

# Synthesis and Characterization of Chitosan-p-t-Butylcalix[4]arene acid

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**Abstract.** The synthesis of chitosan-p-t-butylcalix[4]arene acid was done with DIC (N, N'-diisopropylcarbodiimide) as the coupling agent. The structural analysis of the chitosan-p-t-butylcalix[4]arene acid was conducted by spectrophotometer Fourier Transform Infra Red (FTIR) and X-Ray Diffraction (XRD). Meanwhile, the surface area was investigated by Surface Area Analysis, the Scanning Electron Microscope (SEM) analysed the surface morphology, and also the melting point temperature was determined. FTIR analysis on Chitosan-p-t-butylcalix[4]arene provides an overlapped absorption of -OH and -NH groups at 3438.26 cm<sup>-1</sup>. Meanwhile, a C = C aromatic bond present at 1480.43 cm<sup>-1</sup>. XRD analysis shows some broaden peaks due to the amorphous phase of the prepared material. The prepared material is a brownish yellow solid, odorless and porous. The melting point, surface area, and the average pore radius are above 300 °C, 9.42 m<sup>2</sup> / g, and 52.5938 Å, respectively.

## 1. Introduction

Chitosan has been widely used as an adsorbent because of its ability to bind metal ions and the possibility of relatively easy retrieval of metal ions bound to chitosan by using a particular solvent. The advantage of chitosan is its ability for multi handling absorption [1]. However, Chitosan is highly soluble in a particular solvent such as acid. It could be a weakness due to its low stability. Therefore, to improve the quality of chitosan by modifying chitosan is required in order to reduce solubility in a liquid waste. Because a liquid waste may have various pH condition, therefore chitosan must be modified to become a material with low soluble property even under acidic condition, and the modified chitosan will have ability to be used as adsorbent. A study conducted by Meriatna in 2008 [2] found that the metal wastewater of metallic coating industry has a pH of 5 that still does not meet the quality standards permitted by the Government pursuant to under KEP-51/MENLH/10/1995. In addition, Research on the utilization of chitosan has always improved both in pure chitosan and chitosan modified, primarily in its application as heavy metal adsorbents. Types of chitosan form as adsorbents in flakes [3-4] and powder [5-6], while modified chitosan forms of crosslinked chitosan [6-7].



Increasing the ability of chitosan as adsorbent can be done through cross-linking method, binding crown ether compounds as cross-linker, or cross-connecting of chitosan with calix[4]arene to form a chelate polymers [8-9]. Chitosan modification can also be carried out by binding the cross-linking of macromolecular crown ether compounds to chitosan as has been done by Tabakci and Yilmaz (2008) [10] by cross-connecting between chitosan and calix[4]arene to form chelate polymers. Other modification of chitosan was performed with calix [4] crown by Xiaoting [11] and with calix[4]resorsinarene by Jumina [12].

Modification of calixarene such as by add carboxyl groups to all four hydroxyl group in the p-t-butylcalix[4]arene compounds. This modification will produce p-t-butyl calix[4]arene acid that can be used as a phosphate ion adsorbent [13]. Our previous research on chitosan modification was to attach a macromolecule compound of p-t-butylcalix[4]arene to the chitosan molecules [14]. The produced material was used as adsorbent for Remazol Yellow FG [15], Procion Red MX 8B [16], and also Cd ions [17].

This study aims to synthesize chitosan-p-t-butylcalix[4]arene acid by binding p-t-butylcalix[4]arene acid to chitosan with DIC as a coupling agent, to analyze the structure of the prepare material and also to characterize its properties. The presence of acidic groups in the produced compound is expected to increase the adsorption capacity even larger than our previous research[14].

## 2. Experimental

### 2.1. Ingredients:

All chemical used in this reaseach were procured from E. Merck except special ones, Chitosan (PT Biotech Surindo) and , DIC, Dichloromethane, HCl 37%, Methanol, Ethanol, Chloroform, NaOH Gas N<sub>2</sub> (PT Samator Gas), p-t-butylcalix[4]arene [14].

