RASĀYAN *J. Chem.*
Vol. 18 | No. 2 |779-787| April - June | 2025
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNTHESIS AND CHARACTERIZATION OF ABSOLUTE ASYMMETRIC CATIONIC POLYMERIZATION

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ABSTRACT
This study aims to find a new type of polymerization that has not been found before. In this study, two female students were selected, namely Janah and Febriani. Polymerization was carried out by polymerizing eugenol using H_2SO_4-CH_3COOH. Based on the results of ^1H NMR and IR, three compounds were obtained, namely conformational transition polyeugenol and conformational transition chiral crystals polyeugenol. The results of the polymerization obtained the conformation transition of polyeugenol and showed that humans and days affect the results obtained. This polymerization is a new type of polymerization and is named Absolute Asymmetric Cationic Polymerization.
Keywords: Eugenol, Conformational transition, Polyeugenol, Chiral crystal, Humans, Days.
RASĀYAN *J. Chem.*, Vol. 18, No.2, 2025

INTRODUCTION

Most everyday encounters with chirality include wearing shoes or shaking hands, appreciating the taste of artificial sugar in a soft drink, or seeing the snail's right-handed spiral or the Go unnoticed in the bindweed garden. Despite this, there is no obvious direct relationship between this macroscopic chirality and the chirality at the molecular level. Absolute asymmetries in synthesis are one amazing phenomenon that has a connection to everyday life.[1] However, one of the world's leading producers of oil is Indonesia. In addition, Indonesia uses over half of the world's clove leaf oil. In oil, the proportion of eugenol, also called 3-(4-hydroxy-3-methoxyphenyl) propene, is fixed at 80–90% by weight. In India, a kind of Ayurveda known as Lavang uses cloves.[2-5] Additionally, polyeugenol material has the potential to create new beneficial chemicals. In 2004, Rahim synthesized eugenol-based polyacetylene which was cationic polymerized using the $BF_3.OEt_2$ catalyst.[2] Rahim published a study on absolute asymmetric synthesis related to the polymerization of eugenol, which is based on the synthesis of eugenol-based propargylamide.[5] The monomers were synthesized using triphosgene and produced chiral crystals and this includes absolute asymmetric synthesis. In this study, polymerization was carried out with a mixture of H_2SO_4-CH_3COOH which is expected to produce chiral crystals and includes a new type of cationic polymerization. One type of cationic polymerization known is living polymerization which is indicated by a polydispersity index (Mw/Mn) ~ 1.[6-8] This is the same as that produced by Rahim but the results obtained are not linear like living polymerization and the molecular weight measured is very low. Cationic polymerization will be tried which is related to life, namely humans and days. With this study, it is expected to obtain a new type of cationic polymerization which is consequently of interest to both the commercial and academic communities. The purpose of this study is to synthesize and characterize new types of polymerizations that are related to absolute asymmetric synthesis.

EXPERIMENTAL

Material and Methods

In this study, we used various materials such as Eugenol 99.99% obtained from Happy Green Co., aquadest, ethyl acetate, n-hexane, sulfuric acid (concentrated), methanol, acetic acid, anhydrous sodium sulfate.

http://doi.org/10.31788/RJC.2025.1829155

General Procedure
Polimerisasi Eugenol
10 grams of eugenol were weighed and put into a 250 mL beaker. Then 2.5 mL of H_2SO4-CH_3COOH solution was added with a ratio of 4:1 (monomer: catalyst) while continuing to stir using a magnetic stirrer. The addition of catalyst was done little by little. The formation of the polymer was indicated by the release of thick white smoke and the presence of polymer attached to the walls of the beaker. Polymerization was stopped by adding 4 drops of methanol to the mixture so that the polymer thickened and hardened. The resulting polymer was put into a 250 mL Erlenmeyer flask and then 40 mL of ethyl acetate and 20 mL of n-hexane were added. 100 mL of distilled water was added and then left for 5 minutes. The bottom layer was collected and the top was washed 3 times. Observed the separation using the same ethyl acetate-hexane, left overnight and put in an oven (110 ^oC) to evaporate the solvent and weighed the results. For the bottom layer that dissolves in water, it is put in an oven for two days at a temperature of 110 ^oC to evaporate the solvent and water. The people are 2 two women and every day for 6 days, a 1-day break and continued and a 2-day break was continued again. Molecular weight was measured for the first day using GPC, ^1H NMR, and Oswald viscometer. Measured using FTIR, ^1H NMR, SEM, and XRD for the first day's samples. This research was conducted from *August 12, 2024,* to *August 22, 2024,* in the basic chemistry laboratory of the Chemistry, Pharmacy, and Biology Department, FMIPA, Tadulako University.

