Synthesis of poly pyridine-2-ylmethyl 2-(eugenoxy) acetate (PMEOA) as a metal mixture carrier

M C Djunaidi¹,*, H Cahyono¹, Ismiyarto¹, D Siswanta² and Jumina²
¹Chemistry Department, Faculty of Science and Mathematics, University of Diponegoro, Semarang, Indonesia
²Chemistry Department, Faculty of Science and Mathematics, Gadjah Mada University, Yogyakarta, Indonesia

*E-mail: choliddjunaidi@live.undip.ac.id

Abstract. The synthesis of poly pyridine-2-ylmethyl 2-(eugenoxy) acetate (poly (PMEOA)) as a metal mixture carrier by BLM (Bulk Liquid Membrane) method has been conducted. The synthesis began with the conversion of eugenol to acid followed by the synthesis of pyridine-2-ylmethyl 2-(eugenoxy) acetate (PMEOA) ester. The monomer synthesis results were characterized by FTIR and GC-MS along with NMR. Polymerization of the ester produced poly (PMEOA). The resulting polymer was characterized using FTIR and NMR. Both of the synthesis products (monomers and polymers) were tested for their selectivity towards metal mixtures with Bulk Liquid Membrane Method (BLM) extraction. The results obtained show the difference in selectivity and effectiveness of its extraction ability. Mainly in the improvement of the heavy metal ions transport effectiveness resulted by the use of poly (PMEOA).

1. Introduction
Indonesia is a country with vast tropical forest areas and a wide variety of natural resources. Thus, the development of biological resources is necessary, especially in the field of chemistry. One type of plant that can be utilized in regards to this study is cloves (Eugenia caryophyllata). Cloves yield the most eugenol compared to cinnamon and nutmeg. Eugenol (C₁₀H₂₂O₂) (figure 1) has a higher value than clove oil but Indonesia still imports eugenol although being the largest clove oil exporter in the world [1].

Figure 1. Eugenol structure (2).
Polymerization of natural compounds such as eugenol that produces polyeugenol is a relatively new thing to do. Earlier studies about the synthesis of poly methyl thiazole eugenoxo ethyl acetate) (PMTEEA) from eugenol showed the ability of eugenol derived membrane to transport metal ions thus proved its capability for the recovery of wastewater [3]. The development and utilization of such polymer now undergo further studies [3–4] one of which is the use of active N polyeugenol as a liquid membrane in heavy metal recovery.

The active N compound is hoped to be used as a carrier compound in heavy metal recovery, such as Cr\(^{3+}\), Cd\(^{2+}\), and Cu\(^{2+}\), and be selective towards one of them. Each of those metals (Cr\(^{3+}\), Cd\(^{2+}\), and Cu\(^{2+}\)) represent groups of hard, soft, and borderline (between hard and soft) acids, respectively. The carrier compound works is based on the HSAB theory (theory of acid-base grouping based on hardness and softness) which states that hard metal ions (in this case Cr\(^{3+}\)) commonly form a stronger complexes with hard donor atoms and soft metal ions (in this case Cd\(^{2+}\)) will form a stronger complexes with soft donor atoms [3–6]. Thus, based on the theory of HSAB, it is hoped that the compounds with N donor atoms originating from pyridine carbinol will be selective towards borderline metal (Cu\(^{2+}\)).

Earlier studies done on heavy metal recovery using bulk liquid membrane (BLM) technique showed promising results as it was proven to be capable of removing heavy metal from wastewater with a satisfying result [7–10]. Another study used the polymer inclusion membrane to remove toxic heavy metal from wastewater [11–12]. So far, the bulk liquid membrane is the easiest to perform compared to other types of liquid membrane due to its simplicity and great membrane stability although it is known that BLM has inferior solute fluxes and high membrane resistance [7].

The selectivity of separation in a liquid membrane technique was determined by the complex stability of metal ions and carrier compounds. The donor atom type (active group) contained in the carrier compound (ligand structure), which matches the electron ion metal configuration [13–17] and pH of the solution [5–15] will determine the stability of the complex. The efficiency and selectivity of transport will be improved by the use of carrier compound [18]. In this study the synthesis of the carrier compound N-group and its polymerization will be carried out and the its effectiveness as a carrier compound will be studied.