### 2.2. Instruments:

X-Ray Diffraction (XRD) type Bruker D8, Fourier Transform Infra Red (FT-IR, Shimadzu type FT-IR-8201 PC), Surface Area Analyzer (SAA) Quantachrome Nova 1200e, Scanning Electron Microscopy (SEM, Inspect-S50 EDAX)

### 2.3. Procedure:

2.3.1. *Characterization of chitosan.* Characterization of chitosan was done by determining ash content (ASTM Standard E, 1755) and deacetylation degree by baseline method formulated by Baxter et al. [18].

2.3.2. *Synthesis of p-t-calix[4]arene acid.* A total of 50 mL of dry acetone was added to a round bottom flask containing 0.16 g (0.25 mmol) p-t-butylcalix[4]arene, 0.29 g (2.35 mmol) of chloroacetic acid, 0.36 g (2, 35 mmol) NaI and 0.43 g (3.25 mmol) of K<sub>2</sub>CO<sub>3</sub>. The mixture was refluxed for 24 hours at a temperature of 60 °C and after that the mixture was filtered. The filtrate was then evaporated at room temperature and obtained crystals.

2.3.3. *Synthesis of chitosan-p-t-calix[4]arene acid.* The p-t-calix[4]arene acid (0.60 mmol; 0.38 gram), chitosan (0.55 gram), DIC coupling agent (1.30 mmol; 0.20 mL) and dichloromethane (20 mL) were pour into a flask and stirred at room temperature for 3 x 24 hours under atmospheric nitrogen conditions. Then, the mixture was cooled, filtered and washed successively with dichloromethane and methanol three times. The product was dried at 45 °C for 3 hours and stored in the desiccator. Structural analysis was performed by FTIR Shimadzu type FT-IR-8201 PC) and XRD (brand and specification). Those both analysis is important to investigate whether the functional groups and the diffraction pattern are matched well with the targeted compound. Meanwhile, the material characterization was conducted to investigate the specific

surface by SAA analysis, the surface morphology through SEM (SEM, Inspect-S50 EDAX) analysis, and also the solubility of compound by conducting a solubility test. The solubility test was carried out with a solution at various pH of 2, 4, 6, 8 and 10.

### 3. Results And Discussion

#### 3.1. Characterization of chitosan

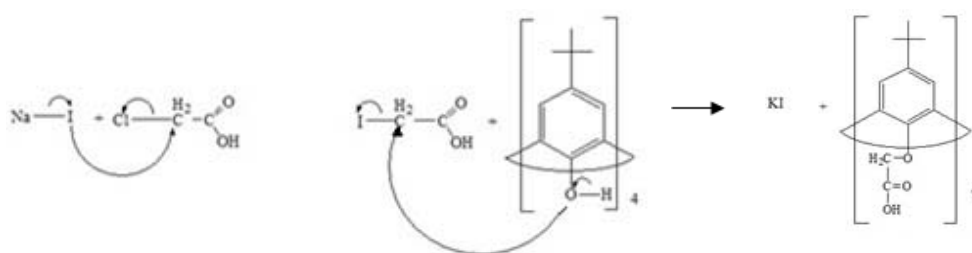
Characterization of chitosan was done by determining the degree of deacetylation and determining chitosan ash content. The chitosan characterization results are shown in Table 1.

**Table 1.** Results of Chitosan characterization

Description	Result
Form	Powder
Color	Brownish white
Smell	Odourless
Ash Content	1.07+0.27%
Degree of Deacetylation	89.93 /