Determination of Molecular Weight Using Viscometer
The polymers were dissolved in ethanol to a concentration of 0.02 g/mL in a 50 mL flask. Ethanol was subsequently added to each of the five sections of the polymer at the following concentrations: 0.01500, 0.01000, 0.00500, 0.00250, and 0.00125 g/mL. The percentage of pure ethanol solvent in an Ostwald viscometer was then used to calculate the concentration of the polymer solution, producing the following results: t0, t1, t2, t3, t4, t5, and t6. Using the Poisseuille equation (ηsp/C) against C, it was discovered. The curve was then extrapolated to zero concentration (C = 0) to yield [η]. The Mark-Houwink equation (η = K.Ma) was used to calculate the molecular weight of the polymer, taking into account the corresponding K and a.

Determination of Molecular Weight Using GPC
Sample Preparation
Dissolve the polymer in a suitable solvent (mobile phase), ensuring it is completely dissolved without degradation or aggregation.

Injection
Inject a small amount of the polymer solution into the GPC system.

Separation
As the polymer solution passes through the column, molecules are separated based on their size. Larger molecules elute first because they are too large to enter the pores of the stationary phase and take a shorter path. Smaller molecules take longer because they can penetrate the pores and interact more with the stationary phase.

Detection
A detector measures the concentration of polymer molecules as they elute from the column. The elution time is recorded and plotted as a chromatogram.

Determination of Molecular Weight Using ^1H NMR
Identify End-Group Signals
Polymers often have specific signals for end-group protons and repeating unit protons. For example, in a polymer like polystyrene, you can identify the signal corresponding to the end-group protons (e.g., a methyl group) and the signal for the repeating unit (e.g., aromatic protons from the styrene units). Integration of Signals: The integral of the NMR peak gives the relative number of protons contributing to that peak. By comparing the integration of the end-group signal (representing a fixed number of protons, often 3 for a

methyl group) to the repeating unit signal (representing the protons in each monomer unit), you can determine the degree of polymerization (DP).

$$DP = \text{Integral of end-group protons} / \text{Integral of repeating unit protons}$$

Molecular Weight Calculation: Once the degree of polymerization (DP) is known, the molecular weight (Mn) can be calculated using the formula:

$$Mn = DP \times M_{\text{repeat unit}} + M_{\text{end groups}}$$

DP: Degree of polymerization, determined from the ratio of integrals.
M repeat unit: Molar mass of the repeating unit (e.g., 104.15 g/mol for styrene).
M end groups: The molecular weight of the end groups.

Detection Method

Structure of polymers and M_n were used Spectrometer NMR JNM-ECZ500R (500 MHz) and Functional groups were used FTIR Spectrometer Thermo Scientific Nicolet iS10, Mn of polymer were used GPC (Tosoh) and Viscometer Ostwald, Morphology analysis was used SEM (JSM-6510LA), Crystallinity analysis was used XRD BRUDER AXS D8 ADVANCE ECO.

RESULTS AND DISCUSSION

Polymerization of Eugenol

This polymerization shows that the results are different on different days and people (Fig.-1). So, people and tribes affect the results obtained. Likewise, the molecular weight of different polymers also has different molecular weights and is linearly related to the results obtained. Interestingly, the molecular weight measured using GPC did not show a polymer, as well as the results of molecular weight measurements using ^{1}H NMR. These results follow the research of Rahim e*t al.,* in 2004 where it was first found that the conformational transition of polyeugenol showed low molecular weight polymer by using GPC.[3] However, in measurements with the Oswald Viscometer, the molecular weight obtained was very different whereas the results obtained showed that the polymer had ultra-high molecular weight. These results were reported for the first time by comparing molecular weight by GPC, ^{1}H NMR, and viscometer for a transition conformation eugenol-based polymer. From a physical perspective, this material is very hard, so it is concluded that this sample is a polymer.