2. Methodology
The active N polyeugenol obtained from the synthesis would be used as a carrier compound in heavy metal recovery by a liquid membrane technique. The 30 ppm metal mixture containing Cr\(^{3+}\), Cu\(^{2+}\), and Cd\(^{2+}\) will act as the feed phase and HCl as the receiving phase. The pH of the receiving phase was made constant (pH 1). Quantitatively, the remaining heavy metals as well as those taken up were determined by AAS.

2.1. Materials
Eugenol (Sigma Aldrich), BF\(_3\) diethyl ether (Sigma Aldrich), SOCl\(_2\) (Sigma Aldrich), Pyridyl carbinol (Sigma Aldrich), NaOH (E-Merck), Chloroacetic acid (E-Merck), Chloroform (E-Merck), Methanol (E-Merck), Diethyl ether (E-Merck), Aquadest, CrCl\(_3\), 6H\(_2\)O (E-Merck), CuCl\(_2\), 2H\(_2\)O (E-Merck), CdCl\(_2\), 2H\(_2\)O (E-Merck)

2.2. Instrumentation
Analytical balance (Mettler-200), pH meter (HACH E C20), Atomic Absorption Spectrophotometer (Perkin Elmer AA 400), FT-IR (Nicolet 360), GC-MS (Shimadzu prestige 21), \(^1\)H NMR (Jeol PMX 60), reflux apparatus.

2.3. Synthesis of eugenoxo acetic acid
A total of 5 g (0.03 mol) of eugenol was put into a 100 mL boiling flask, then 33% NaOH solution (33 g NaOH in 100 mL) as much as 17.5 mL (0.144 mol) was added. The mixture was stirred for approximately 30 minutes, and 12.5 mL of 50% chloroacetic acid solution (50 g of 100 mL water)
(0.066 mol) was added gradually while being stirred constantly. The mixture was heated in a water bath with temperature 80-90°C. The heating took 2 hours, then the mixture was cooled and acidified with HCl 6 M to pH 1. Furthermore, it was extracted with diethyl ether 3 times, 50 mL each. The ether extract result was combined and extracted with 5% (w/v) of sodium bicarbonate 3 times, 30 mL each. Later the water layer was acidified with HCl 6 M until it reached pH 1. Filtering, drying, and weighing were done afterward. The results obtained were tested for melting point and identified with FTIR and GC-MS.

2.4. Synthesis of Pyridin-2-ylmethyl 2-eugenoxay acetate
A total of 3 g (0.0135 mol) of eugenox acetic acid (EOA) was introduced into a 100 mL three-neck flask with auxiliary equipment (funnel, reflux). The EOA was added with 1.6 mL (2,624 g, 0.022 mol) of thionyl chloride dropwise. Then the mixture was refluxed for 150 minutes in a warm water bath (40°C) and allowed to cool. Next, 2 mL (2,262 g, 0.0207 mol) of pyridyl carbinol was added dropwise to the mixture and refluxed again in a warm water bath (40°C) for 60 min. After it had cooled the results obtained were dissolved in chloroform and washed with water. The extraction results were dried with anhydrous sodium sulfate, filtered and then evaporated to remove the remaining solvent. The results obtained were tested for melting point and identified with FTIR and GC-MS.

2.5. Polymerization
A total of 2 g (0.00639 mol) of pyridin-2-ylmethyl 2-eugenoxacetate was introduced in a three-necked flask (100 mL) and then added with 1 mL of BF$_3$ diethyl ether for every hour as much as 0.25 mL of BF$_3$ diethyl ether. After the reaction process had lasted for 4 hours, the polymerization was discontinued with the addition of 0.5 mL of methanol. The precipitate formed is dissolved in chloroform, then washed with distilled water until neutral. After that, it is dried using Na$_2$SO$_4$ anhydrous to attract the water. The solvent was then evaporated and weighed. The obtained polymer was analyzed by FTIR.

