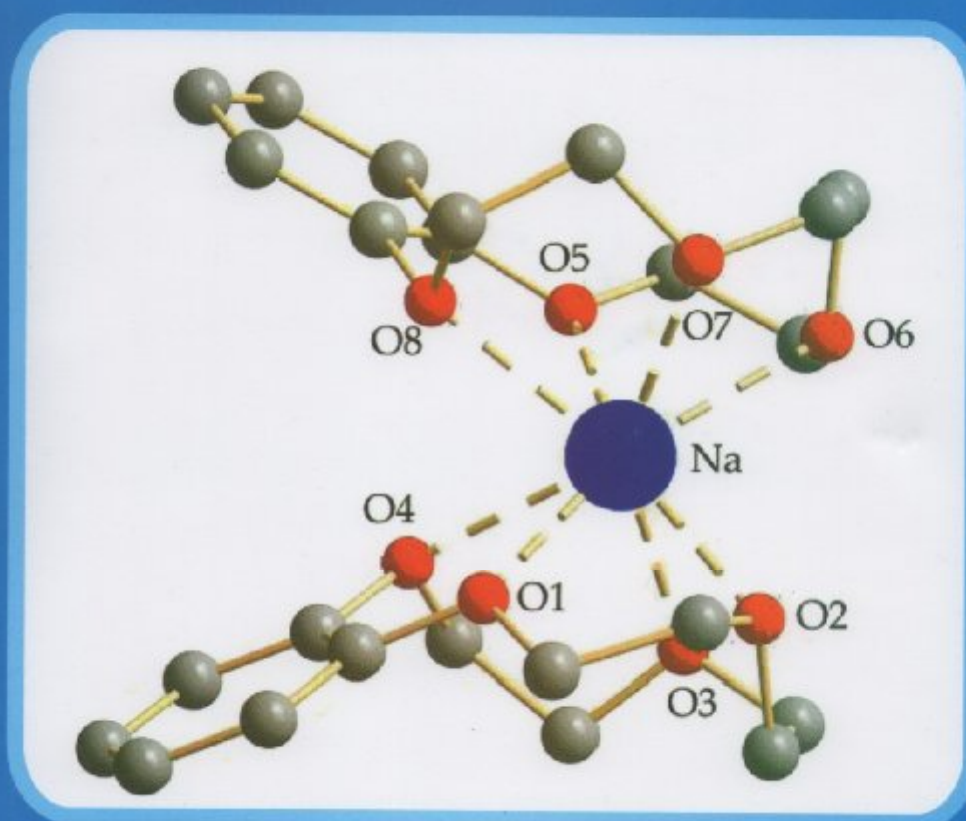


ISSN 1411-9420

Accredited by DIKTI
No : 108/DIKTI/Kep/2007

Indonesian Journal of Chemistry

Vol. 10, No. 1, March, 2010



Indo. J. Chem.