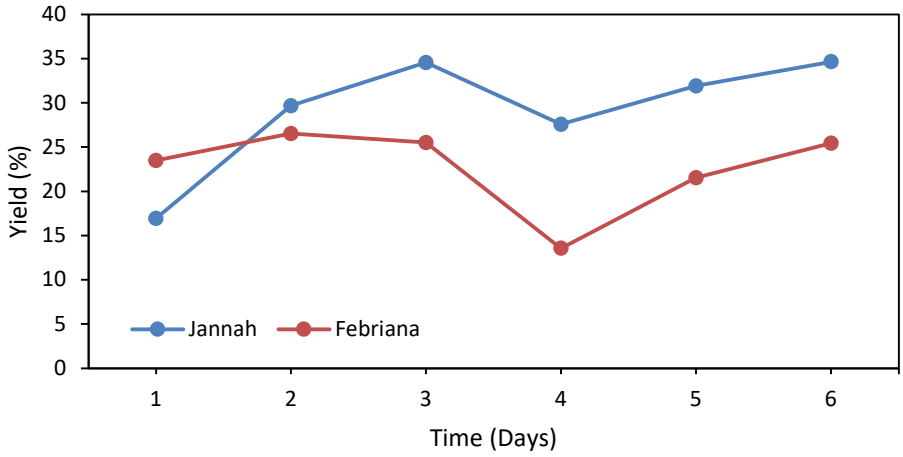


Fig.-1: Yield of Polymerization of Eugenol

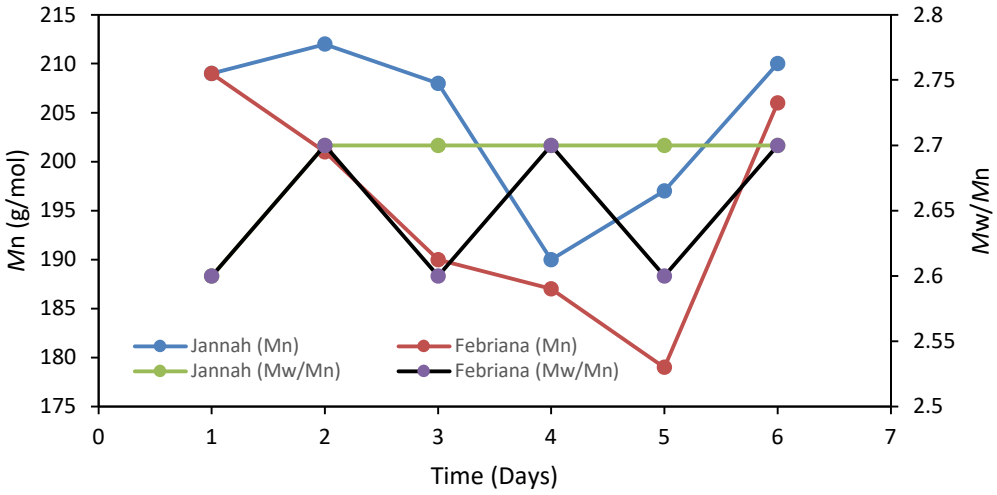


Fig.-1A: M_n and M_w/M_n of Conformational Transition Polyeugenol

GPC data from the conformational transition of polyeugenol synthesized by Jannah and Febriana differed on the second to sixth day and showed that the polymer synthesized by Jannah had a higher molecular weight (M_n) than that synthesized by Febriana and in accordance with the percentage yield produced (Fig-1A). Interestingly, for the first polymerization, the molecular weight was the same and this needs further research because the ^{1}H NMR results for the chiral crystals synthesized by Febriana produced a different spectrum from that obtained by Jannah. The Polydispersity Index (M_w/M_n) is also interesting because for the first day, the M_w/M_n obtained by both were the same and for Febriana it fluctuated regularly. For Jannah it is also interesting because the Polydispersity Index is constant for the second to seventh day except for the first day. There was an anomaly on the first day as well as its ^{1}H NMR (Fig.-9A) and the peak for OH shows that two splittings indicate two chiral crystals, namely (-) and (+) and the magnitude is not the same. This is also interesting to study further considering that the asymmetric absolute synthesis produces optically active compounds without the influence of the presence of optically active compounds.[1]