#### 3.2 Synthesis of p-t-calix[4]arene acid

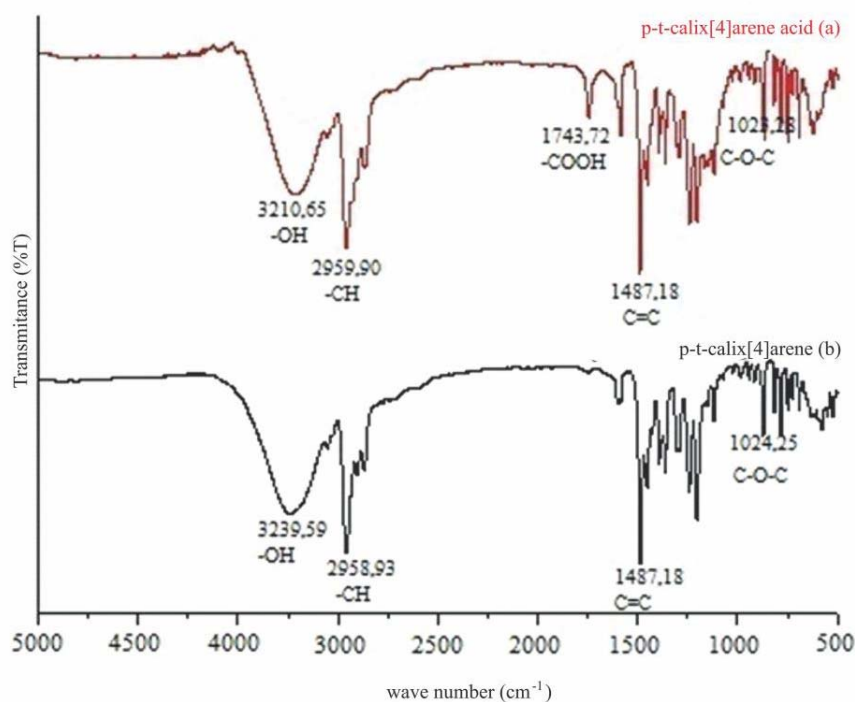
The carboxyl groups addition to p-t-calix[4]arene produced a white and odorless powder. The reaction occurred during synthesis was etherification reaction, in which the addition of the carboxyl group causes the formation of ether compound. The formation of ether lead to release some Cl atoms from chloroacetic acid and atom I from NaI. The  $\text{Na}^+$  atom is a very electropositive ion that can be binded to a highly electronegative Cl atom to produce NaCl. Chlor (Cl) atom of chloroacetic acid is replaced by atom I of NaI. The addition of a  $\text{K}_2\text{CO}_3$  base caused the proton to escape from p-t-calix[4]arene, and also caused I atom to be detached and reacted with K to form KI. The residual chloro acetic acid having a positive partial C atom then attacked the negative partial O at p-t-calix[4]arene to enter the carboxyl group. The description on reaction mechanism is depicted in Figure 1.



**Figure 1.** Mechanism of the synthesis reaction of p-t-calix[4]arene acid

The success of synthesis can be known by analyzing the structure of p-t-calix[4]arene acid using FTIR as shown in Figure 2. in the spectrum shows a sharp absorbance at  $3210.65\text{ cm}^{-1}$  refers to -OH adsorption of carboxylic acids. The absorption indicates that the -OH group was in considerable amount. A peak at  $1087.28\text{ cm}^{-1}$  is a typical C-O-C-ether absorbance. The adsorption of the -COOH group peak at  $1743.72$

