

The Synthesis, Characterization and Properties of Calix [6] arene-Based Polymer

Susy Yunita Prabawati, Jumina, Sri Juari Santosa, and Mustofa

Abstract—Novel poly-calix[6]arenes have been synthesized by direct polymerization of calix[6]arene through allyl groups at lower rim to yield poly-monoallyloxy-calix[6]arene (PMK[6]H) and poly-diallyloxy-calix[6]arene (PDK[6]H). The characterizations and properties of polymers were observed by means of melting point, FTIR and ^1H NMR spectrometers. Physicochemical properties were determined by scanning electron microscope (SEM) and surface area analyzer (SAA). ^1H NMR spectrum showed that the allyl group had been incorporated to the lower rim of the calix[6]arene. As expected, at the ^1H NMR spectrums of polymers, the existence of vinyl protons signal which resonate at δ 5.9 ppm (=CH-) and δ 5.0-5.2 (C=CH₂), were disappeared, indicating that the vinyl groups had been polymerized. The polymers were obtained as brown and brownish green crystals with the melting point of 199-201 and 108-110 °C, respectively. With a tunnel-like structure of the polymers, they can be used as adsorbents to trap heavy metal ions.

Keywords— adsorbents, calix[6]arene, poly-calix[6]arenes,

I. INTRODUCTION

THE development of calixarene chemistry has tremendously increased in the last decade especially after Gutsche revealed that calixarenes can be considered as “baskets” to be used to trap molecules or ions [1]. The unique geometry and the presence of active groups in calixarenes, allowing these compounds can be used for various purposes.

The uniqueness of the calixarenes structure allows these compounds can act as “host-guest” for the molecule or ion. Kunsagi-Mate (2005) had shown that calix[6]-Na-hexasulphonat successfully used to trap *p*-nitro-phenol [2]. Calix[n]arenes can also be used as adsorbent for dye waste or heavy metals [3].

Generally, there are two synthesis strategies that can be done to improve the affinity of calixarenes in forming complexes with metal ions. Firstly, synthesize calixarenes by including the polar ionophores groups such as carboxyl, amide, nitrile, halide and phosphate. However, calixarenes with these groups belong to the calixarenes soluble in water, so this is not consistent with use as an adsorbent that should not be soluble in water. Secondly, synthesize calixarenes with highly polar groups, but to suppress their solubility in water, it can be done through calixarenes immobilized on a polymer or by synthesize the calixarenes polymer [4].

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Various studies have been done in this synthesize calixarenes polymers. Trivedi *et al.* (2002), had made the synthesis of calix[6]-hydroxyamide based polymer and it can be used to trap the metal ions of uranium, thorium and cerium [5]. Adsorption properties of the polymer calix[6]-1.4-crown had also been reported by Yang *et al.* (2005) for soft cations such as Cu (II), Co (II) and Ni (II) [6].

Calixarene immobilized on a polymer had also been carried out to conduct a cross connection between chitosan and calix[4]arene to produce a chelate polymer [7]. The results of this synthesis was used to adsorb the heavy metal cations and dichromate anions, apparently resulting polymer has adsorption capacity is higher (80-93%) than chitosan (25-33%). A similar study was conducted by Tabakci and Yilmaz [4] who did calixarene immobilized on silica gel and the polymer was also be able to trap the Cu(II) with satisfactory results.

Jumina *et al.* (2007) suggested the possibility of such alkenyl groups include allyl groups at the lower rim of tetrahydroxy-calix[4]arene to produce monoallylcalix[4]arene [8]. Furthermore, Utomo (2009) had been polymerized this compound under acidic conditions to produce poly-propylcalix[4]arene that were not soluble in water [9]. Utilization of this polymer as adsorbent for Pb(II) and Cr(III) appeared to indicate that the adsorption capacity was much greater than the monomer. Subsequent research conducted by Handayani also succeeded in synthesizing a compound of poly-5-allylcalix[4]arene and showed good results in absorbing heavy metal cations [10].

Based on previous research, in this research, it will be conducted the synthesis of a series of poly-calix[6]arene. The synthesis of calix[6]arene was much easier than other calixarene. The synthesize of poly-calix[6]arene was started by substituting one allyl group and the two allyl groups at the lower rim of the calix[6]arene. In the polymerization process, the presence of one allyl group would form a linear polymer, while the presence of two allyl groups would form a cross link polymer.