Vol. 10

No. 1

PP 1-142

Yogyakarta
March 2010

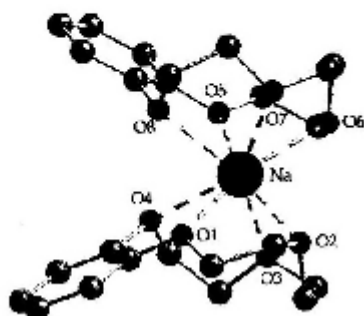
ISSN
1411-9420

CONTENTS

Adsorption of Am-241, Cs-137 and Sr-90 Radionuclides with Bentonite-Humic Acid Immobilized Yield (<i>Adsorpsi Radionuklida Am-241, Cs-137 dan Sr-90 dengan Hasil Imobilisasi Bentonit-Asam Humat</i>) by Kris Tri Basuki and Muzakky	1-7
Preparation and Characterization of Iron Sulphide Thin Films by Chemical Bath Deposition Method by Anuar Kassim, Tan Wee Tee, Dzulkefly Kuang Abdullah, Alan Mohd. Sharff, Ho Soon Min, Gwoe Siew Yong, and Saravanan Nagalingam	8-11
Synthesis and Characterization of Crosslinked Polyacrylamide (PAAM)-Carageenan Hydrogels Superabsorbent Prepared by Gamma Radiation (<i>Sintesis dan Karakterisasi Hidrogel Superabsorben Poliakrilamida (PAAM) Benjolan Silang - Karagenan Hasil Iradiasi Gamma</i>) by Erizal	12-19
Use of Nanosized Chromium Doped TiO₂ Supported on Zeolite for Methylene Blue Degradation by Aeri Ameta, Indu Bhatt, Rakshit Ameta, and Suresh C. Ameta	20-25
Synthesis of Mesoporous Titania by Potato Starch Templated Sol-Gel Reactions and Its Characterization by Canggih Selya Budi, Indriana Kartini, and Bambang Rusdianso	26-31
Influence of Cyanide on Removal of Copper Ion from the Solution by Photocatalytic Reduction Method with TiO₂ Suspension by Endang Tri Wahyuni, Mudasir, and Tenia Avia Gusman	32-35
Short Communication: Activated Carbon from Durian Seed by H₂PO₄ Activation: Preparation and Pore Structure Characterization by Amri Ismail, Hanggara Sudrajat, and Desi Jumlianti	36-40
Synthesis and Characterization of Mesoporous Aluminosilicates Al-MCM-41 and Investigation of Its Thermal, Hydrothermal and Acidity Stability by Suyanta, Narsito, Endang Tri Wahyuni, and Triyono	41-45
Note: Separation of Penicillin G from Fermentation Broth by Emulsion Liquid Membrane Technique (<i>Pemisahan Penisilin G Hasil Fermentasi dengan Teknik Membran Cair Emulsi</i>) by Imam Santoso, Bachri Amran, and Apriliana Laili Fitri ³	46-50
Integrated Gas-Liquid Separator-Reactor for Determination Sn(II) at Trace Levels in Solution (<i>Reaktor Separator Gas-Cair Terintegrasi untuk Penentuan Sn(II) pada Level Renik dalam Larutan</i>) by A. Setioto Panggabean, M. Bachri Amran, Buchari, and Subur P. Pasaribu	51-57
Alkylaryketone Homologous Series for Determination of Kovats Retention Indices with RP-HPLC using Acetonitrile/Water System by Rinaldi idroes	58-63
Isotopic Characterization of Organic Materials Leached from Leaves in Water of Mundaring Weir Dam by Markus Heryanto Langsa	64-68
Separation of Fe (III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) Metal Ions using Poly(Eugenyl Oxycetic Acid) as an Ion Carrier by a Liquid Membrane Transport Method (<i>Pemisahan Ion Logam Berat Fe(III), Cr(III), Cu (II), Ni(II), Co(II), dan Pb(II) Menggunakan Pengemban Ion Polii(Asam Eugenil Oksisasetat) dengan Metode Transpor Membran Cair</i>) by La Harimu, Sabirin Matsjeh, Dwi Siswanta, and Sei Juani Santosa	69-74
Decrease of Colour and COD Content of the Liquid Waste Product from the Jeans Washing Industry by Chitosan and <i>Trametes versicolor</i> (<i>Penurunan Kadar Warna dan COD Limbah Cair Industri Pencucian Jeans dengan Menggunakan Kitosan dan Jamur Lapuk Putih (<i>Trametes versicolor</i>)</i>) by Rumohang Bulan, Merai Suryani Sinaga, and Damianti	75-79
Adsorption Kinetics of Pb(II), Cd(II) and Cr(III) on Adsorbent Produced by Protected-Crosslinking of Humic Acid-Chitosan (<i>Kinetika Adsorpsi Pb(II), Cd(II) dan Cr(III) pada Adsorben Produk Pengikatan-Silang Terproteksi Asam Humat/Kitosan</i>) by Dewi Umariangrum, Uripito Triano Santoso, Radna Nurmasari, and Rahmat Yunus	80-87
Immobilization of Humic Acid on Chitosan Beads by Protected Cross-Linking Method and Its Application as Sorbent for Pb(II) (<i>Imobilisasi Asam Humat pada Pearls Kitosan dengan Metode Pengikatan-Silang Terproteksi dan Aplikasinya sebagai Adsorben Pb(II)</i>) by Radna Nurmasari, Uripito Triano Santoso, Dewi Umariangrum, and Taufiqur Rohman	88-95

CONTENTS (Continued)

