Synthesis and functionality of eugenol-based polyacetylenes

E A Rahim¹, F Sanda²

¹ Department of Chemistry, Tadulako University- Central Sulawesi , Palu, Indonesia
² Department of Chemistry and Materials Engineering, Faculty of Chemistry, Material and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

Email: erwin_abdulrahim@yahoo.com

Abstract. Eugenol is an inexpensive natural ingredient, which contains a functional group of phenolic hydroxyl and allyl, and is to be a major component of chemical synthesis which is environmentally friendly. The future of semiconductor materials can serve as smart textiles, lab on chip, portable compact screen, skin cancer treatment. With cheap and easy-to-obtain basic materials in Indonesia this polymer is increasing in price. In the future the helical polymer becomes a very useful material. Thus this material has a good prospect to be developed in Indonesia.

1. Introduction
Eugenol (4-allyl-2-methoxyphenol) is the main component (80% by weight) of clove oil found in Indonesia and widely used as perfumes, antioxidants, medicines, foods and flavouring [1-2]. Eugenol is an ingredient inexpensive nature, containing hydrophilic and allyl phenolic functional groups, and is expected to be a major component of chemical synthesis which has eco-friendly properties. Some researchers have also used eugenol in the synthesis of chemical polymers. Ciszewsky and Milczarek have synthesized polieugenol with electropolimerization and used this polymer as Chemo and Biosensor [3-5]. Bailly and his friends [6] have synthesized bisphenol a polycarbonate/eugenol siloxan copolymer. On the one hand, polyacetylene and its derivatives are attractive, since polyacetylene containing double bonds on the main chain has properties as electrical conductor, chemical reactivity and membrane to separate the gas. As a form of continuous development in this field, we are now in an era of electronic plastics that was previously imaginable only through science fiction [7]. This background stimulates the authors to study the polymerization, properties and functions of eugenol-based polymers, which are inexpensive and environmentally friendly natural materials.

Eugenol can be obtained by distilling the clove leaf. Furthermore, with a simple reaction modified functional groups into monomers containing triple bonds. There are two types of synthesized bonding monomers. Namely optically active and not optically active compound. Polymerization of monomers containing a non-optically active compound was carried out using a transition metal catalyst i.e. Rh, Mo and W. Effective polymerization with Rh and Mo catalysts and obtained polymers of moderate molecular weight. Eugenol-based polymers exhibit soluble properties in organic solvents, stable up to 150 °C and polymers with stable helical structures up to 90 °C. Polyacetylene based eugenol are low-cost and environmentally friendly polymer candidates for advanced technology purposes [8-11]. Optically active helical polymer exhibits a large specific rotational and circular dicroism. Eugenol, an...
inexpensive base material containing a hydroxyl phenolic reactive functional group and allyl, appears to be a key component in the synthesis of organic chemistry and chemical polymers with eco-friendly properties. The polymer has properties as a semiconductor. Semiconductors are materials that can conduct electrical current. Its function, among others, is used as an electronic device such as television, radio, computers and movies etc. Besides it can also function as a solar cell which is the energy source of the future. The future of semiconductor materials can serve as smart textiles, lab on chip, portable compact screen, skin cancer treatment. With cheap and easy-to-obtain basic materials in Indonesia this polymer is increasing in price. In the future the helical polymer becomes a very useful material. For now its main function is as a catalyst and chiral introduction in the pharmaceutical industry. Thus this material has a good prospect to be developed in Indonesia.

2. Experimental

2.1. Material and Methods
Eugenol 99 % was purchased from Indesso.com Indonesia, [Rh(nbd)2Cl] was purchased from Wako Japan, [Rh+] was synthesized according to literature [8,9,10]. MoCl5 was purchased from Wako Japan. NaOH was purchased from Indesso.com Indonesia. K2CO3 was purchased from Indesso.com Indonesia. Propargyl chloride, Propargyl amide, L-Alanine, HCOOH, Triphosgene was purchased from Wako, Japan. BF3.OEt was purchased from Indesso.com Indonesia.

2.2. General procedure
All Polymers was purified by HPLC. Monomer synthesis and polymer synthesis were synthesized according to literature.

2.3. Detection Method
1H NMR, IR, CD spectroscopy, elemental analysis were used for detection of structure and properties of monomer and polymer.

