Synthesis of a Series of Calix[6]arenePolymers from*p*-*ter*-butylphenol

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Abstract

*A research has been conducted to synthesize ofa series of novel calix[6]arene-based polymers **2a-c**using p-tert-butylphenol as a starting material. It was of interest to study calix[6]arene and its derived polymers which have cavity size larger than calix[4]arene.The synthesis was carried out in several steps i.e (1) formation of p-tert-butylcalix[6]arene from p-tert-butylphenol, (2) treatment of p-tert -butylcalix[6]arene with allyl bromide under alkaline condition to yield compound **1a**, (3) esterification of **1a** to yield **1b**, (4) hydrolysis of **1b** with chloride acid to yield **1c** and (5) polymerization of **1a-c**by treatment with concentrated sulfuric acid to yield a series of polypropyl-calix[6]arenes**2a-c**. The structures of those products were observed by means of melting point, FTIR and ^{1}H NMR spectrometers. The ^{1}H NMR spectra showed that one allyl group had been incorporated to the lower rim of the p-tert-butylcalix[6]arene.The polymers **2a-c**wereobtained as brownish crystals with the melting point of 199-201; 99-101; and 101-103 ^{o}C respectively. With a tunnel-like structure of the polymers, they can be usedas adsorbents to trap heavy metal ions.*

Keywords: p-tert-butylphenol, p-tert-buthylcalix[6]arene, esterification, hydrolysis, andpolypropyl-calix[6]arenes.

1. Introduction

Calixarenes are an important class of macrocyclic molecules in supramolecular chemistry [1-2]. These compounds are cyclic oligomer of phenols linked by methylene bridges and have active groups such as –OH groups arrange the molecules. Because of the unique molecular geometry of calixarenes, its can be used as catalyst [3], ion exchange and adsorbent forcation, anion, or neutral molecule [4,5].

The development in calixarene chemistry in mainly due to the possibilities of functional modifications at the upper or lower rim to yield new macro molecules.The reactions used to modify the lower rim of calixarenethat binding hydroxygroups, include the esterification and etherification [6, 7]. Richard et al. [8], has also succeeded in modifying the lower rim of calix[6]arena by substituting the OH groups with a carboxylic acid groups.

Calixarene compounds can be used as adsorbent for heavy metal ions by modify its functional groups polar (hydrophilic groups) such as carboxyl, sulphonate, nitro, amino, amide, halide, and phosphate.To increase its polarity, it's also possible to incorporate alkenyl groups such as an allyl groupat the lower rim ofcalixarene. Ho, *et al* [9] and Shu, *et al* [10] have shown that the two allyl group at the lower rim of calix[4]arene could be incorporated by addition of allylbromide, while Kusumawardani [11] also reported that a resin derived calix[4]arenei.e.,tetra-*p*-propenyltetraester-calix[4]arene and tetra-*p*-propenyltetra-carboxylicacid[4]arenecould be successfully synthesized by first entering the four allyl groups at the lower rim of calix[4]arene.

In order to keep functioning as an effective adsorbent and solubility in water is reduced, it can be immobilized the calixareneon a polymer or by synthesize the polymers of calixarene.Jumina, *et al* [12] has reported that the monoallylcalix[4]-arene can be polymerized under acidic conditions to generate the corresponding polypropyl-calix[4]arene polymer. Furthermore, Utomo [13] reported that the capability of this polymerto trap heavy metal cations such as Pb (II) and Cr (III)) cationsare significallygreater thanthat of the monomer. Based on this phenomenon, it would be interesting to study calix[6]arene with cavity size larger than calix[4]arene, and its polymerization as well as the polycalix[4]arene in regards to ability to trap heavy metals. Herein, we wish to report the synthesis of a series of calix[6]arene polymers from *p*-*tert*-buthylphenol.

2. Experimental Section

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.

Instruments

Melting points were obtained with anelectrothermal 9100 Model Digital Melting Point apparatus,wasobtained at theLaboratory of Chemistry, StateIslamicUniversitySunanKalijaga of Yogyakarta.Infrared (IR) spectra were recorded on a Shimadzu FTIR 8201 PC Spectrophotometer and refer to KBr disks. ^{1}H NMR spectra were obtained in the designated solvent ($CDCl_3$) on a JEOL-MY500 proton Nuclear MagneticResonanceSpectrometer.