Oxidation Kinetics and Quantification Method of Cholesterol using Cholesterol Oxidase Enzyme Catalyst by Ipi Izul Falah, Ritmaleni, and M. Utoro Yahya	96-101
Adsorption of an NH₃ Molecule on Cr(111) Surface by QCMP 116 Program by Charles Banon	102-105
Ab Initio Investigation of 12-Crown-4 and Benzo-12-Crown-4 Complexes with Li⁺, Na⁺, K⁺, Zn²⁺, Cd²⁺, and Hg²⁺ by Yahmin, Hamo Dwi Pranowo, and Ria Armunanto	106-109
Synthesis and Cytotoxicity Test of Several Compounds of Mono Para-Hydroxy Calixarene (Sintesis dan Uji Sitotoksitas Beberapa Senyawa Mono Para-Hidroksi Kalikon) by Indyah Sulistyio Arty	110-115
Conformational Studies of Lignans from <i>Durio oxleyanus</i> Griff. (Bombacaceae) by Rullyansyah, Lynette K Lambert, and Mary J Gerson	116-121
Synthesis of Tetra-<i>p</i>-propenyltetraester-calix[4]arene and Tetra-<i>p</i>-propenyltetraester-calix[4]arene from <i>p</i>-<i>t</i>-Butylphenol by Triana Kusumaningsih, Jumina, Dwi Siswanta, and Masitofa	122-126
Synthesis of Poly-5,7-dialkyl-25,26,27,28-tetrahydroxycalix[4]arene by Desi Suci Handayani, Jumina, Maulidan Firdaus, and Triana Kusumaningsih	127-131
The Effect of Formaldehyde Exposure and Yogurt Supplementation on Profile and Character of Hepar Tissue Protein of Rats (<i>Rattus norvegicus</i>) (Efek Paparan Formaldehid (Formalin) dan Suplementasi Yogurt Terhadap Profil dan Karakter Protein Hepar Tikus (<i>Rattus norvegicus</i>)) by Chanif Mahdi and Aulaniam	132-137
USFDA-Guideline Based Validation of Testing Method for Rifampicin in Indonesian Serum Specimen by Tri Joko Raharjo, Tri Wahyudi, and Sismindari	138-141



Cover picture :

See Yahmin et al., page 106

Three dimension structure of Benzo-12-crown-4-Na⁺ complex

SYNTHESIS OF POLY-5,7-DIALLYL-25,26,27,28-TETRAHYDROXYCALIX[4]ARENE

Desi Suci Handayani^{1,*}, Jumina², Maulidan Firdaus¹, Triana Kusumaningsih¹¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan Surakarta 57126, Indonesia²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

Received December 16, 2009; Accepted January 12, 2010

ABSTRACT

The synthesis of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene were performed in experimental series as follows: (1) Cyclotetramerization of *p*-*t*-butylphenol with NaOH and paraformaldehyde to *p*-butylcalix[4]arene, (2) Debutylation of *p*-butylcalix[4]arene using AlCl₃ and phenol to tetrahydroxycalix[4]arene, (3) Allylation reaction using allylbromide to diallyloxy-dihydroxycalix[4]arene, (4) Claisen rearrangement reaction, (5) Cationic polymerization to diallylcalix[4]arenes. All of the synthesized products were analyzed by means of IR spectrometer and ¹H-NMR spectrometer. The result of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene synthesis was white crystals having m.p. 205-207 °C in 80.95% yield. The synthesis of 5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene gave light yellow crystals having m.p. 214-216 °C in 78.67% yield. The polymerization gave poly(5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene) having m.p. 338-340 °C, in 60% yield. Its estimated has a relative molecular weight of 18,738 g/mol with the number of unit repetition about 37 monomer units.

Keywords: Diallylation, polymerization, Poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene

INTRODUCTION

Calixarenes are belonging to macrocyclic molecules for example crown ether and cyclodextrin [1]. These compounds have active groups arranged in unique molecular geometry in the form of vase or pot in which can be used as host of cation, anion, and neutral molecule [2]. Calixarenes in water system can also be utilized as a surfactant and acid catalyst [3].