2.6. Measurement of molecular weight of the polymer
A total of 1 g of poly(pyridin-2-ylmethyl 2-eugenoxacetate) was dissolved in methanol to a concentration of 0.04 g/mL. The solution was then diluted with methanol into three different concentration: 0.02 g/mL; 0.01 g/mL and 0.005 g/mL. The viscosities of the pure solvent (methanol) ($\eta_s$) and various concentrated polymer solutions were measured using Ubbelohde viscometer, thus $t_0$, $t_1$, $t_2$, $t_3$ and $t_4$ were obtained. Through calculations, relative viscosity ($\eta_{rel}$) and specific viscosity ($\eta_{sp}$) were obtained. Then, a reduced viscosity ($\eta_{sp}/C$) versus concentration (C) graph was created. The graph was then extrapolated to a zero concentration that an intrinsic viscosity [$\eta_{in}$] was obtained. With the equation of Mark-Houwink-Sakurada [$\eta$] = KM$^a$ (23), the relative molecular mass of polyeugenol can be calculated with the price K = 11x10$^2$ and a = 0.725 (19).

2.7. Preparation of the feed solution
Parent-Solution Preparation:
1. Cr (III) solution 500 ppm was prepared by dissolving CrCl$_3$.6H$_2$O 0.6407 g in aquadest in a 250 mL volumetric flask.
2. Cu (II) solution 500 ppm was prepared by dissolving CuCl$_2$. 2H$_2$O 0.3352 g in aquadest in a 250 mL volumetric flask
3. Cd (II) solution 500 ppm was prepared by dissolving CdCl$_2$. H$_2$O 0.2240 g in aquadest in a 250 mL volumetric flask

2.8. Feed solution preparation
A metal mixture was prepared by taking Cr (III), Cu (II), and Cd (II) solutions from the parent solutions, each 6 mL, diluted in a 100 mL aquadest in a volumetric flask. The metal mixture solution was then measured using a pH meter.
2.9. Preparation of the receiving solution
A total of 0.8 mL of a concentrated HCl 12 M solution was diluted with aquadest in a 100 mL volumetric flask. The acidity of the diluted solution was tested using pH meter.

2.10. Preparation of the liquid membrane
In this study, BLM testing was conducted three times. Two of which were based on the two-separate mass of PMEOA used which were 0.3 g and 0.7 g in 30 ml of chloroform each, whilst the other used 0.7 g of Poly-PMEOA in 30 mL of chloroform.

2.11. Recovery process
A solution containing 30 mL of PMEOA or PolyPMEOA was inserted in a U-tube placed between the feed and receiving phases, 13 mL each, then stirred for 24 hours.

2.12. pH measurement
After the feed phase and the receiving phase underwent the stirring process, pH measurements were taken

2.13. AAS analysis
Analysis of the metal ion contents in the feed phase and the receiving phase after they had been separated was carried out with an atomic absorption spectrometer.

3. Results and discussions

3.1. Polyeugenol with active N group
The results of the synthesis of poly (pyridine methyl eugenox acetate) and its performance as carrier compounds in metal ion transport Cd\(^{2+}\), Cu\(^{2+}\), and Cr\(^{3+}\) will be discussed.

3.1.1. Synthesis of eugenox acetic acid (EOA)
Eugenox acetic acid was purified by extraction using diethyl ether to remove polar impurities and with NaHCO\(_3\) to remove nonpolar impurities such as acidic compounds and forming water-soluble salts. Eugenox acetic acid formed from the synthesis was a brownish-white precipitate with a yield of 73\% and a melting point of 88-93°C (figure 2). The solubility test with the organic compounds at temperature of 28°C indicates that the compound is soluble in ether, chloroform, methanol, and slightly soluble in benzene.