Procedure

Synthesis of *p*-t-butylcalix[6]arene

p-*tert*-Butylcalix[6]arene were prepared from *p*-*ter*-butylphenol according to the procedures reported previously [14]. Recrystalization from chloroform-methanol afforded a white solid crystal :3.5 g, 65.47%, m.p. 370-372 ^{o}C; IR (KBr) 3425 cm^{-1}(OH stretching), ν (C=C aromatic)= 1627 cm^{-1}, (*t*-butyl)=1365 cm^{-1} and ν(methylene group)= 1481 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 10.5 **(**s,1, ArOH), δ 7.10 (m,2, ArH), δ 3.9 (s,2, CH_2), δ 1.27 (s, 9, $C(CH_3)_3$).

Synthesis of *p*-*t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-hydroxycalix[6]arene (1a)

A mixture of 4.86 g (5 mmol) of *p*-*t*-butylcalix[6]arene, 0.621 g (4,5 mmol) K_2CO_3, 0.714 mL (8.25 mmol) allylbromide, and 100 mL of dry acetone was refluxed under dry N_2 condition for 48 hours. The precipitate was filtered and acetone was evaporated. The residue was recrystallized with $CHCl_3$ and CH_3OH to yield *p*-*t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-hydroxycalix[6]arene, afforded 4.402 g (86.99 %) of yellow crystals: mp178-180^{o}C; IR (KBr): 3387 cm^{-1}(OH stretching), ν(vinyl group,C=CH_2) 987 cm^{-1};^{1}H-NMR ($CDCl_3$), δ 7.06-7.24 (m, 12, ArH), δ 5.9 (m, 1, C=CH-C), δ 5.06-5.2 (m, 2H, C=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, $C(CH_3)_3$).

Synthesis of *p*-*t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-estercalix[6]arene (1b)

Into a three-necked flash equipped with a reflux condensor, it was added 0.263 g (0.25 mmol) of **1a**; 0.2875 g (2.35 mmol) ethyl-2-chloroacetic; 0.355 g (2.35 mmol) NaI; 0.425 g (3.25 mmol) K_2CO_3, and 50 mL of dry aceton.The mixture was refluxed for 24 h.

The resulting mixture was allowed to cool, K_2CO_3wa filtered off and aceton was evaporated. The residu was dissolved in chloroform, and then washed with 3 x 25 ml HCl 1 M and 1 x 25 mlsaturated NaCl. The solution was dried with Na_2SO_4 anhydrous and chloroform was evaporated. The product was characterizedby means of FTIR, ^{1}H-NMR.

Synthesis of *p-t*-butyl-37-monoallyloxy-38,39,40,41,42-penta-carboxylic-acidcalix[6]arene (1c)

A mixture of **1b**(1.2 mmol; 1.73 g); 0.5 g KOH and 50 ml of ethanolwas refluxed under dry N_2 condition for 24 hours. The resulting mixture was allowed to cooland acidified with HCl 1 M. The precipitated was filtered off. The product was characterizedby means of FTIR, ^{1}H-NMR.

Polymerization of monoallyloxycalix[6]arene

To 1 g of**1a-c** 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 **2a-c** which was dried in a desiccator.

3. Result and Discussion

3.1 Syntheses and characterizations

Synthesis of *p-t*-buthyl-37-monoallyl-38,39,40,-41,42-pentahydroxy-calix[6]arene (**1a**) was carried out by refluxing 1.1 equivalent of allyl bromide and 0.6 equivalent of K_2CO_3 in dry aceton for 48 h under N_2atmosphere.The product of this reaction was obtained as yellow crystals with the melting point of 178-182^{o}C. The scheme ofthesyntheticroute of **1a**wasshowed in Figure 1.

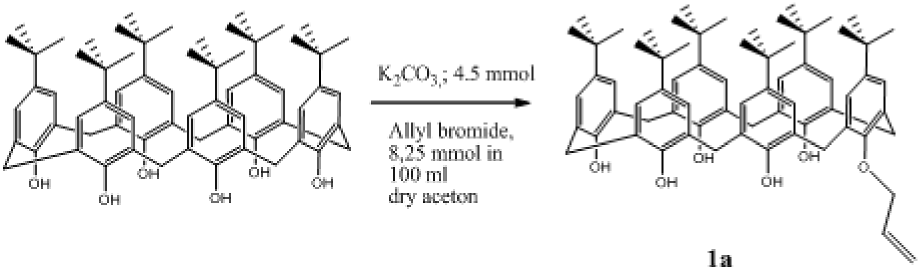


Figure 1. Scheme of the synthetic route of **1a**

Esterification of **1a** was performed using K_2CO_3, NaI and 2-ethylchloroacetate reagent. The esterification product to yield **1b**was obtained as yellow crystals with the melting point of 164-166^{o}C. Furthermore the synthesis of **1c** was done by hydrolysis reaction of **1b** and the product of this reaction was obtained as yellow white crystals with the melting point of 143-145^{o}C.