Based on its characteristic structure and its function of calixarenes structures, this compound has many great attentions in supramolecular chemistry especially for the synthesis of its derivative. Haverlock et al. [4] had been synthesized calix[4]arene-bis(benzocrown-6) which was reported having transport ability for Francium ion. Synthesis of 5,17-bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(1-propyloxy)-25,27-calix[4] monocrown-6 was synthesized and was reported able to trap metal cation i.e. Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Mg²⁺, Ca²⁺, dan Sr²⁺ [5]

Functionalized calixarenes have previously been prepared by the direct substitution route [6] and the *p*-Claisen rearrangement route [7-8]; the present work adds another procedure for introducing various groups onto the *p*-position of the calixarene framework. *p*-tert-Butylcalix[4]arene (Fig. 1 (1)) can be prepared in good yield by the base-induced condensation of tert-butylphenol and formaldehyde [9]. Aluminum chloride-

catalyzed removal of the tert-butyl groups proceeds in excellent yield [7-8].

Monoalkylation of calix[4]arenes to the corresponding monoalkyl ethers **2** (Fig. 1) can be performed directly by reaction with an excess of alkylating agent in the presence of 1.2 equivalents of a weak base (CsF) in N,N-dimethylformamide (DMF) [10], as an alternative for the selective dealkylation of di- or tetraalkylated calix[4]arenes with Me₃SiI [11]. A stronger base like K₂CO₃ in acetonitrile gave not only the monoalkyl ethers (**2**) but also the 1,3-dialkyl ethers (**3**) (Fig. 1). Selective alkylation of two diametrically located phenol rings is possible in good yields by reacting calix[4]arenes with 2 equivalents of alkylating agent in acetonitrile, in the presence of 1 equivalent of K₂CO₃ [12-13]. All the products (**3**) are obtained in the cone conformation and further alkylation does not take place. Alkylation of calix[4]arenes with an excess of NaH in DMF and 2.2 equivalents of alkylating agent leads to the 1,2-dialkoxycalix[4]arenes (Fig. 2 (**4**)) (in the cone conformation) in acceptable yields, besides tetrasubstituted calix[4]arenes and starting material [14]. Among the upper rim functionalized methods, Gutsche and his coworker reported that the allyl group could be introduced by the Claisen rearrangement route (**5**) [8].

It has been mentioned that the ability of calixarenes to function as host molecules, extractant, adsorbent, and complexing agent are due to the presence

* Corresponding author. Email address : desi_sh2006@yahoo.co.id

** Postgraduate Student of Chemistry Department, Faculty of Mathematic and Natural Sciences, Universitas Gadjah Mada

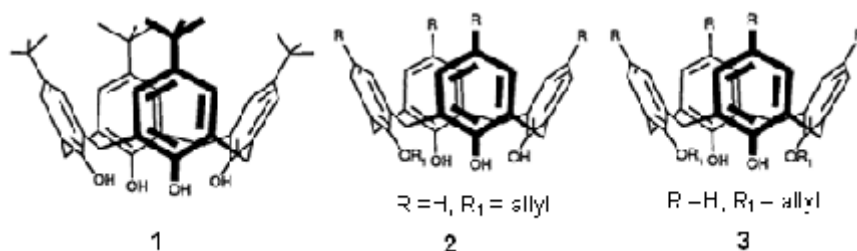


Fig 1. Structures of (1) p-t-butylcalix[4]arene, (2) monoallyloxycalix[4]arene, (3) 1,3-diallyloxycalix[4]arene

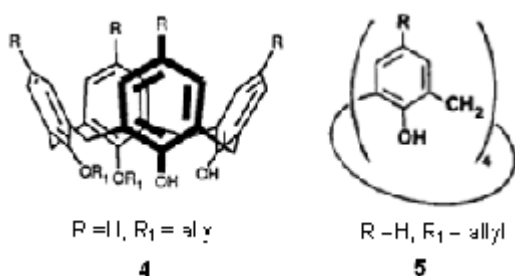


Fig 2. structures of 1,2-diallyloxycalix[4]arene (4) and diallylcalix[4]arene (5)

of cavity and donor atoms in the molecule. Accordingly, it could be expected that such functions would be greatly enhanced when the molecule does exist in a polymeric state. This occurs as the total volume of the cavity and the number of donor atoms in calixarene polymeric materials would be exponentially multiplied compared to those of calixarene monomer. This is the reason why we are interested to synthesize polypropylcalix[4]arene polymers. Based on this phenomenon, this research was carried out to synthesize calix[4]arene polymers having two allyl groups. Due to the existence of the two allyl groups, cross link reaction between calix[4]arene was taken place. This makes the molecules immobile and it can be predicted that the adsorption process for heavy metal cation will be higher.

