis carried out the cationic polymerization reaction step of eugenol and LMA proposed is shown in Figure 1.

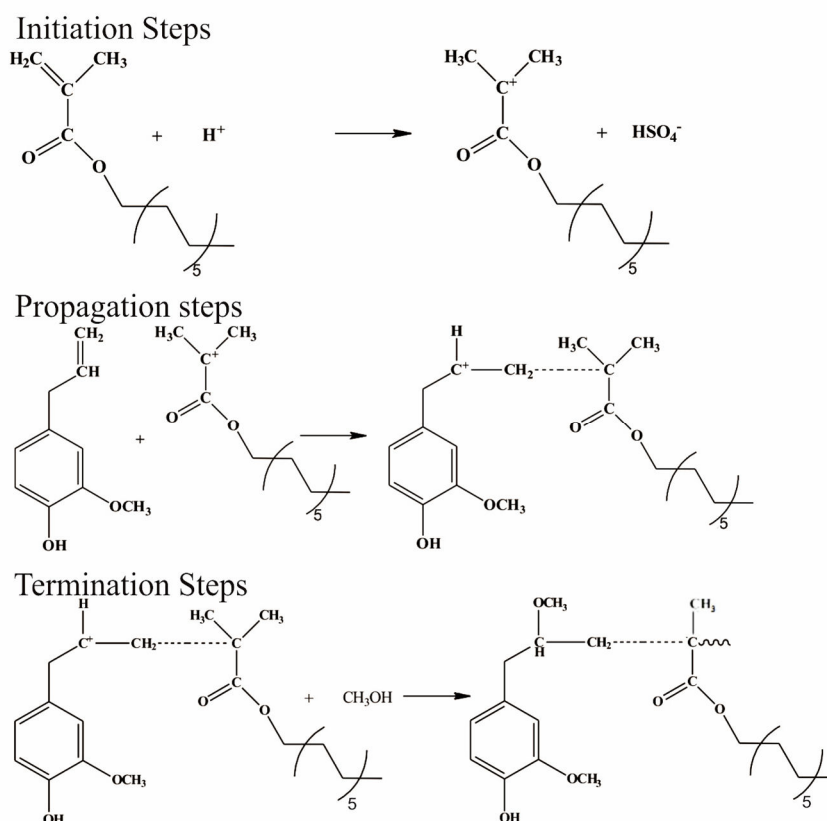


Figure 1. Scheme of the synthesis of cationic polymerization of eugenol and LMA

The initiation stage is carried out by the formation of carbocation on a tertiary C vinyl group from LMA due to initiation of H_2SO_4 . This initiation stage can occur either through the eugenol monomer or LMA because both have a vinyl group that can form a carbocation. However, the propagation stage will be greatly influenced by the stability of the formed carbocation; the more stable ion will increase

the reaction rate [10]. In both monomers can form a carbocation, but according to McMurry [14], the carbocation on the tertiary C atoms is more stable than at the C atom of the secondary and the primary. Therefore initiation of LMA is more proposed to form an active carbocation. The second stage is the propagation stage; the elongation takes place through the end of the reactive carbocation that initiates the other monomer continuously until the termination or chain runs out. At the propagation stage, the eugenol monomer and LMA opened the double bond and form a covalent bond with reactive carbocation at polymer end [10]. This propagation process will affect the length of the polymer chain and its relative molecular weight. The last stage of the polymerization process is the termination stage, at this stage, the chain elongation process is stopped by the addition of methanol. The $-\text{OCH}_3$ group of methanol will interact with the carbocation at the end of the polymer and stopped the formation of covalent bonds of the vinyl group by carbocation [6]. Physical identification of the co-poly(Eg-LMA) from polymerization were obtained brown powder in 32.03 % yields and melting point at $96 - 97^\circ\text{C}$. The solubility test of the co-poly(Eg-LMA) showed that the polymer could not soluble in water but soluble in nonpolar solvent (chloroform, diethyl ether, and benzene).

3.2. FTIR analysis

The FTIR spectra of eugenol, LMA, and co-poly(Eg-LMA) monomers are shown in figure 2. IR spectra of the eugenol monomer had characteristics of hydroxyl group uptake at 3448 cm^{-1} , double bond benzene ring at 1612 cm^{-1} and methoxy group ($-\text{O}-\text{CH}_3$) at 1034 cm^{-1} . The peak for absorption of $\text{C}=\text{C}$ vinyl groups was present in wave numbers 1637 , 995 and 914 cm^{-1} . While in LMA monomer spectra the identified characteristic waveforms were $\text{C}=\text{O}$ carbonyl acryl absorption at 1722 cm^{-1} , $-\text{C}-\text{O}-\text{C}-$ methacrylate at 1296 and 1165 cm^{-1} . The LMA also had a vinyl group uptake at 985 cm^{-1} .