As monomers, **1a-c** were polymerized with concentrated sulfuric acid to yield polymer **2a-c**. The synthetic route of polymers were illustrated inFigure 2. The polymers **2a-c**were obtained as brown, brownish white and brown crystals respectively.

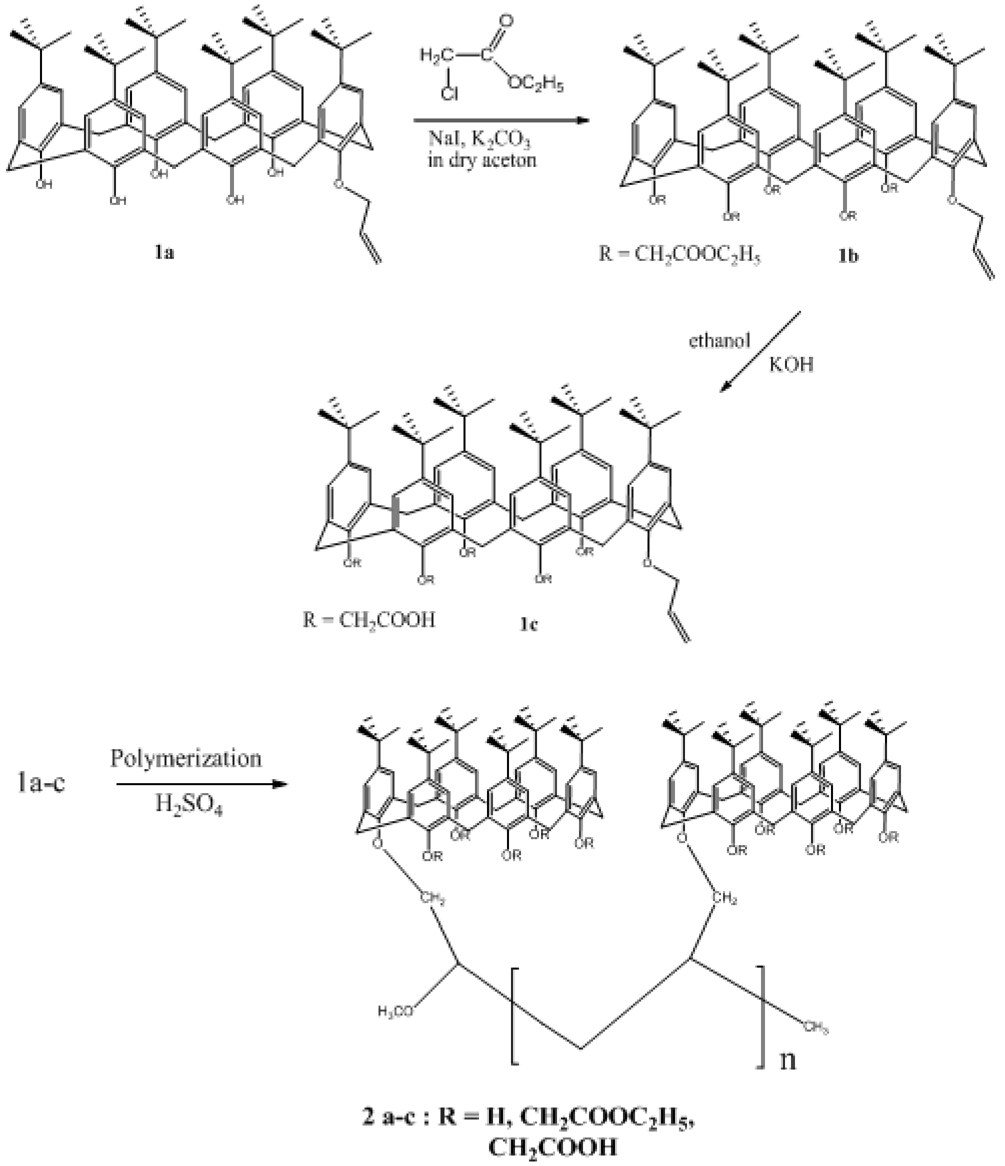


Figure 2. Scheme of thesyntheticroute of polymer 2a-2c.