Table-1: Comparison of Molecular Weight of Conformational Transition Polyeugenol

Run	Name Person	Day	M_n with GPC[(a)] (Mw/Mn)	M_n with ^{1}H NMR	M_w with Viscometer
1	Jannah	1	209 (2.6)	440	n.d
2	Febriana	1	209 (2.6)	470	1.1 x 10^6
3	Jannah	2	212 (2.7)	490	n.d
4	Febriana	2	201 (2.7)	440	n.d
5	Jannah	3	208 (2.7)	n.d	n.d
6	Febriana	3	190 (2.6)	n.d	n.d
7	Jannah	4	187 (2.7)	n.d	n.d
8	Febriana	4	190 (2.7)	n.d	n.d
9	Jannah	5	197 (2.7)	n.d	n.d
10	Febriana	5	179 (2.6)	n.d	n.d
11	Jannah	6	210 (2.7)	n.d	n.d
12	Febriana	6	206 (2.7)	n.d	n.d

n.d = not determined, (a) Determined by GPC (THF elution, PSt standard).

Structure of Polyeugenol

Using IR and ^{1}H NMR spectroscopies, the structure of polyeugenol produced using H_2SO_4-CH_3COOH was investigated. According to FTIR examination, the absorption disappeared at wavenumbers 1637 and 995 cm^{-1}, which was characteristic of the vinyl group's absorption. It did not occur at the polyeugenol spectrum (Fig.-2).