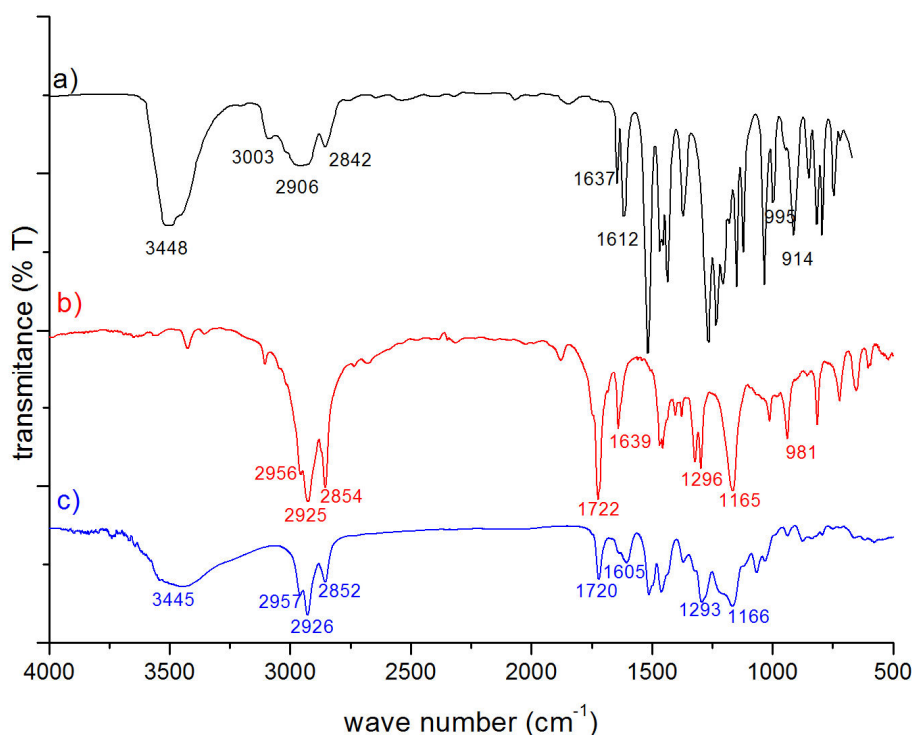


Figure 2. Infra-red spectrum of (a) eugenol, (b) LMA and (c) co-poly(Eg-LMA)

The spectra of co-poly(Eg-LMA) showed a hydroxyl group at 3445 cm^{-1} which are estimated to be $-\text{OH}$ of eugenol because the LMA has no hydroxyl group. The sharp peak at the 1720 cm^{-1} wave number indicated that the presence of a $\text{C}=\text{O}$ carbonyl group that was initially absent in the eugenol monomer. The peaks of the vinyl double bonds seen in the eugenol and LMA monomer spectra of

wave numbers 1637, 1639, 995 and 985 cm^{-1} are no longer present in the co-poly(Eg-LMA) spectra. While the uptake of the vinyl monomer group at 914 cm^{-1} shifts to 936 cm^{-1} and is not completely lost. Aran [15], indicates that the group vinyl is not completely lost and shifted because the end of the chain is more or less disproportionately. Based on the existing FTIR spectra analysis, it can be said that the eugenol polymerization process with LMA is successfully done by opening the double bond $\text{C}=\text{C}$.