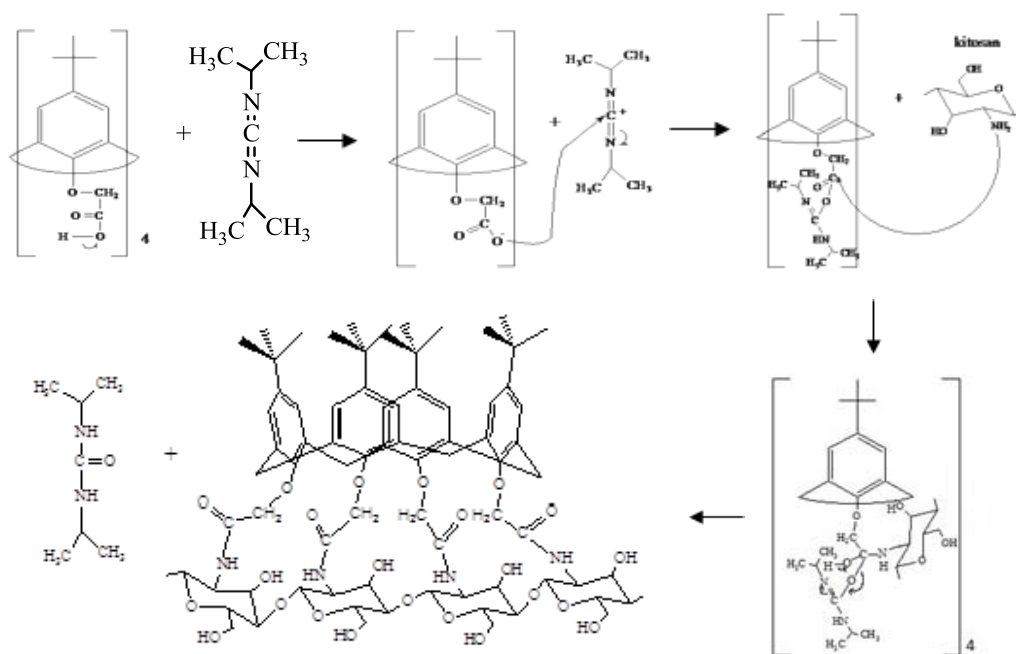
$\text{cm}^{-1}$  indicates the presence of carboxylic acid group in the chloro acetic acid compound. Meanwhile, the presence of the aromatics  $\text{C}=\text{C}$  groups is shown by absorbance at  $1487.18\text{ cm}^{-1}$ .



**Figure 2.** FTIR spectra of p-t-calix[4]arene acid (a) and p-t-calix[4]arene (b)

### 3.3 Synthesis of chitosan-p-t-calix[4]arene acid.

Synthesis of chitosan-p-t-calix[4]arene acid was using DIC as a coupling agent. According to Han and Young-Ah Kim (2004) N, N'-diisopropylcarbodiimide (DIC) is a linear carbodiimide compound that will easily bind two organic compounds [19]. The reaction was carried out at room temperature under atmospheric nitrogen to avoid side reactions with oxygen. The binding process of chitosan with p-t-calix[4]arene acid occurred through a substitution reaction with DIC as an intermediate agent and will reform at the end of the reaction. The resulting compound of the synthesis was a brownish yellow solid, odorless and has a yield of 67.29%. Possible reactions are shown in Figure 3.