EXPERIMENTAL SECTION

Materials

Most of organic compounds utilized in this research were commercial products of high purity purchased from Merck, and used as such without any further purification.

Instrumentation

Structure identifications were performed using infra red spectrometer (IR Shimadzu 8201 PC) and $^1\text{H-NMR}$ spectra were recorded at room temperature on JEOL-MY500 spectrometer. The relative molecular weight a polymer could be determined using Ubbelohde viscometer.

Procedure

Synthesis of p-tert-butylcalix[4]arene

p-t-butyl-calix[4]arene was prepared according reported to procedures reported previously [15]. Recrystallization from CH_3Cl and CH_3OH afforded 57.83% of a white crystal: m.p 343-345 °C (literature 344-346 °C); FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3178.5, $\nu_{\text{C=C}}$ 3024 and 1604.7, ν_{CH_2} 1456.8, ν_{CH_3} 1361.7.

Synthesis of 25,26,27,28-tetrahydroxycalix[4]arene

Powdered agregat of p-t-butylcalix[4]arene (13.3 g; 20 mmol) was dissolved in 125 mL toluene in a three neck round bottom flask equipped with a nitrogen flow pipe. In the mixture was added 9.02 g (96 mmol) powdered phenol and 14 g (105 mmol) AlCl_3 anhydrous. The mixture was stirred at room temperature for 1 h under slow nitrogen atmosphere. The mixture was cooled at ice bath and 250 mL HCl 0.2 N solution was added to be followed by stirring for 30 min. Organic layer was collected. The excess of toluene was evaporated and methanol was added until a solid was formed. Recrystallization from CH_3Cl and CH_3OH afforded 6.16 g (72.64%) of a white crystal: m.p 310-312.5 °C; FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3159, $\nu_{\text{C=C}}$ 1593.1 and ν_{CH_2} 1456.8.

Synthesis of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene

25,26,27,28-tetrahydroxycalix[4]arene (1.06 g, 2.5 mmol) was dissolved in acetonitrile. K_2CO_3 (0.34 g, 3 mmol) and allylbromide (0.67 g, 5.6 mmol) were then added. The mixture was refluxed for 24 h under nitrogen atmosphere (the reaction was monitored using TLC until the starting material spot disappear). The solvent was removed, the residu was dissolved in chloroform and washed with diluted HCl, and solvent was then removed. The product was recrystallized from CH_3Cl and CH_3OH afforded 1.02 g (80.95%) of a white crystals: m.p 205-207 °C; FTIR ($\text{KBr}/\text{cm}^{-1}$) ν_{OH} 3410.15, $\nu_{\text{C=C}}$ 1651.07, ν 987.55 and 925.83 (specific for vinyl group); $^1\text{HNMR}$ (500 MHz, CDCl_3) δ : 8.0027 (-OH, 4H), 7.2595–6.6631 (H Ar, 12H), 6.2756–6.2414 (-CH allyl, 2H), 5.8124–5.4139 (=CH₂ Vinyl, 4 H), 4.5596–

4.3114 (-CH₂- bridge, 8H), and 3.4021–3.37464 (-CH₂-allyl, 4H).

Synthesis of 5,17-diallyl-25,26,27,28-tetrahydroxycalix[4]arene

25-27-diallyloxy-26,28-dihydroxycalix[4]arene (1.5 g) was dissolved in 20 mL N,N-diethylanilin and refluxed for 3 h. The mixture was cooled and poured in 20 mL ice water. Concentrated HCl (25 mL) was then added and the obtained solid was filtered. The solid was recrystallized using dichloromethane-methanol afforded 1.18 g (78.67%) of a light yellow crystals : m.p 214-216 °C; FTIR (KBr/cm⁻¹) ν_{OH} 3179.97, $\nu_{C=C}$ 1635.64 and 1604.77, ν 995.27 (specific for vinyl group); ¹HNMR (500 MHz, CDCl₃) δ : 10.2260 (-OH, 4H), 7.0787-6.7584 (H aromatic, 10 H), 5.8931-5.8588 (-CH allyl, 2 H), 5.0790-5.0949 (-CH₂- allyl, 4 H), 4.2760-3.4998 (-CH₂-bridge, 8 H), and 3.2016-3.1882 (=CH₂ vinyl, 4 H).