![Figure 2. Eugenoxacetic acid.](image-url)
3.1.2. FTIR analysis of eugenoxy acetic acid
The results of the analysis with an infrared spectrometer can be seen in figure 3. The absorption bands at 3400 and 3500 cm⁻¹ indicate the presence of OH groups. The spectrum range of 3100-3000 cm⁻¹ is the C-H stretching band of aromatic compounds that indicates the presence of aromatic compounds, the absorption band 1600-1475 cm⁻¹ is the C=C vibration of the aromatic ring and the range of 800-900 cm⁻¹ indicates that the aromatics are substituted. The absorptions at 1635 cm⁻¹, 997 cm⁻¹, and 915 cm⁻¹ are the absorption bands of the vinyl group (RHC=CH₂). While the carbonyl acid group is indicated by the absorption at 1727 cm⁻¹.

![Figure 3. FTIR spectrum of EOA compound](image)

Based on the absorption bands on the FTIR spectrum, it can be concluded that the compound being analyzed contains substituted aromatic nuclei, OH, methylene, vinyl and carbonyl groups of acids.

3.1.3. GC-MS Analysis of Eugenoxy acetic (EOA)
The gas chromatography-mass spectrometer (GC-MS) analysis of the EOA sample from the synthesis gave 4 peaks, each with a retention time of 3.491; 5.321; 7.941; and 9.388 minutes. By looking at the MS data it can be summarized that EOA appears at the fourth peak, with a retention time of 9.388 minutes and the area of 99.33% (figure 4).

The synthesized eugenoxy acetic acid resulted as a compound that has a mass spectrum with molecular ion M⁺ of m/z = 222, which is the relative molecular mass of eugenoxy acetic acid. The fragmentation pattern formed from the molecular ion peak of eugenoxy acetic acid compound is shown as follows (figure 5).
Figure 4. (a) Gas chromatography of the EOA compound (shown by peak number 4) and (b) mass spectrum of EOA compound at a retention time of 9.388 min.

Figure 5. Fragmentation pattern of EOA compound.
3.2. Synthesis of pyridin-2-ylmethyl 2-(eugenoxo)acetate (PMEOA)

The pyridine methyl eugenoxo acetate (PMEOA) compound was synthesized from EOA. Eugenoxo acetic acid is a carboxylic acid that can react with alcohol to form esters. However, because the esterification reaction is reversible [20], the resulting yield was less than satisfactory. A good yield can be obtained using another esterification method that converts eugenoxo acetic acid to acid chloride using thionyl chloride first, then the newly formed acid chloride is reacted with alcohol. Chloride acid presence could be known due to its effect to the solution pH, making it acidic. This method can produce esters with a yield of above 80% [21].

![Figure 6. Pyridine methyl eugenoxo acetate (PMEOA).](image)

![Figure 7. Formation reaction of pyridyl methyl eugenoxo acetate (PMEOA).](image)
The PMEOA formed is a black fragrant-smelling thick liquid (figure 6) with a yield of 89%. The mass density of PMEOA is 1,246 g/mL. The solubility test using organic compounds at temperature 28°C showed that this compound dissolves in chloroform and benzene but is difficult to dissolve in n-hexane and methanol.

The PMEOA esterification mechanism can theoretically be explained by the following stages of the reaction (figure 7).

3.2.1. FTIR Analysis of pyridin-2-ylmethyl 2-(eugenox) acetate (PMEOA)
The analysis result of pyridin-2-ylmethyl 2-(eugenox) acetate using FTIR can be seen in figure 8. The formation of the ester can be known from the infrared spectrum at the wavenumber of 1763.64 cm\(^{-1}\), which is the spectrum of the carbonyl ester group. As opposed to carbonyl acid, ester has a larger wave number. Another evidence of ester formation is the loss of the characteristic spectrum of the hydrogen bond of the OH group which forms a wide band at a wavenumber of about 3500 cm\(^{-1}\).

![Figure 8. FTIR spectra of PMEOA compound.](image)

3.2.2. GC-MS analysis of PMEOA
The results of the synthesis PMEOA sample analysis by gas chromatography-mass spectrometer (GC-MS) (figure 9) gave 2 peaks, each with a retention time of 18.552 and 24.778 min. By looking at the MS data it can be seen that PMEOA appears at the second peak with retention time of 24.778 minutes and an area of 99.27%.