The elemental analysis data and molecular weight of polymer **2a-c** were shown in Table 1. The relative molecular weight (M_n) for each polymers were obtained by UbbelohdeViscometer. The M_n of polymers **2a-c**were approximately 25,000-30,000 g/mol. The structure of all these deductions wereconfirmed by IR and ^1H NMR spectrum.

Table 1. Results of the polymerized products

Compounds	Results			
	m.p (°C)	Color	Rel. Mol. Weight	(n)
Poly-monoallylcalix[6]arene (**2a**)	199-201	brown	30,182	30
Poly-monoallyl-pentaestercalix[6]arene (**2b**)	99-101	brownish white	27,228	19
Poly-monoallyl-pentacarboxylic-acidcalix[6]arene(**2c**)	101-103	brown	24,612	19

3.2 IR spectrum

The structures of compound **1a-c** were confirmed by IR spectrumthat showed in Figure 3. At the IR spectrum of **1a**, it was showedthat a strong broad band of the -OH groups appeared at 3387cm^{-1} and the absorption at 1203.58 cm^{-1}, indicating the presense of C-O derived from the bond between C benzene ring with hydroxyl oxygen atoms. This is supported by a strong absorption peak at 987.55 cm^{-1}, indicating the presence of vinyl terminal.

On the other hand, at the IR spectrum of **1b**, it can be seen that the absorption band at 3387 cm^{-1} of the hydoxyl group (-OH) dissappeared indicating that the esterification reaction has taken place. The characteristic absorption of carbonyl group (C=O) and (C-O-C) of ester appeared at 1759.08 cm^{-1}and 1200-1100 cm^{-1}, respectively. These data of IR spectrum certainly suggested that the hydroxyl groups were well esterifisized to yield*p*-*t*-buthyl-37-monoallyl-38,39,40,-41,42-pentaester-calix[6]arene (**1b**).

The successful synthesis of **1c**was showed by appearence absorption band at 3425.58 cm^{-1}, which is characteristicfor -OH groups. This indicated that the ester groups were hydrolyzed to carboxylic acid. The existence of carbonyl groups (-C=O) were showed at 1743.65 cm^{-1}and the absorption at 1473.62 cm^{-1} indicated the existence of methylene groups.