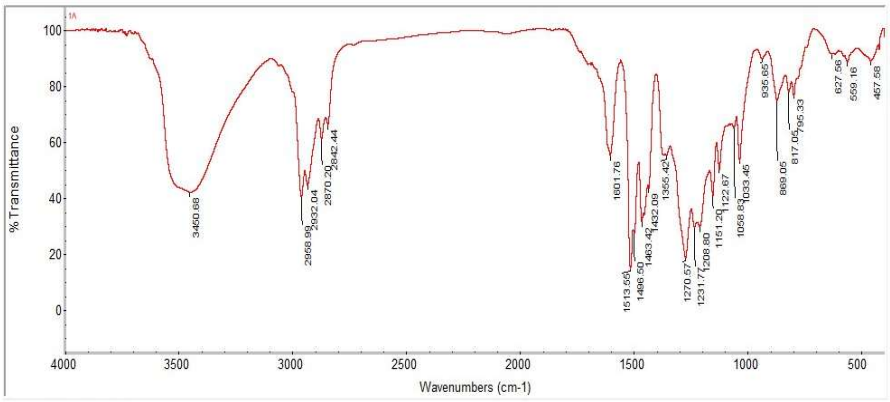


Fig.-2: IR Spectrum of Conformational Transition Polyeugenol

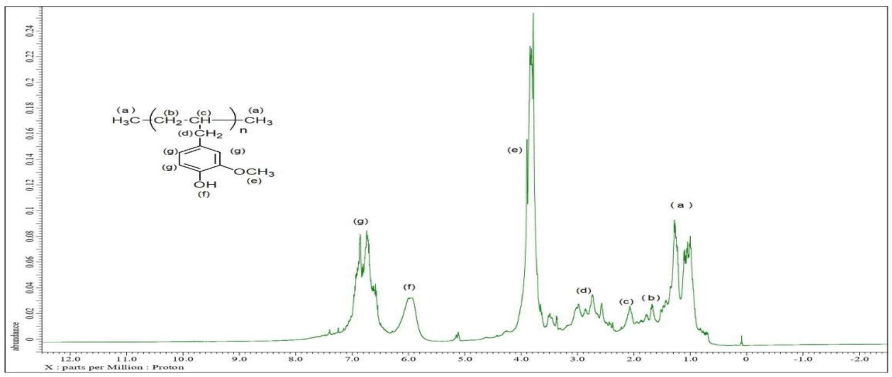


Fig.-3: ^{1}H NMR of Conformational Transition Polyeugenol

Thus, it suggested that polyeugenol was forming. Furthermore, it was evident that polymerization had occurred since the vinyl group's proton resonance at 5 ppm was not apparent (Fig.-3). The splitting of the methoxy group indicates of conformational transition of the methoxy group [9] and all ^{1}H NMR of polyeugenol and crystal chiral polyeugenol show the splitting of the methoxy group. We conclude that the polymer has the conformational transition of the methoxy group. The IR and ^{1}H NMR of chiral polyeugenol crystals binding H_2SO_4 can be seen from the IR and ^{1}H NMR spectra in the image and the IR and ^{1}H NMR spectra are similar (Fig.-4 and Fig.-5).

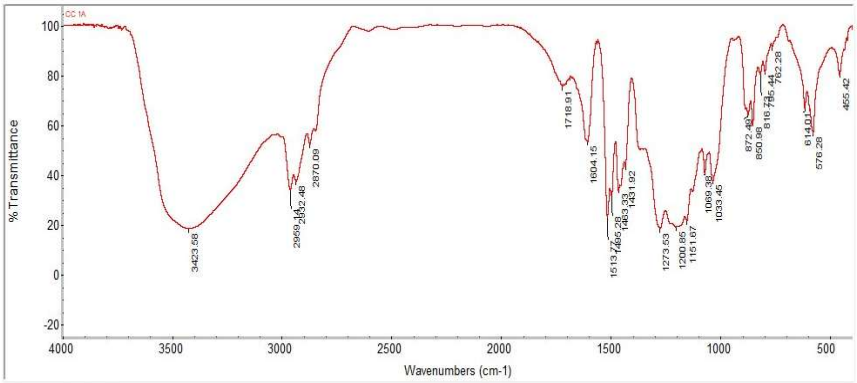


Fig.-4: IR of Conformational Transition Crystal Chiral of Polyeugenol

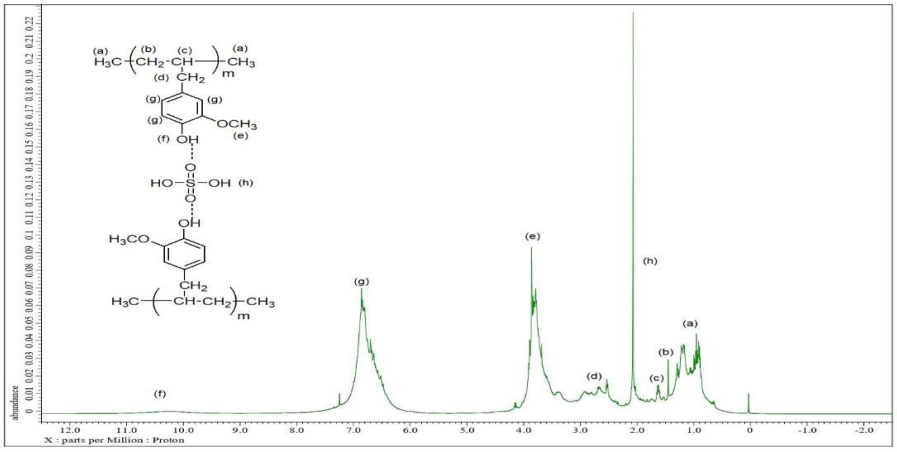


Fig.-5: ^{1}H NMR of Conformational Transition Crystal Chiral Polyeugenol

The reaction can be written as follows:

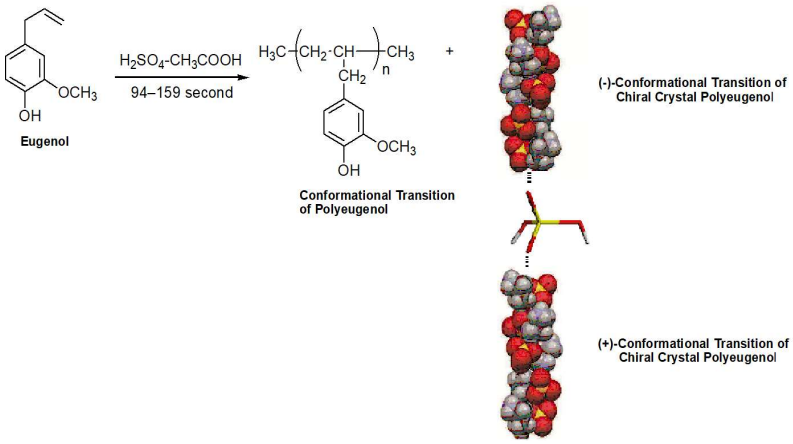
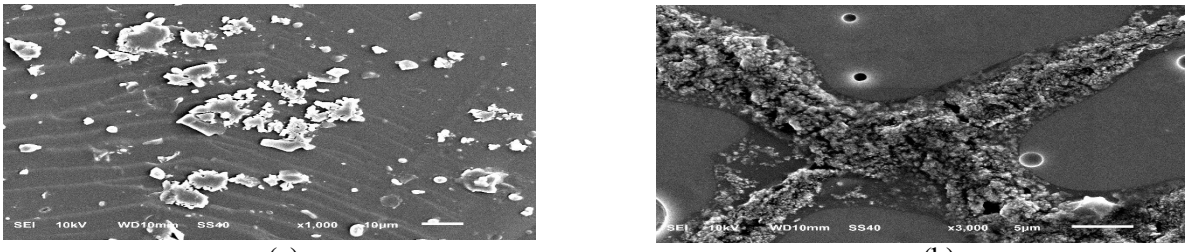


Fig.-6: Absolute Asymmetric Cationic Polymerization of Eugenol

SEM Analysis

SEM analysis shows that the conformational transition of polyeugenol has fewer crystals than the conformational transition of chiral crystal polyeugenol, and the chiral crystal structure can be seen in the SEM image in Fig.-7(b).



(a) (b)

Fig.-7: SEM Analysis of Conformational Transition of Polyeugenol and Chiral Crystal Polyeugenol

XRD Analysis

The crystallinity of the conformational transition of polyeugenol shows two peaks and is similar to each other the crystallinity is 32.1% and the crystallinity of conformational transition chiral crystal polyeugenol is 10.5%. However, both show that the degree of crystallinity is low but the sample is very hard so this is support that the sample is polymer, not dimer or oligomer.