Based on the results of FTIR and GC-MS analysis, it can be concluded that pyridyl methyl eugenox acetate compound had formed with relative purity of 99.27% and a relative molecular weight of 313 g/mol.
3.3. Polymerization of pyridin-2-ylmethyl 2-(eugenoxo)acetate (PMEOA)

The polymer of pyridin-2-ylmethyl 2-(eugenoxo) acetate (PMEOA) has successfully been synthesized using the BF₃-diethyl ether catalyst with monomer: catalyst = 2:1. The polymerization of pyridyl methyl eugenoxo acetate resulted in the formation of a black gel-like solid with a 100% yield.

The determination of the relative molecular mass of poly(pyridyl methyl eugenoxo acetate) (poly(PMEOA)) was based on the viscosity measurement of each solution. Intrinsic viscosity [η] determination was based on the equation: \( \eta_0/C = [\eta]^0 + k[\eta]^2 C \) [23]. Accordingly, the intercept of the intrinsic viscosity [η].

The relative molecular mass was calculated by the Mark-Houwink-Sakurada equation\( [\eta] = K MW^a \) [24], with the price K = 11x10⁻³ and a = 0.725 [20]. From the calculation result, the relative molecular mass of poly(PMEOA) is 4924 with a degree of repetition n \( \cong 16 \).

3.3.1. FTIR analysis and NMR of poly pyridin-2-ylmethyl 2-(eugenoxo)acetate poly (PMEOA)

FTIR analysis (figure 10) showed that the loss of vinyl spectra at wave number 915 cm⁻¹, 997 cm⁻¹ and 1648-1638 cm⁻¹ indicates that polymerization has occurred. Other evidence of polymerization can be seen from the \(^1\)H NMR spectra of the poly(PMEOA) compound and compared it with its monomers. The \(^1\)H NMR used the frequency of 60 MHz. Occurrence of polymerization is characterized by loss of shifting chemical δ = 5.2 ppm in a monomer which is a signal of a hydrogen attached to a vinyl and the emergence of δ = 1 ppm (multiplet) on the polymer spectra, which is a signal of hydrogen atoms bond to the polymer backbone (-CH₂-CH₂-) (figure 11). This reinforces the addition of the addition polymerization reaction.

Figure 9. (a) Gas chromatography of PMEOA compound and (b) mass spectrum of PMEOA compound at a retention time of 24.778 min.
Figure 10. Spectra FTIR poly (PMEOA).

Figure 11. Spectra of \(^1\)H NMR: (a) PMEOA and (b) polyPMEOA.
3.4. Metal mixture transport using the BLM technique

In this study, metal ion transport was studied by using the U pipe. The feed phase of 13 mL contained a mixture of metal ions, namely Cr (III), Cd (II), and Cu (II) each 30 ppm (pH 3.31). The liquid membranes used were PMEOA esters (0.0023 and 0.001 mol) and Poly PMEOA (0.0023 mol) in 30 mL of chloroform solvent. The receiving phase was controlled at pH 1 (13 ml of HCl 0.1 M solution). During the process, the system was stirred at a constant speed for 24 hours.

In the recovery process of heavy metals with the bulk liquid membrane (BLM) technique, there were changes in pH in the feed and receiver phases. These pH changes indicate an exchange mechanism of metals and H⁺ ions between the two phases, as shown in the following reaction mechanisms (figure 12 and table 1).

![Figure 12. Mechanism of transport in liquid membrane.](image)

### Table 1. Changes of pH values between the initial and final condition in BLM.

| Membrane   | pH of feed phase | pH of receiving phase |
|------------|-----------------|----------------------|
|            | Initial pH      | Final pH             | Initial pH | Final pH |
| PMEOA-1    | 3.31            | 1.79                 | 1.00       | 1.50     |
| PMEOA-2    | 3.31            | 2.54                 | 1.00       | 1.41     |
| PolyPMEOA  | 3.31            | 1.37                 | 1.00       | 1.37     |

Description:
- PMEOA-1: PMEOA with a mass of 0.7 g
- PMEOA-2: PMEOA with a mass of 0.3 g
- Poly (PMEOA): Polymer of PMEOA with a mass of 0.7 g

3.4.1. Metal transport by monomeric ligands

In this study, PMEOA monomers were used in two different levels of concentrations to test the selectivity and effectiveness of metal transport by using the BLM technique. The metal mixture transport results are shown in table 2.