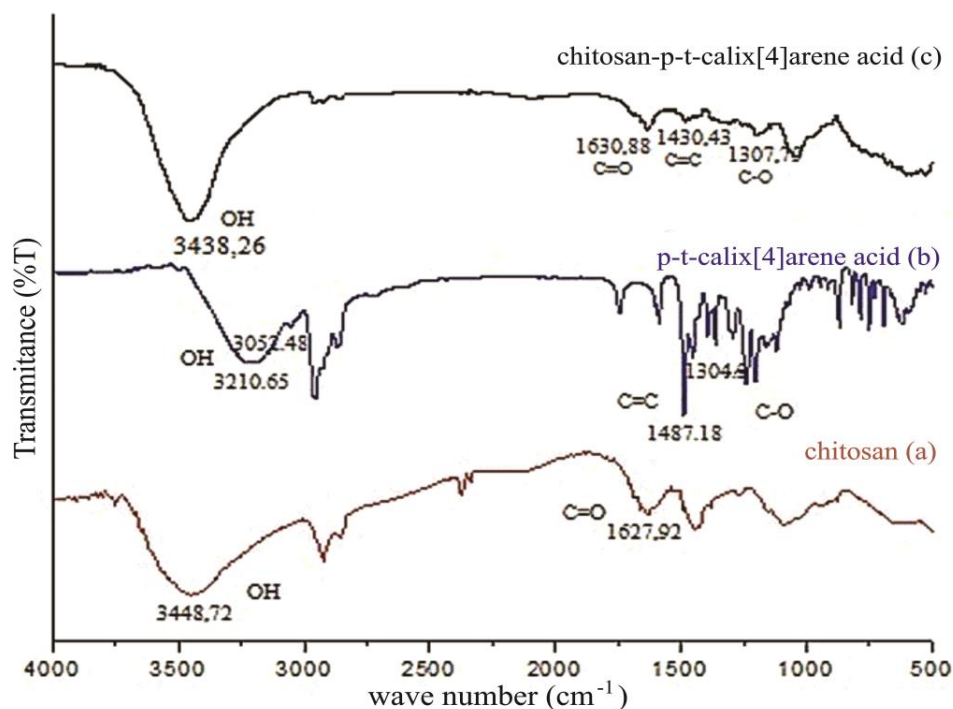


chitosan with p-t-calix[4]arene acid

**Figure 3.** Possible reaction of binding chitosan with p-t-calix[4]arene acid

The reaction mechanism as described in Figure 3 is as follows at first, there is a proton release on the hydroxyl group present in the p p-t-calix[4]arene acid, irrespective of  $H^+$  thus causing a partially negative charged O atom. One of  $C = N$  on the DIC coupling agent is cut off into a single bond resulting in a carbocation. Atom O of p-t-calix[4]arene acid a partially negative arena attacks the carbocation of the DIC coupling agent. The bonding results between p-t-calix[4]arene acid with DIC will then react with the  $NH_2$  group of chitosan through nucleophilic substitution. Atom N on chitosan has a lone pair electron that is nucleophile and will attack the carbocation. The result of a nucleophile attack to a carbocation produces a secondary amine by releasing a DIC coupling compound.

Analysis structure of the synthesis of p-t-butylcalix[4]arene acid using FTIR obtained spectra shown in Figure 4, while functional group analysis is shown in Table 2.

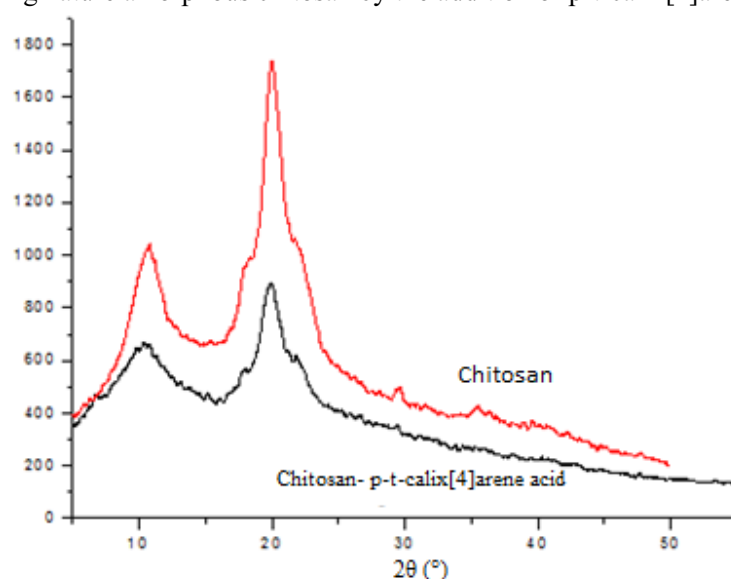


**Figure 4.** Spectra of chitosan (a), p-t-calix[4]arene acid (b) and chitosan-p-t-calix[4]arene acid (c)

**Table 2.** Analysis functional group of chitosan-p-t-calix[4]arene acid synthesis

Wave number (cm <sup>-1</sup> )			Functional group
Chitosan	p-t-calix[4]arene acid	Chitosan-p-t-calix[4]arene acid	
3448.72	-	3438.26	$\nu$ -NH
-	3210.65	-	$\nu$ Hydroxy -OH
-	3052.48	-	$\nu$ -CH stretching aromatic (sp <sup>2</sup> )
2924.09	2959.90	2926.14; 2957.93	$\nu$ -CH stretching asymmetric (sp <sup>3</sup> )
2854.65	2867.31	2855.73	$\nu$ -CH stretching symmetric (sp <sup>3</sup> )
1627.92	-	1630.88; 1697.43	$\nu$ C=O, N Acetyl (-NHCOCH <sub>3</sub> )
-	1487.18	1480.43	$\nu$ C=C aromatic
1442.75; 1381.03	1452.46; 1361.8	1381.09; 1437.99	$\nu$ -CH Bending symmetrically (sp <sup>3</sup> )
-	1304.9	1307.79	$\nu$ -CH stretching
1026.13	1023.28	1038.71	$\nu$ C-N