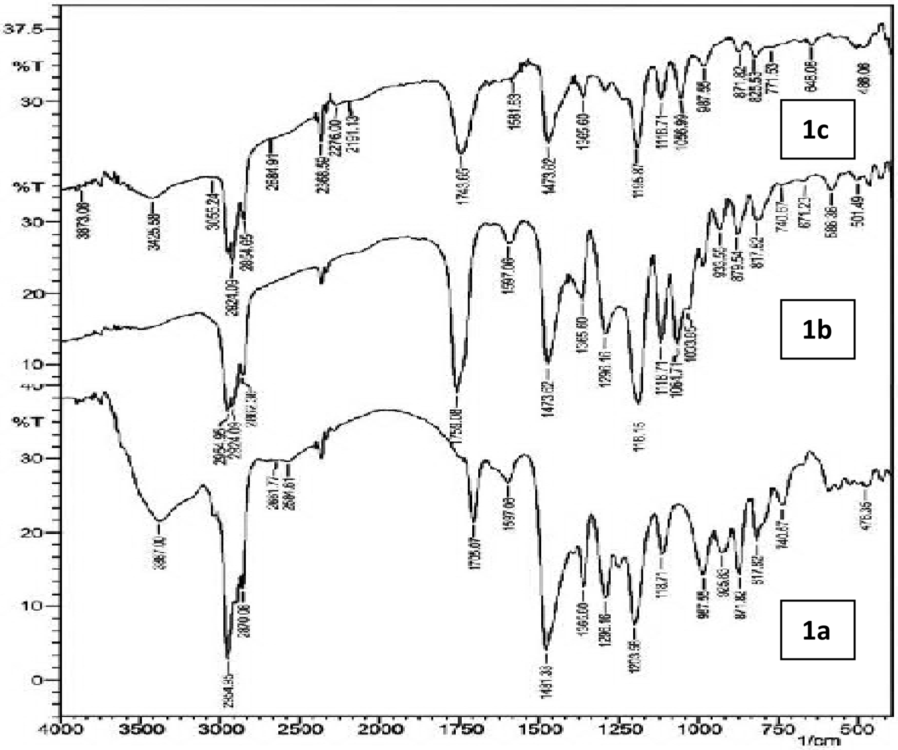


Figure 3.IR Spectrum of 1a, 1b and 1c

The structure of polymers2a-c werealso characterized by IR. In the IR spectrum, the absorption peaks of vinyl were disappeared which mean almost all of the vinyl groups were polymerized.

3.3 ^{1}H NMR spectrum

^{1}H NMR spectrum of compound **1a** showed in Figure 4. Its showed 6 (six) signals depicting 6 differrent 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 (-CH=) and signal at δ 5.0-5.2 ppm refers to terminal proton resonance of allyloxy (=CH$_2$) group. This supported by the integration of ^{1}H NMR spectrum shows the number of the ether linkages of the monoallyl ether was 1. This indicated that onlyone allyl group had been incorporated to the lower rim of the *p*-*t*-butylcalix[6]arene to form **1a**.

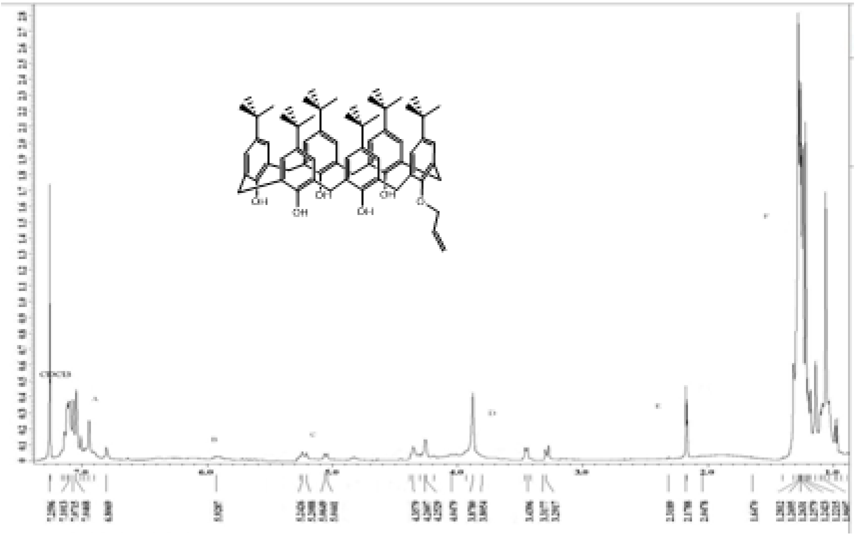
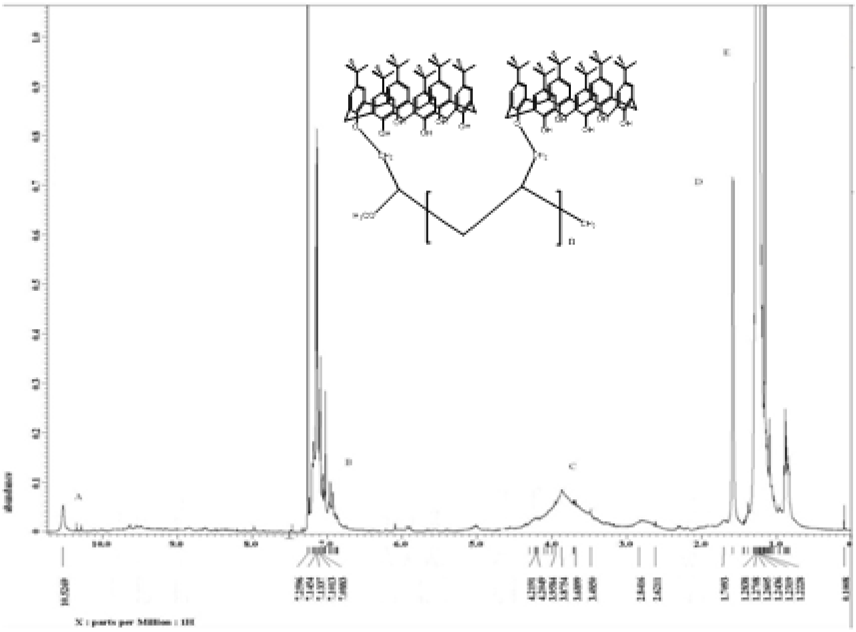