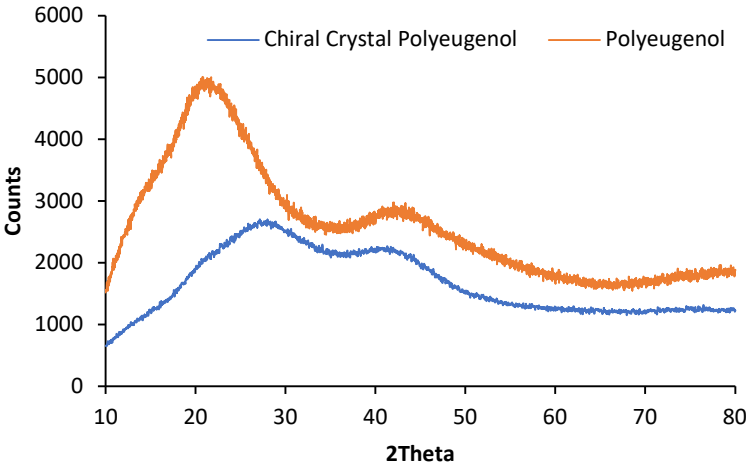
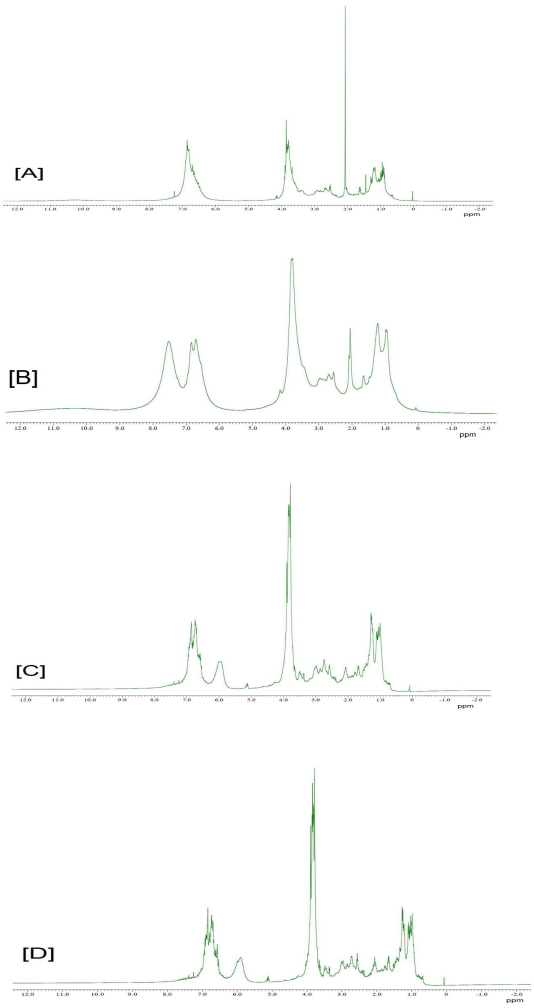


Fig.-8: XRD Analysis of Conformational Transition of Polyeugenol and Chiral Crystal Polyeugenol

Effect of Human Beings and Day to the Result of Polymer

Eugenol polymerization was carried out by 2 women named Jannah and Febriana. The polymer results obtained were different. In general, the amount of polymer produced was greater for Jannah compared to Febriana. With ^{1}H NMR, the influence of humans on the results obtained can be seen. All ^{1}H NMR of Polyeugenol were not the same effected by human beings and day. Interestingly ^{1}H NMR in Fig.-9B is different from another polymer.



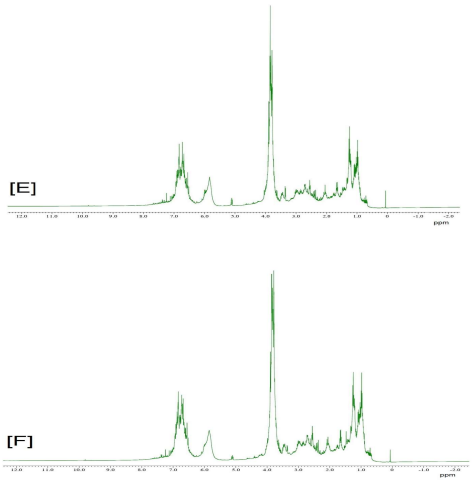


Fig-9: ^{1}H NMR of Polymer: (A) Chiral Crystal 1st Day (Jannah), (B) Chiral Crystal 1st Day (Febriana), (C) Conformational Transition Polyeugenol 1st Day (Jannah), (D) Conformational Transition Polyeugenol 1st Day (Febriana), (E) Conformational Transition Polyeugenol 5th Day (Jannah), (F) Conformational Transition Polyeugenol 5th Day (Febriana).

CONCLUSION

Polymerization of eugenol with H_2SO_4-CH_3COOH catalyst is a new type of cationic polymerization that produces conformational transition polyeugenol and conformational transition chiral crystals polyeugenol. Person and day affected the molecular of the polymer and ^{1}H NMR**.** This type of polymerization is reported for the first time and we named it "Absolute Asymmetric Cationic Polymerization". This polymer can be applicable as advanced materials.

ACKNOWLEDGMENTS

EAR is grateful for the support provided by the DRTPM Ministry of Education, culture, research, and Technology Indonesia with contract number 095/E5/PG.02.00.PL/2024.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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[RJC-9155/2024]