II. EXPERIMENTAL SECTION

A. Material

All the chemicals used in this study were the highest purity available from Merck or Aldrich chemical companies and were used without further purification.

B. Instruments

Melting points were obtained with an electrothermal 9100 Model Digital Melting Point apparatus, was obtained at the Laboratory of Chemistry, UIN Sunan Kalijaga of Yogyakarta. Infrared (FTIR) spectrums were recorded on a Shimadzu FTIR 8201 PC Spectrophotometer and refer to KBr disks. ^1H NMR spectrum were obtained in the designated solvent (CDCl_3) on a JEOL-MY500 proton Nuclear Magnetic Resonance Spectrometer.

C. Procedure

Synthesis of *p*-*t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-hydroxycalix[6]arene

p-*t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-hydroxycalix[6]arene (calixarene **1**) were prepared from *p*-*ter*-butylcalix[6]arene according to the procedures reported previously [11]. Recrystallization from chloroform-methanol afforded 4.40 g (86.99 %) of yellow crystals: mp 178-180 °C; FTIR (KBr): 3387 cm^{-1} (OH stretching), ν (vinyl group, $\text{C}=\text{CH}_2$) 987 cm^{-1} ; ^1H -NMR, 500 MHz (CDCl_3), δ 7.06-7.24 (m, 12, ArH), δ 5.9 (m, 1, $\text{C}=\text{CH}-\text{C}$), δ 5.06-5.2 (m, 2H, $\text{C}=\text{CH}_2$), δ 3.2-4.3 (s and dd, 12H, ArCH_2Ar), δ 2.1 (s, 2H, OCH_2C) and δ 1.2 (s, 54, $\text{C}(\text{CH}_3)_3$).

Synthesis of *p*-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene

p-*t*-butyl-37,40-diallyloxy-38,39,41,42-tetrahydroxycalix[6]arene (calixarene **2**) were prepared according to the procedures reported previously [12]. The residue was recrystallized with CHCl_3 and CH_3OH to yield a yellow white crystals: mp 141-143 °C; FTIR (KBr): 3410 cm^{-1} (OH stretching), ν (vinyl group, $-\text{C}=\text{CH}_2$) 925 cm^{-1} ; ^1H -NMR 500 MHz (CDCl_3), δ 7.06-7.24 (m, 12, ArH), δ 6.80 (m, 2, $\text{C}=\text{CH}-\text{C}$), δ 5.33-5.52 (m, 4H, $\text{C}=\text{CH}_2$), δ 4.24-4.49 (d, 4H, OCH_2C), δ 3.82-3.89 (d, 4H, ArCH_2Ar), and δ 1.2 (s, 54, $\text{C}(\text{CH}_3)_3$).

Polymerization of calix[6]arene

To 1 g of calixarene (**1** and **2**) in 100 mL chloroform was added concentrated sulfuric acid (0.1 mL) in 0.25 mL portions every 30 minutes. The reaction mixture was stirred at for 8 h and the polymerization was terminated by adding 0.5 mL of methanol. The mixture was decanted and the precipitate was dissolved in diethyl ether and washed until neutral. The chloroform layer was washed until neutral and combined with the ether layer. The combined layers were dried with anhydrous Na_2SO_4 and evaporated to yield the polymers i.e. PMK[6]H and PDK[6]H which were dried in a desiccator.

III. RESULT AND DISCUSSION

A. Synthesis and characterizations

As monomers, calixarene **1** and calixarene **2** were polymerized with concentrated sulfuric acid at room temperature to yield poly-monoallyloxy-calix[6]arene (PMK[6]H) and poly-diallyloxy-calix[6]arene (PDK[6]H). The synthetic routes of polymers were illustrated in Fig. 1. The polymers i.e. PMK[6]H and PDK[6]H were obtained as brown and brownish green crystals, respectively.