Polymerization reaction

5,17-diallyl-25,26,27,28-tetrahydroxycalix[4]arene (0.15 g) was dissolved in 15 mL chloroform in a 100 mL three neck round bottom flask equipped with condenser and a nitrogen flow pipe. Concentrated Sulfuric acid (0.4 mL) was then added (it was done 4 times every 30 min for polymerization process each 0.1 mL). Polymerization was performed for 5 h (the reaction was monitored using TLC). The polymerization was terminated by adding 0.5 methanol. Chloroform layer was washed using water until neutral, dried over Na₂SO₄ anhydrous, evaporated the solvent and dried in an exicator. The product was brown solid afforded 60%: m.p 338-340 °C; FTIR (KBr/cm⁻¹) ν_{OH} 3178.69, $\nu_{C=C}$ 1604.77. The disappearances of vinyl (-CH=CH₂) group at 995.27 cm⁻¹ as well as absorption at 1635.64 cm⁻¹.

Relative molecular weight of poly-5,17-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene

Molecular weight determination of poly-5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene was done by udelahde viscometry methods based on time flow measuring in chloroform as the solvent. Various concentration had been made in 0.075; 0.150; 0.300; dan 0.600 g/L.

RESULT AND DISCUSSION

The synthesis of *p-t*-butilkaliks[4]arene was carried out using a previously reported method [15]. The synthesis was performed using *p-t*-butylphenol, formaldehyde and NaOH as the catalyst. The scheme of the reaction depicted in Fig. 3.

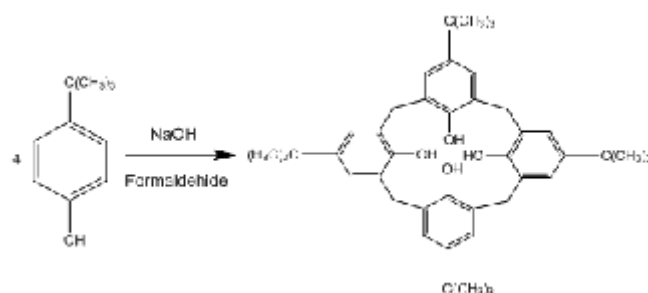


Fig 3. Reaction scheme of *p-t*-butylcalix[4]arene synthesis

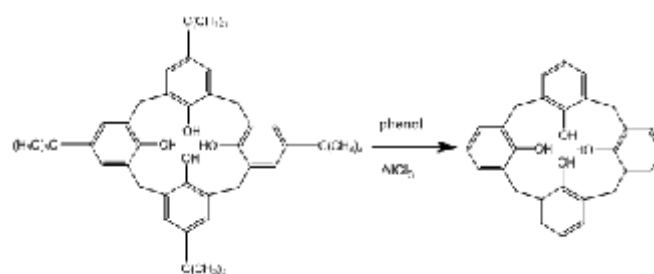


Fig 4. Debutylation of *p-t*-butylcalix[4]arene



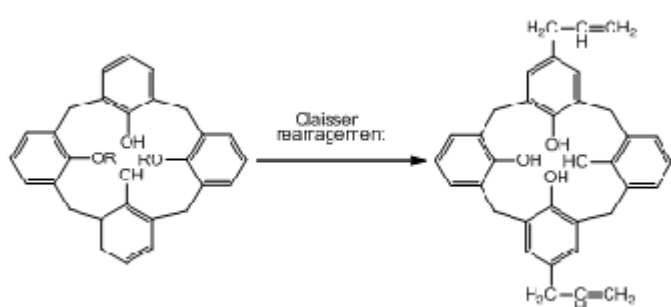
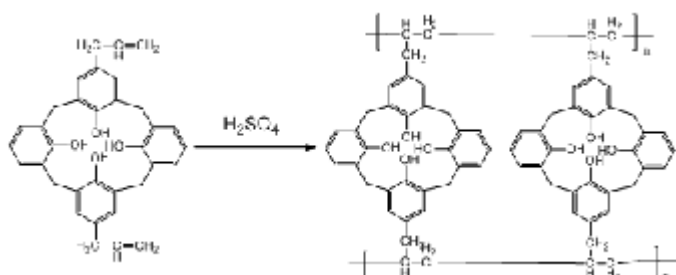
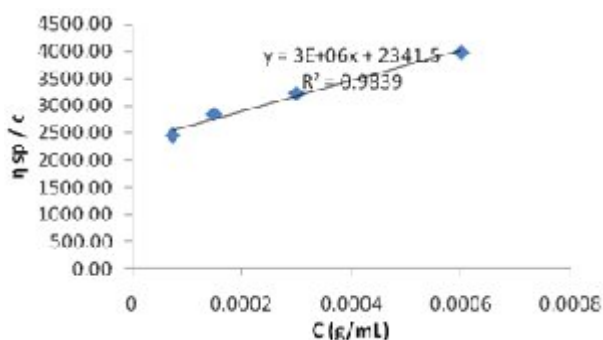
Fig 5. Allyloxy of 25,26,27,28-tetrahydroxycalix[4]arene

