

## Modification and Characterization of a New Polymer Chitosan-p-t-butylcalix[4]arenes

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### Abstract

Modification of chitosan by p-t-butylcalix[4]arenes has been conducted using a nucleophilic substitution reaction between chitosan, p-t-butylcalix[4]arenes and N,N-diisopropyl carbodiimide (DIC) in reagent dichlorometane at room temperature and under nitrogen atmosphere. Analysis structure of the chitosan-p-t-butylcalix[4]arenes is determined with spectrophotometer Fourier Transform Infra Red (FTIR) and X-ray diffraction. The melting point, surface area and morphological analysis are also conducted on the prepared materials. The prepared chitosan-p-t-butylcalix[4]arenes is white brown powder with melting point of 238 °C. The FTIR spectrum shows a peak at 3346.50 cm<sup>-1</sup> that indicates the presence of the N-H bonds of secondary amine. The diffraction patterns shows the presence of charge and shift in 2θ. It indicates that the modification proceed successfully. The result of surface area analysis shows that chitosan-p-t-butylcalix[4]arenes is macroporous material with average of pore radius of 673.6 Å and the surface area of 16.352 m<sup>2</sup>/g. SEM analysis shows that chitosan-p-t-butylcalix[4]arenes also confirm that the materials has porous surface.

*Key words:* modification of chitosan, polymer, p-t-butylcalix[4]arene

### 1. Introduction

Chitin waste is not optimally utilized at recent. Chitosan is the main derivative of chitin obtained by deacetylation process. Deacetylation proces aims to remove acetyl groups from chitin by heating in a high concentrate alkaline solution<sup>1</sup>. The elimination of acetyl groups during deacetylation process allows production of a free amino group which causes the chitosan to be polycationic<sup>2</sup>. Chitosan can be used as adsorbent<sup>3</sup>, removal of metal ions Cd, Cu and Zn in water<sup>4</sup> and drug delivery systems<sup>5</sup>. Increased ability of chitosan can be done with modify the chitosan.

A modification through crosslinking chitosan with p-t-butylcalixarenes is an alternative to increase the performance of chitosan. Modification of chitosan with calixarene has been done by Tabakchi and Mustafa<sup>6</sup> who synthesize compound of Calix[4]arenes (p-t-butylcalix[4]arenes with the group dinitrile mono-carboxylate)-based chitosan. The modified material is

used to adsorb some heavy metal cations such as Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup> and Pb<sup>2+</sup> and dichromate anions. Meanwhile, Li et al.<sup>7</sup> synthesized calixarene linked to chitosan and found that the adsorption capacity of the Ag<sup>+</sup> and Hg<sup>2+</sup> are higher than chitosan without calixarene. p-t-butylcalix[4]arenes compound is a calixarene compound which is derived from phenol and it is known as the best host molecule after cyclodextrin and crown ether that can be applied broadly. p-t-butylcalix[4]arenes compounds have been synthesized by single phase with induced base using with the main material from derived phenolic compounds, aldehydes and base catalyst<sup>9</sup>.

This research was conducted to synthesize p-t-butylcalix[4]arenes using optocoupler DIC in modifying chitosan. Based on the structure p-t-butylcalix[4]arenes that are hollow and high selectivity towards metal ions, it is expected that the polymer chitosan-p-t-butylcalix[4]arenes have high adsorption capacity towards heavy metal waste.

## 2. Experiment

### 2.1 Materials

The materials used were p-t-butylcalix[4]arenes [9], crab shell chitosan (LIPI), sodium hydroxide (Merck), DIC (Merck), hydrochloric acid pa (Merck), acetic acid pa (Merck), nitrogen gas (PT Samator gas), dichloromethane pa (Merck), methanol pa (Merck), and whatman filter paper 42 (Merck).

### 2.2. Instrumentation

Fourier Transform Infra Red (FTIR) Prestige-21 Shimadzu, X-Ray Diffractometer (XRD) Bruker D8, Surface Area Analyzer (SAA) Quantachrome Nova 1200e and Scanning Electron Microscopy (SEM) Jeol JSM 6360.