### Table 2. Influence of carrier membrane concentrations in metal transport.

| Metal ions | % Transport in Feed Phase | % left in Feed phase | % left in Membrane |
|------------|---------------------------|----------------------|--------------------|
|            | PMEOA-1 | PMEOA-2 | PMEOA-1 | PMEOA-2 | PMEOA-1 | PMEOA-2 |
| Cd (II)    | 43.53   | 25.70   | 59.00   | 84.50   | ~ 0     | ~ 0     |
| Cu (II)    | 87.54   | 73.03   | 16.39   | 17.42   | 28.85   | 9.55    |
| Cr (III)   | 0.60    | 2.01    | 92.51   | 97.99   | 6.89    | ~ 0     |
Based on the above table, it can be seen that Cu (II) metal ions were the most metal to be transported to the receiving phase, followed by Cd (II) and Cr (III) metal ions, respectively. This conforms with the theory of HSAB which states that hard acid metals bind more strongly with hard bases, while soft acid binds more strongly with a soft base, and borderline acid binds more strongly with a borderline base. Cu (II) is a borderline acid metal ion, thus it can bind to an active N ligand which is a stronger borderline base than any other metal ion.

In this study, we studied the influence of the carrier concentration on metal transport by comparing the number of metal ions transported based on the different membrane concentrations which are 0.023 g/mL and 0.01 g/mL. The experimental results showed that, in general, the performance of metal transport would increase with the increase of the carrier compound concentrations. This behavior may be related to the greater chance of metal ions to bind to the carrier at greater concentration.

The advantage of BLM compared to SLM or ELM techniques are that this method sufficiently enables the study of the transport mechanism and the influence of the carrier structure in its efficiency and selectivity [13]. Looking at the data of the percentage of metal ions left in the membrane, Cu(II) appeared to be having the most ions left in the membrane (28.85 in PMEOA-1 and 9.55 in PMEOA-2) which shows that the ligand creates a stronger bond with Cu (II) in comparison to the other metal ions. This suggests the selectivity of the PMEOA ligand towards Cu (II) and that the transport mechanism occurred is based on the HSAB theory. HSAB theory was also applied in the studies of carriers made from the derivatives of eugenol with eugenol monomer of active N and S groups for the separation of Cu (II) and Cd (II) [4].

3.4.2. Metal transport by polymeric ligands

The first polymer used in the metal ion transport test in this study was soluble in chloroform. The second polymer could not be tested as it did not find a suitable solvent for the recovery process. A suitable solvent should have a greater density than water and is insoluble or has very small solubility in water. The recovery process of metal ions is shown in table 3.

Table 3. Percentage of metal ions in feed phase, receiving phase and membrane.

| Metal ions | % transport in the feed phase | % left in the feed phase | % left in the membrane |
|------------|-------------------------------|--------------------------|------------------------|
| Cd (II)    | 54,98                         | 63,32                    | ~ 0                    |
| Cu (II)    | 47,17                         | 53,17                    | ~ 0                    |
| Cr (III)   | 45,58                         | 51,48                    | 2,94                   |

Based on the data above, it can be seen that the amounts of transported metal ions were relatively the same. Thus, there is no indication that shows transport selectivity. However, the overall effectiveness of each of the metal ions were increased compared to their monomer. This suggests that the transport mechanism that occurs is no longer HSAB. Rather, it’s the capture of a metal ion in the bulky polymer structure. The results are different when compared with the eugenol derivative polymers with the active groups N and S that still follow the HSAB theory [3].

4. Conclusions

Based on this research, the following can be concluded:

1. Pyridine methyl eugenoxo acetate carrier compound is selective towards Cu (II) metal ions.
2. Poly (pyridine methyl eugenoxo acetate) can improve the transport effectiveness but not its selectivity towards heavy metal ions.
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