Debutylation is a Friedel-Craft alkylation (retro Friedel-Craft alkylation). Dealkylation of 4 tertier butyl groups of *p-t*-butylcalix[4]arene to 25,26,27,28-tetrahydroxycalix[4]arene is taken place in this reaction. The scheme of the reaction is depicted in Fig. 4. The disappearance of absorption at 1361.7 cm⁻¹ (for methyl group) at tertier butyl group indicated that the debutylation was taken place.

Gutsche and his co-workers reported that the calixarene allyl ethers were able to transform to the corresponding *p*-allylcalixarenes by the heat-induced Claisen rearrangement [8]. It is assumed that the partially *p*-allyl substituted calix[4]arenes could also be prepared from the corresponding partially allyloxylated calix[4]arenes in the same rearrangement. The two diallyl ethers were prepared according to the general procedures reported by Reinhoudt and his co-workers for the calix[4]arene's 1,2-dialkyl ethers and 1,3-dialkyl ethers [14,16]. Calix[4]arene 1,3-diallyl ether **2** was prepared by refluxing calix[4]arene with allyl bromide in CH₃CN in the presence of K₂CO₃. The reaction scheme is illustrated in Fig. 5.

Table 1. η_{sp}/C for Molecular Weight Determination

Conc (g/mL)	t (second)	η_{rel}	η_{sp}	η_{sp} / c
0	10.50			
0.000075	12.43	1.183809524	0.183809524	2450.79
0.00015	14.98	1.426666667	0.426666667	2844.44
0.0003	20.67	1.968571429	0.968571429	3228.57
0.0006	35.60	3.39047619	2.39047619	3984.13

**Fig 6.** Claisen rearrangement of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene**Fig 7.** Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene**Fig 8.** Graphic correlation of C versus η_{sp}/C of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene solution in chloroform

Claisen rearrangement of 25,27-diallyloxy-26,28-dihydroxycalix[4]arene was taken place using the presence of N,N-diethylaniline. The reaction was refluxed at 217 °C for 3 h. The solid product separated

after excess HCl addition to remove the remaining N,N-diethylaniline. The obtained solid was then recrystallized using chloroform-methanol and 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene was obtained. The reaction scheme is illustrated in Fig. 6.

Based on FTIR and HNMR analyses, it can be concluded that Claisen rearrangement was taken place and 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene was synthesized. HNMR spectra from the starting ethers, and the upfield shift of the allylic methylene hydrogen (from $\delta = 3.4$ to $\delta = 3.2$) indicated that allyl moieties had been transferred from the lower rim to the upper rim.

Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene

Polymerization of 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene using H_2SO_4 as the catalyst was carried out at room temperature (29 °C) under nitrogen atmosphere. The scheme of the reaction is depicted in Fig. 7.

The disappearances of vinyl ($-CH=CH_2$) group at 995.27 cm^{-1} as well as absorption at 1635.64 cm^{-1} showed that the polymerization was taken place.

Relative molecular weight of poly-5,7-diallyl-25,26,27,28-tetrahydroxy-calix[4]arene

Observation result for time flow in various concentration of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene and chloroform solvent were calculated from relatively viscosity (η_r), specific viscosity (η_{sp}) and relatively reductive viscosity (η_{sp}/C), as presented in Table 1.

Furthermore, based on Table 1, it can be obtained information about intrinsic viscosity from polymer solution which had been made using Huggins equation: $\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C$. Based on the equation, it

can be made a graphic $\frac{\eta_{sp}}{C}$ versus concentration (C).

By extrapolation to zero concentration, the intercept, intrinsic viscosity, $[\eta]$ of poly-5,7-diallyl-25,26,27,28-

tetrahydroxycalix[4]arene can be obtained as illustrated in Fig. 8.