### 2.3. Procedure

#### 2.3.1. Redeacetylation of chitosan

Chitosan was added by a solution of 45% NaOH in flask with ratio of 10: 1 (v/w) and then heated 120°C for 30 minutes. Once cooled, filtered and washed with distilled water and then dried in an oven at 60°C for 24 hours. Analysis of the synthesis using infrared spectroscopy in the wave number region of 4000-400  $\text{cm}^{-1}$ .

#### 2.3.2. Synthesis of Chitosan- p-t-butylcalix[4]arenes

p-t-butylcalix[4]arene compounds (2.3 mmol), chitosan (1.22 mmol), DIC optocoupler agent (2.4 mmol) and dichloromethane (50 mL) was included in the flask and stirred at room temperature for 3 days under nitrogen atmospheric. The mixture was cooled, filtered and washed successively with dichloromethane, methanol, HCl solution and distilled water three times. Product is dried at 45°C for 3h and stored in a desiccator. Products obtained was structure analysis by FTIR and XRD and determine the melting point.

#### 2.3.3. Characterization

Characterization of modified chitosan-p-t-butylcalix [4] arenes performed with SEM and SAA.

## 3. Result and Discussion

### 3.1. Modification of chitosan with p-t-butylcalix-[4]arenes

Redeacetylation process of chitosan compound was successfully performed by reacting chitosan with concentrated alkaline solution of NaOH 45% (v/w). It produce 85.97 % of redeacetylation chitosan

FTIR spectrum shows that disappearance at 1606  $\text{cm}^{-1}$  which is identified as C=O stretching. The loss of absorption in 1606  $\text{cm}^{-1}$  which is accompanied by the appearance of new absorption at 1597  $\text{cm}^{-1}$  indicate the presence of -NH bending for vibration of  $\text{NH}_2$ . It shows that the acetyl group peaks were separated from amine group ( $\text{NH}_2$ ). It indicates the increasing degree of deacetylation. FTIR spectra of chitosan before redeacetylation and after redeacetylation can be seen in Figure 1.

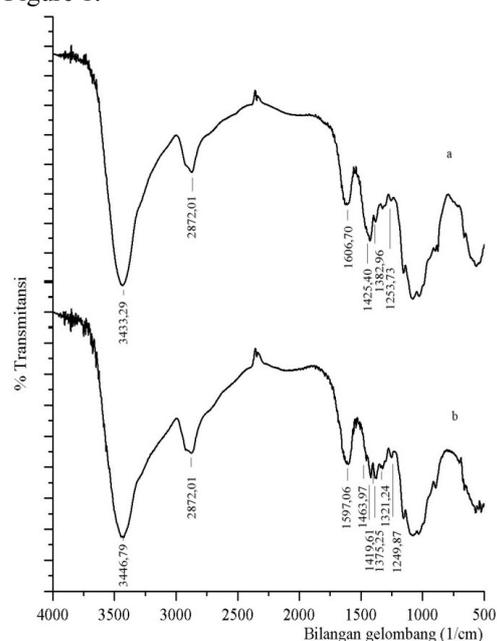


Fig 1. FTIR spectra of chitosan (a) before redeasetilasi (b) after redeasetilasi

The process of redeacetylation chitosan was done by hydrolysis reaction<sup>9</sup>. NaOH solution decomposes into  $\text{Na}^+$  and  $\text{OH}^-$  ions. The presence of oxygen and hydroxyl ions did not initiate rupture of glycoside bond but prefer to attack the electropositive charged carbonyl carbon to produce a primary amine group and by products such as sodium acetate. Redeacetylation of chitosan hydrolysis reaction under alkaline conditions is shown in Figure 2.

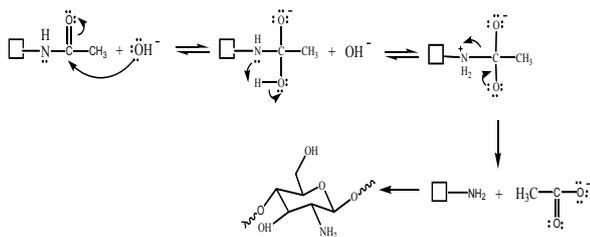


Fig 2. Mechanism reaction of redeacetylation chitosan [3]

Determination of deacetylation degree of chitosan was conducted by using baseline b according to formulation of Baxter<sup>11</sup>. The deacetylation degree of chitosan after redeacetylation process increase from 91.76% to 94.04%. It indicates that the redeacetylation process was proceed succesfully. Chitosan which has a high degree of deacetylation will increase the qualityof the chitosan.