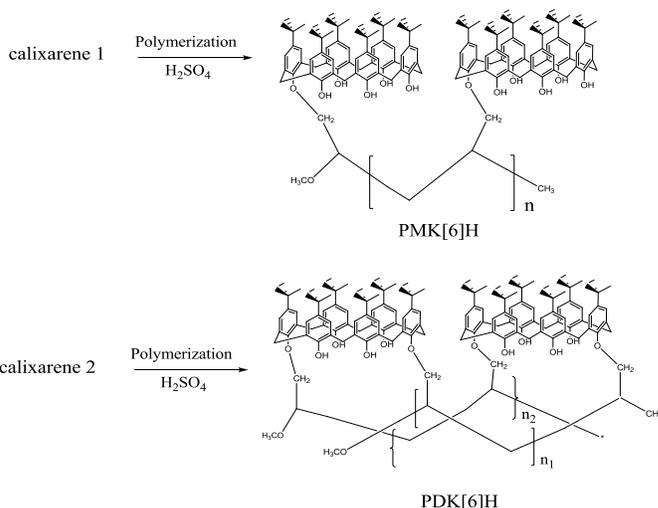


Fig. 1 Scheme of the synthetic route of PMK[6]H and PDK[6]H

The elemental analysis data and molecular weight of polymers were shown in Table I. The relative molecular weight (M_n) for each polymer was obtained by Ubbelohde Viscometer. The M_n of polymers were approximately 12,000-30,000 g/mol with the repetition unit of 30 and 12. The physical properties of polymers were presented in Table I.

TABLE I
RESULTS OF THE POLYMERIZED PRODUCTS

Compounds	Results			
	m.p (°C)	Color	Rel. Mol. Weight	(n)
PMK[6]H	199-201	brown	30,182	30
PDK[6]H	108-110	brownish green	12,510	12

Based on the relative molecular weight of polymers, it was showed that PDK[6]H had repetition unit was relatively smaller than PMK[6]H. This was understandable because PDK[6]H was a branched polymer that have large steric effect when the polymerization was occurred.

B. FTIR spectrum

At the FTIR spectrum of calixarene **1**, it was showed that a strong broad band of the -OH groups appeared at 3387 cm^{-1} and the absorption at 1203.58 cm^{-1} , indicating the presence of C-O derived from the bond between C benzene ring with hydroxyl oxygen atoms. This is supported by a strong absorption peak at 925.83 cm^{-1} , indicating the presence of vinyl terminal. In the FTIR spectrum of the PMK[6]H, the absorption peaks of vinyl were disappeared which mean almost all of the vinyl groups were polymerized. At the FTIR spectrum of calixarene **2** and PDK[6]H the absorption peaks of vinyl were appeared at 925.83 cm^{-1} , indicating the presence of vinyl terminal and in the spectrum of PDK[6]H, that adsorption were disappeared, which mean almost all of the vinyl groups were polymerized.

C. ^1H NMR spectrum

The product of polymers were also characterized by ^1H NMR spectrometer. The ^1H NMR spectrum of calixarene **1** showed in Fig. 2. It's showed 6 (six) signals depicting 6 different types of protons. Signals at δ 7.0-7.2 ppm refers to

proton resonance of benzene groups. Signal at δ 5.9 ppm is predicted from one proton in the middle carbon group ($-\text{CH}=\text{}$) and signal at δ 5.0-5.2 ppm refers to terminal proton resonance of allyloxy ($=\text{CH}_2$) group. This supported by the integration of ^1H NMR spectrum shows the number of the ether linkages of the monoallyl ether was 1. This indicated that only one allyl group had been incorporated to the lower rim of the *p-t*-butylcalix[6]arene to form calixarene **1**. The existences of methylene bridge of calixarene ($-\text{CH}_2-$) protons are shown at δ 3.2-4.3 ppm. The $\text{O}-\text{CH}_2-$ group proton and the proton tert-butyl groups are estimated to resonate at δ 2.1 ppm and δ 1.22-1.28 ppm, respectively.