The obtained intrinsic viscosity value is then added Mark-Houwink equation, $[\eta] = KM_v^a$. K and a is a constant which is depend on the polymer type and solvents. Based on Brandrup [17], K and a value for a certain polymer polypropylene polymer in chloroform at 30 °C are 2.18×10^{-2} mL/g and 0.725, respectively. By adding $[\eta]$, K, and a values to Mark-Houwink equation, it can be obtain that the relative molecular weight (M_v) and total repeated unit (n) of poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene are 18,738 g/mol and 37, respectively.

CONCLUSION

Poly-5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene can be synthesized by the following steps: (1) cyclotetramerization to *p-t-b*-calix[4]arene, (2) Debutylation to 25,26,27,28-tetrahydroxycalix[4]arene, (3) allylation to 25,27-diallyloxy-26,28-dihydroxycalix[4]arene, (4) Claisen rearrangement to 5,7-diallyl-25,26,27,28-tetrahydroxycalix[4]arene and (5) Polymerization. Poly-5,7-diallyl-25,26,27,28-tetrahydroxy calix[4]arene synthesized product was a solid having m.p. 338-340 °C, and molecular weight 18,738 g/mol with repeated unit : 37.

ACKNOWLEDGEMENT

The financial support from Indonesian Directorate General of Higher Education in the form of Hibah Bersaing 2009 is greatly appreciated.

REFERENCES

- Bohmer, V., 1995, Review, *Angew. Chem., Int. Ed. Engl.*, 34, 713-745.
- Linane, P. and Shinkai, S., 1994, *Chem. Ind.*, 811-814.
- Shinkai, S., Mori, S., Koreishi, H., Tsubaki, T., and Manabe, O., 1986, *J. Am. Chem. Soc.*, 108, 2409-2416.
- Haverlock, T.J., Mirzadeh, S., and Moyer, B.A., 2003, *J. Am. Chem. Soc.*, 125, 1126-1127.
- Kim, J.Y., Kim, G., Kim, C.R., Lee, S.H., Lee, J.H., and Kim, J.S., 2003, *J. Org. Chem.*, 68, 1933-1937.
- Gutsche, C.D. and Pagoria P.F., 1985, *J. Am. Chem. Soc.*, 50, 5795-5802.
- Gutsche, C.D., Levine, J.A., and Sujeeth, P.K., 1985, *J. Org. Chem.*, 50, 5802-5805.
- Gutsche, C.D. and Lin, L.G., 1986, *Tetrahedron*, 42, 1633-1640.
- Gutsche, C.D., Iqbal, M., and Stewart, D., 1986, *J. Org. Chem.*, 51, 742-745.
- Groenen, L.C., Ruel, B.H.M., Casnati, A., Verboom, W., Pochini, A., Ungaro, R., Harkema, S., and Reinhoudt, D.N., 1991, *Tetrahedron*, 47, 8379-8384.
- Casnati, A., Arduini, A., Ghidini, E., Pochini, A., and Ungaro, R., 1991, *Tetrahedron*, 47, 2221-2228.
- Van Loon, J.-D., Arduini, A., Verboom, W., Ungaro, R., van Hummel, G.J., Harkema, S., and Reinhoudt, D.N., 1989, *Tetrahedron Lett.*, 30, 2681-2684.
- Collins, E.M., McKervey, M.A., and Harris, S.J., 1989, *J. Chem. Soc., Perkin Trans.*, 1, 372-374.
- Groenen, L.C., Ruel, B.H.M., Casnati, A., Timmerman, P., Verboom, W., Harkema, S., Pochini, A., Ungaro, R., and Reinhoudt, D.N., 1991, *Tetrahedron Lett.*, 32, 2675-2678.
- Gutsche, C.D., Dhawan, B., No, K.H., dan Muthukrishnan, R., 1981, *J. Am. Chem. Soc.*, 103, 3782-3792.
- Van Loon, J.-D., Arduini, A., Coppi, L., Verboom, W., Pochini, A., Ungaro, R., Harkema, S., Reinhoudt, D.N., 1990, *J. Org. Chem.*, 55, 5639-5646.
- Brandrup, J., Immergut, E.H., and McDowell, W., 1975, *Polymer Handbook*, John Wiley and Sons, USA.