The XRD analysis was conducted at  $2\theta = 5^\circ$ - $50^\circ$ . The result of diffractogram obtained was shown in Figure 5. Based on the diffraction pattern obtained, no new diffraction pattern appeared in the Chitosan-p-t-calix[4]arene acid. Change only occurs in intensity. The change of intensity occurs both chitosan peaks of  $10^\circ$  and  $20^\circ$  where at  $2\theta = 10^\circ$  there was a change of intensity from 1040 to 667 and at  $2\theta = 20^\circ$  there is a change of intensity from 1733 to 898. It can be assumed a considerable decrease in intensity indicates that there is an increasing nature amorphous chitosan by the addition of p-t-calix[4]arene acid.



**Figure 5.** Diffractogram of chitosan and Chitosan-p-t-calix[4]arene acid

The p-t-calix[4]arene had a melting point of  $342$ - $344^\circ\text{C}$  [20] whereas its derivatives in the form of p-t-calix[4]arene acid had a melting point of  $292$ - $293^\circ\text{C}$  [13]. The result of the measurements shows a chitosan- p-t-calix[4]arene acid of more than  $300^\circ\text{C}$ .

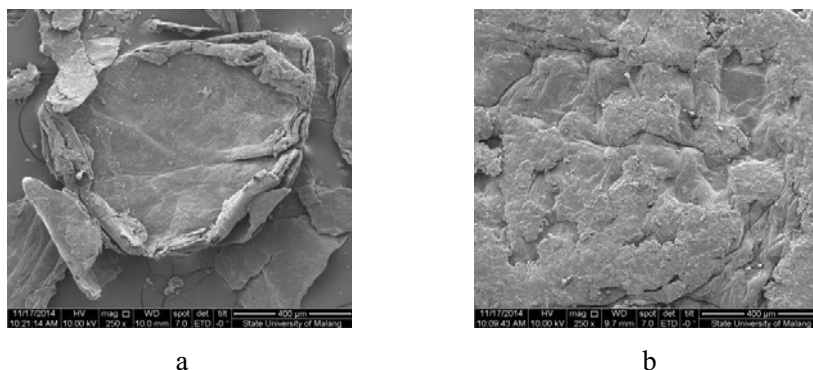
Surface analysis to determine the specific area as well as the pore distribution of chitosan-p-t-butylcalix[4]arene acid with SAA (Surface Area Analyzer). The results of SAA testing are shown in Table 3. The increased surface area of the modified chitosan is due to the presence of an active group of p-t-butylcalix[4]arene acid binding to chitosan.

**Table 3.** Analysis SAA of Chitosan and chitosan-p-t-butylcalix[4]arene acid

Parameter	Chitosan	chitosan-p-t-butylcalix[4]arene acid
Surface area	$6.42\text{ m}^2/\text{g}$	$9.42\text{ m}^2/\text{g}$
Total pore volume	$1.423 \times 10^{-2}\text{ cc/g}$	$2.478 \times 10^{-2}\text{ cc/g}$
Average pore radius	$44.3001\text{ \AA}$	$52.5931\text{ \AA}$

Analysis of surface morphology was done with SEM. The results of analysis using SEM shown chitosan-p-t-butylcalix[4]arene had porous surface morphology as shown in figure 6.





**Figure 6.** Morphology of (a) Chitosan and (b) Chitosan-p-t-butylcalix[4]arene

#### 4. Conclusion

The synthesis of chitosan-p-t-butylcalix[4]arene acid can be conducted with DIC as a coupling agent. The product obtained is a powder with melting point above 300 °C, surface area of 9.42 m<sup>2</sup> / g and an average pore radius of 52.5938 Å.

#### Acknowledgment

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