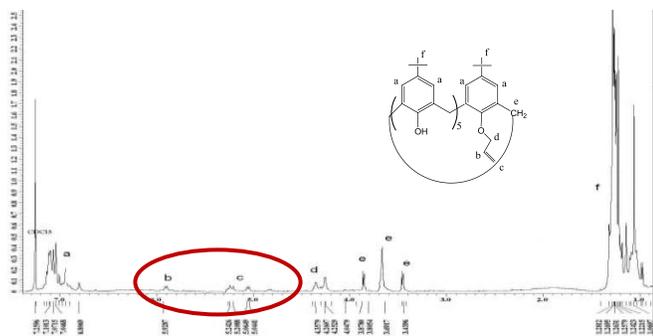


Fig. 2 ^1H NMR 500 MHz spectrum of calixarene **1**

The ^1H NMR spectrum of the PMK[6]H were showed in Fig. 3. As expected, the existence of vinyl protons signal which resonate at δ 5.9 ppm ($=\text{CH}-$) and δ 5.0-5.2 ($\text{C}=\text{CH}_2$), were disappeared, indicating that the vinyl groups had been polymerized. The successful of the reaction can also be proved from the resonate at δ 10 ppm, which indicated the proton resonance of $-\text{OH}$ groups.

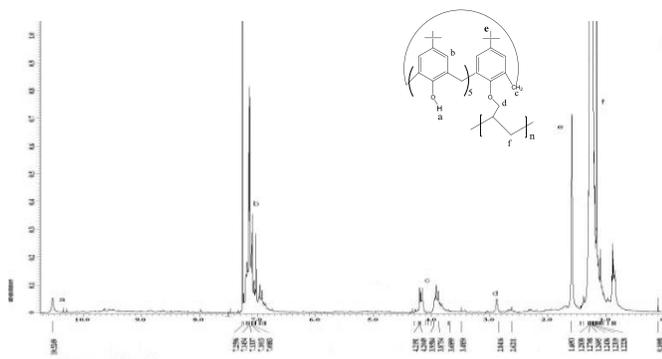


Fig. 3 ^1H NMR 500 MHz spectrum of PMK[6]H

Meanwhile, the presence of allyl group was also shown in the ^1H NMR spectrum of calixarene **2** (Fig.4). As expected, the proton NMR spectrum of PDK[6]H (Fig.5) does not also show the existence of vinyl protons signal which resonate at δ 6.80 ppm ($\text{C}=\text{CH}-\text{C}$) and δ 5.33-5.52 ($\text{C}=\text{CH}_2$), indicating that the vinyl groups had been polymerized.

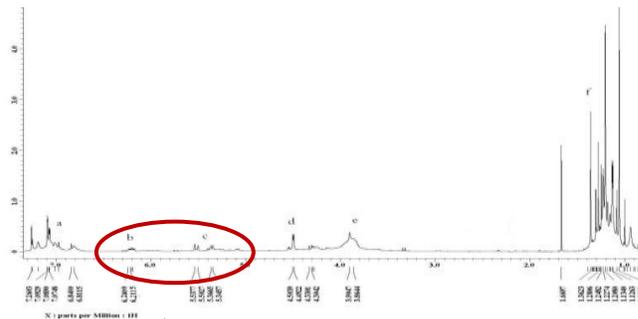
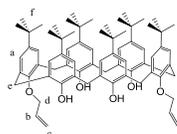


Fig. 4 ^1H NMR 500 MHz spectrum of calixarene **2**

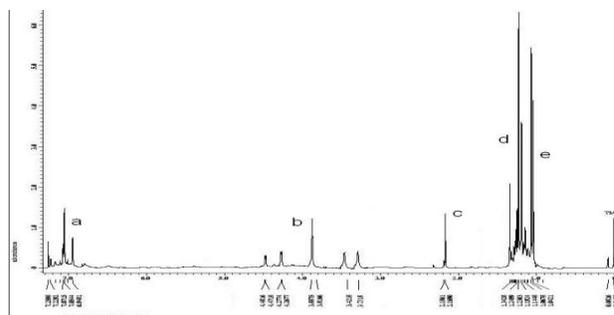


Fig. 5 ^1H NMR 500 MHz spectrum of PDK[6]H

The poly-calix[6]arenes are very possible to be used as adsorbent for heavy metals. The hydroxy groups as active groups are scattered along the polymer chain and can interact with the metal ions. The physicochemical properties of adsorbents such as surface area, pore size, surface morphology, and the conformation of the adsorbent can affect its ability to absorb heavy metals. In this research, the surface morphology of the linear polymer (PMK[6]H) and branched polymers (PDK[6]H) were characterized using Scanning Electron Microscope (SEM) were showed in Fig. 6.