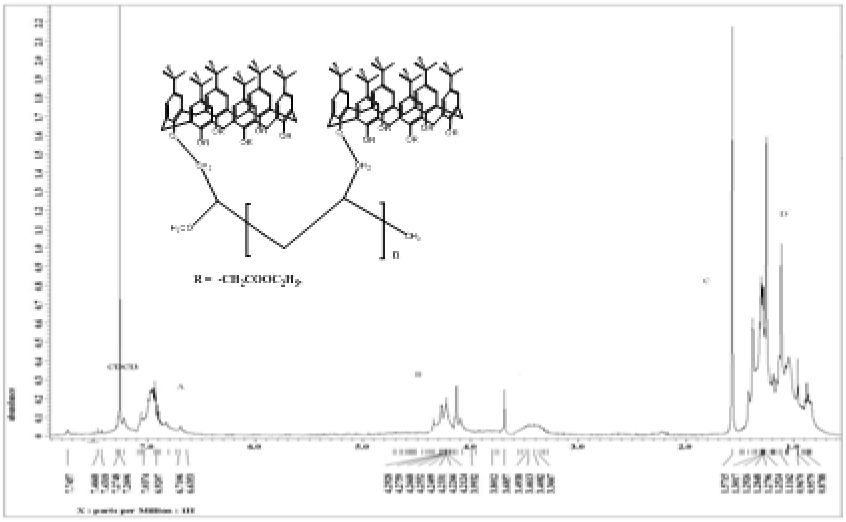
Figure 4.^{1}H NMR 500 MHz spectrum of monoallil-calix[6]arene (**1a**)

The existence of methylene brigde of calixarene (-CH_2-) protons are shown at δ 3.2-4.3 ppm. The O-CH_2- group proton and the proton tert-buthyl groups are estimated to resonate at δ 2.1 ppm and δ 1.22-1.28 ppm respectively.

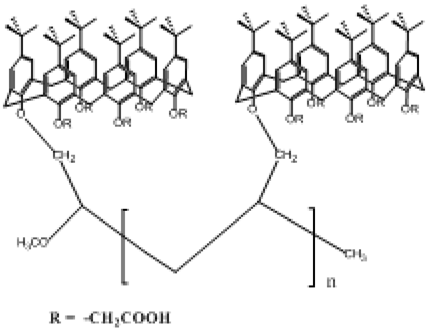
On the other hand, the ^{1}H NMR spectrum of the polymers **2a-c**were showed in Fig. 5. As expected, the^{1}H NMR spectrum does not also show the existence of vinylprotons signal which resonate at δ 5.9 ppm (=CH-) and δ 5.0-5.2 ($C=CH_2$), indicating that the vinyl groups had been polymerized. The successful of the reaction can also be proved fromthe resonate at δ 10 ppm, which indicated the proton resonance of –OH groups. This signal disappeared in ^{1}H NMR spectrum of **2b**which mean almost all of the -OH groups were hydrolyzed.



2a



2b



2c

Figure 5.^{1}H NMR 500 MHz spectrum of **2a-c**

4. Conclusion

The synthesis of three new calix[6]arene-based polymers **2a-c**have been successfully produced from *p*-*t*ert-buthyphenol as a starting material. These polymers can be synthesized by the following steps:(1) cyclohexamerization to *p*-*t*ert-buthylcalix[6]arene; (2) allylation to *p*-*t*-buthyl-37-monoallyl-38,39,40,-41,42-pentahydroxy-calix[6]arene (**1a**); (3) esterification to *p*-*t*-buthyl-37-monoallyl-38,39,40,-41,42-pentaester-calix[6]arene (**1b**); (4) hydrolisis to *p*-*t*-buthyl-37-monoallyl-38,39,40,-41,42-pentacarboxylic-acidcalix[6]arene(**1c**); and (5) polymerization of **1a-c** to yield polymers **2a-c**. Based on IR and ^{1}H NMR analyses, it can be concluded that the synthesis of a series of calix[6]arene polymers were successfully produced. The polymers were obtained as brownish crystals with the relative molecular weight for each polymers were approximately 25,000-30,0000 g/mol.

5. Acknowledgement

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