3. Results and Discussion

3.1. Monomer Synthesis
Eugenol-based monomers have been synthesized with eugenol as a starting material (figure 1). Propargyl eugenolate (1) has been synthesized from eugenol and propargyl chloride in the presence of K2CO3 in the ethanol medium. This is a simple reaction that produces monomer 1 with a yield of 54%. The monomer analogue with the 1-propenyl group as the allyl group substitute (2) has been synthesized with a yield of 51% yield. Polymerization of 2 with BF3.OEt2 produces a polymer containing the eugenol (3) group with Mn 500-1,200 and a yield of 25-95%. Eugenol can be transformed to isoeugenol by means of isomerization using a base. The use of alkaline conditions includes RhCl3 catalyst at 20 °C with 92% yield within 2 hours. Eugenol methylation with dimethyl sulphate in NaOH yields methyl eugenol in 95.5% yield. Methyl eugenol is a sex attraction for several types of flies, among others, Dacus dorsalis. The addition reaction of metal eugenol and continued by hydrolysing using NaOH produce chiral alcohol compounds. Monomer 4 has been synthesized in three step reaction with triphosgene, L-alanine and propargyl amine yielded 70%. The transformation of the allyl and hydroxyl groups of eugenol as the starting material is essentially a highly economical material.
3.2. Polymer Synthesis
The polymerization of 1 and 2 with Rh and Mo catalyst yields poly (1) and poly (2) polyacetylene of medium molecular weight ranging from the range of 12,100 to 38,400, however the W catalyst produces very little yield with a low $M_n$ (figure 2). Poly (3) has been synthesized from 3 with Rh catalyst. $N$-propargylamide with a substituent chiral derivate eugenol compound (4) has been polymerized with a rhodium-zwitterions catalyst in tetrahydrofuran producing a polymer of a moderate molecular weight of 17,300 with good results. Since rhodium catalysts always produce polyacetylene with cis-transoidal structures [10], polyacetylene with eugenol based also has this structure. Trans polyacetylene can be synthesized by isomerization using heat.

3.3 Material Properties
Eugenol-based polyacetylene soluble in common organic solvents and stable up to 150 °C. The Poly eugenol derivatives (4) dissolve well in CH$_2$Cl$_2$, CHCl$_3$, THF, acetone, benzene, toluene, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Poly (4) has a large specific rotation that
is $\alpha$ D = -2011° in CHCl$_3$. Because it has a large specific rotation and circular dicroism signal (CD) it can be concluded that poly (4) forms one handed helical structure. Poly (1) to Poly (3) showed widespread UV-Vis absorption at 300-450 nm and poly (4) showed cotton and UV-vis effects at 400 nm (figure 3). Solvents and temperatures can tune the helical structure of poly (4).

![Figure 3](image_url) CD Spectrum of poly (4) measured in toluene at 20 °C - 90 °C

4. Conclusions
Eugenol is a cheap natural ingredient, containing hydroxyl phenol and allyl reactive groups and is to be a major component in organic synthesis and environmentally friendly chemical polymers. Eugenol-based polyethylene can be applied as an electronic plastic and in the pharmaceutical industry. The continuation of research in synthesizing new polymers from eugenol ingredients and developing new functions should be continued.

Acknowledgements
E A Rahim acknowledge the support of Faculty of Mathematics and Natural Science, Tadulako University, Indonesia.

References
[1] Philips R W 1982 Skinners Science of Dental Materials; Philadelphia
[2] Fujisawa S and Kadoma Y 1997 Journal of Biomaterials 18 701–703
[3] Ciszewsky A, and Milczarek G 1998 Journal of Electroanlysis 10 791–793
[4] Ciszewski A, and Milczarek G 1999 J. Anal. Chem. 71 1055–1061
[5] Hagenaars A C, Bailly C H, Schneider A and Wolf B A 2002 Polymer 43 2663–2669
[6] Ciszewski A, and Milczarek G 2001 J. Anal. Chem. 13 860–867
[7] Lam W Y, and Tang B Z 2005 Acc. Chem. Res. 38 754
[8] Abdul Rahim E, Sanda F, and Masuda T 2004 Journal of Macromolecular Science, Part A 41 133-141
[9] Abdul Rahim E, Sanda F, and Masuda T 2004 Polymer Bulletin 52 100
[10] Abdul Rahim E, Sanda F, Masuda T 2006 J. Polym. Sci. A Polym. Chem. 44 810-819
[11] Tabata M, Sone T and Sadahiro Y 1999 Macromolecular Chemistry and Physics 200 265–282.