3.3. $^1\text{H-NMR}$ analysis

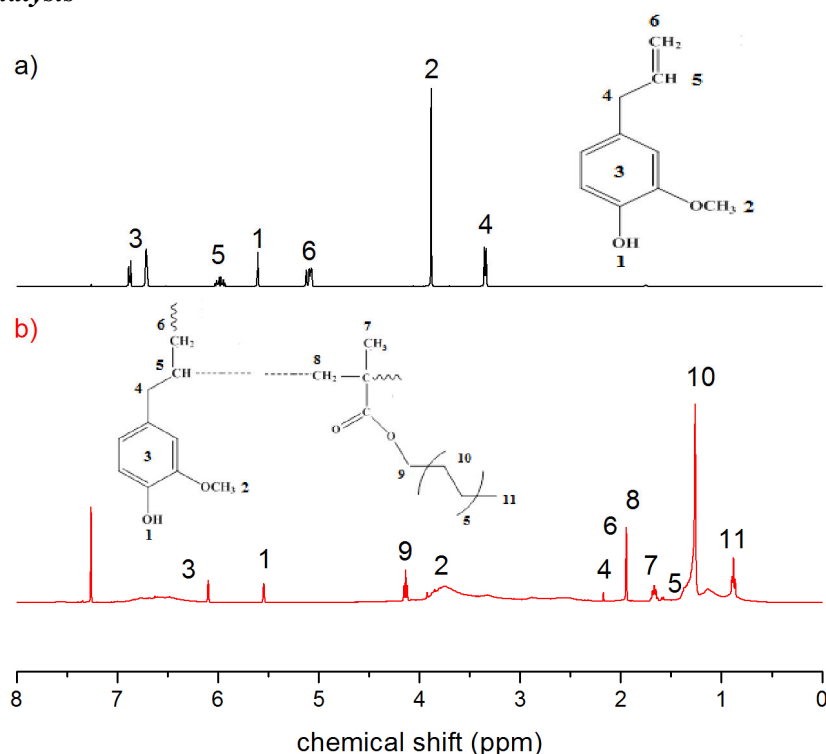


Figure 3. $^1\text{H-NMR}$ spectrum of (a) eugenol and (b) co-poly(Eg-LMA)

Eugenol and co-poly(Eg-LMA) monomers identified with $^1\text{H-NMR}$ can be seen in Figure 3. The proton NMR showed chemical shift signals at 0.88 and 1.26 ppm from the methyl of acrylic chain and overlapping of methylene ($-\text{CH}_2-$) chain. Also, the chemical shift at 3.92 ppm is a proton signal of the methoxy ($-\text{O}-\text{CH}_3$) group, the signal at 5.54 ppm for the hydroxyl ($-\text{OH}$) group, and the proton signal at 6.10 ppm from benzene ring. These proton signals were characteristic functional groups of eugenol in the identified polymer. The identification of successful polymerization processes in co-poly(Eg-LMA) was demonstrated by the loss proton signal of vinyl eugenol group at 5.97, and 5.08 ppm and the appearance of chemical shifts at 2.50 - 3.00 ppm which are proton signals for double bonding changes from vinyl group becomes a single bond [16]. Identification Based on the identification made known that co-poly(Eg-LMA) has been successfully established.

3.4. Average Molecular Weight of co-poly(Eg-LMA)

The molecular weight of a polymer is a very important thing because it will affect the physical properties and its application in life. The determination of average molecular weight (\bar{M}) of co-poly(Eg-LMA) was performed based on the measurement of its viscosity with an Ostwald viscometer. Measurements were made on 4 solutions with different concentrations: 0.01; 0.005; 0.0025; and 0.00125 g/mL. The results obtained from the measurement of the flow time using an Ostwald viscometer at the five concentration variations are shown in table 1. Measurements are made at room temperature.

Table 1. Flow time of copoly(Eg-LMA) using an Ostwald viscometer

Concentration (g/mL)		0	0.00125	0.0025	0.005	0.01
Copoly (Eg-LMA)	t (s)	15.77	16.16	16.58	16.97	17.14
		15.80	16.28	16.60	17.04	17.25
		15.81	16.31	16.66	17.20	17.33
	t _{average} (s)	15.793	16.250	16.613	17.070	17.240

The calculation using the Mark-Houwink equation based on the data from the measurement of the flow time using an Ostwald viscometer. Average molecular weight (\bar{M}) of co-poly(Eg-LMA) is 42020 with the degree of polymerization by 200.

4 Conclusion

Copoly (Eg-LMA) have been successfully synthesized via cationic polymerization using H₂SO₄ as an initiator under anitrogen atmosphere without any reaction medium. FTIR analysis revealed that the absorption of the vinyl group from the monomers disappear at the wave number 1637-1639 and 985-995 cm⁻¹ and also ¹H-NMR on the chemical shift 5.97 and 5.08 ppm. Based on the results analysis it is seen that the polymerization process reacted only via an opening of the vinyl group. Copoly(Eg-LMA) were obtained brown powder in 32.03 % yields and melting point at 96 – 97 °C, which can not soluble in water but soluble in chloroform, diethyl ether, and benzene. The average molecular weight of co-poly(Eg-LMA) also investigated using Ostwald viscometry obtained theaverage molecular weight of co-poly(Eg-LMA) of 42020 with the degree of polymerization by 200 Variation amount of the each component and the physical properties still need to be evaluated to produce material with better functional properties.

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