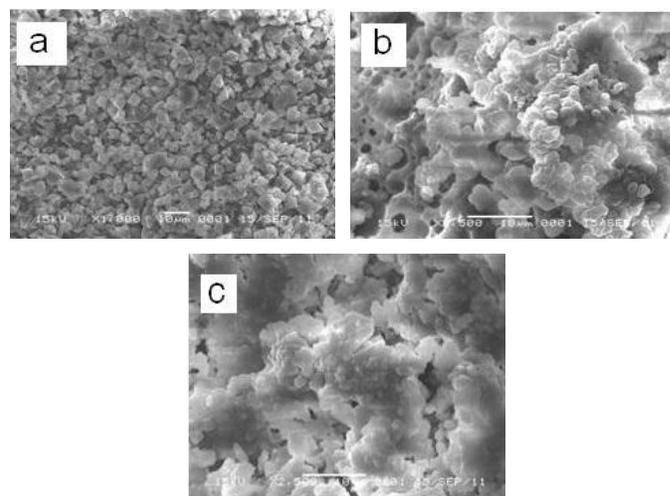


Fig. 6 SEM analysis of calix[6]arene (a), PMK[6]H (b), and PDK[6]H (c)

The morphology of the calixarene compound change after *p-t*-butylcalix[6] arene was transformed into polymers. These three compounds showed the porous morphology structure. The surface morphology of calix[6]arene showed a rough solid surface, and after the polymerization, the morphology of

the polymer becomes more porous and regular. PMK[6]H had more regular pore texture than PDM[6]H. This was also supported by SAA analysis that was listed in Table II.

TABLE II
SURFACE AREA AND POROSITY ANALYSIS

Poly-calix[6]arenes	Surface Area (m ² /g)	Total Pore Volume x 10 ⁻³ (cc/g)	Average Pore Radius (Å)
PMK[6]H	2,197	4,368	39,765
PDK[6]H	0,957	2,087	43,594

Specific surface area of PMK[6]H was also greater than PDK[6]H. Thus in general it can be said that the a linear calix[6]arene polymer tends to be more regular than a branched polymer that are more complex. This seems to be caused by the presence of a large steric hindrance in branched polymer, so that the structure becomes more complex and tend to close the pores of the compound.

One of the factors that also play a role in the adsorption process is the compatibility between the adsorbent and adsorbate size. Suitability size can play a role in the process leading to the formation of a stable interaction, though in the end that determines the stability of the interaction is an unsuitable nature of the hard-soft acid-base. In calixarene compounds, suitability measure is meant to be a measure of the suitability of the calixarene cavity diameter with diameter of heavy metal cations. Table 3 contains the value of the theoretical diameter of PMK[6]H and PDK[6]H obtained based on calculations using the MM AMBER method with HyperChem program.

TABLE III
THE DIAMETER OF PORE OF CALIX[6]ARENE MONOMER

Poly-calix[6]arenes	Diameter of pore (Å)
PMK[6]H	6,711
PDK[6]H	6,422

Based on the data from Table III, it is known that the cavity diameter of the monomer of PMK[6]H greater than PDK[6]H. The size compatibility between the metal ions can cause the adsorbate and adsorbent is at a distance effective to do the interaction, so the capability to adsorb metal ions becomes greater. Meanwhile, the heavy metal cations diameter ranged from 1.94 to 2.4 Å [13]. In aqueous solution, metal ion prefers hydrated form. In the hydrated state, the metal ion will have a larger diameter ions. Based on this results, it could be concluded that poly-calix[6]arenes can be used as adsorbent for heavy metal cations.

IV. CONCLUSION

Based on the FTIR and ¹H NMR analysis, it can be concluded that the synthesis of a series of calix[6]arene-based polymers i.e. PMK[6]H and PDK[6]H were successfully produced. The polymers were obtained as brown and brownish green crystals with the relative molecular weight for each polymer was 30,182 and 12,510, respectively. The physicochemical properties of PMK[6]H and PDK[6]H

showed that a linear calix[6]arene polymer tends to be more regular than a branched polymer that are more complex. Based on physical properties of calix[6]arene polymers, it can be regarded as a potential adsorbent in the application of heavy metals wastewater treatment.

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