Modification of chitosan with pt-butylcalix[4]arenes produce chitosan-p-t-butylcalix-[4]arenes in the form of brownish white powder with a melting point of 238 °C and a yield of 93.383%. This compound was synthesized using a solvent of dichloromethane at room temperature and under nitrogen atmospheric conditions. Drainage of nitrogen gas is used to expel water vapor or other gases that may interfere the reaction.

Based on the FTIR spectra can be acquired information regarding the functional groups. FTIR spectra are shown in Figure 3 can be interpreted that there is absorption at 3419 cm<sup>-1</sup> which indicates the presence of OH group absorption. OH group is derived from chitosan which has been bound to the pt-butylcalix[4]arenes. Absorption at 3346 cm<sup>-1</sup> indicates the presence of a secondary amine NH bond. This is reinforced by the loss of uptake of primary amine NH vibration at 1597 cm<sup>-1</sup> accompanied by the appearance of the amide II vibration at 1624 cm<sup>-1</sup>. FTIR spectra of the compound chitosan modified chitosan-p-t-butylcalix[4]arenes are shown in Figure 3.

The shift and the emergence uptake of p-t-butylcalix[4]arenes and chitosan in chitosan- p-t-butylcalix[4]arenes spectra showthat the synthesis of modified chitosan compounds have been successfully. Indications of changes in the structure of the compound marked on the XRD diffractogram shown in Figure 4.

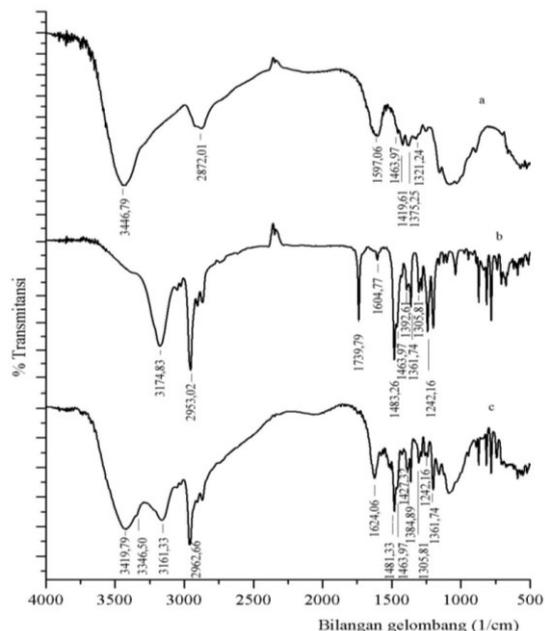


Fig 3. FTIR spectra of (a) chitosan, (b) p-t-butylcalix-[4]arenes (c) chitosan-p-t-butylcalix[4]arenes.

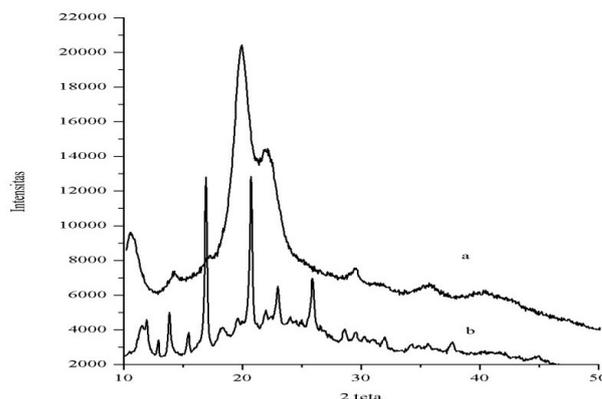


Fig 4. XRD diffractogram of (a) chitosan and (b) chitosan-p-t-butylcalix[4]arenes

Compounds synthesized chitosan-p-t-butylcalix-[4]arenes have high peaks at 2θ ie 16.9353 ° and 20.7386 ° while the peak of chitosan at 2θ 10,4027°, 19,7542° and 21.9466 °. The results of XRD diffractogram of chitosan-p-t-butylcalix[4]arenes and chitosan obtained at 2θ shifting and the icreasing of intensity. The shift in 2θ of chitosan-p-t-butylcalix[4]arenes which was caused by deformation of strong hydrogen bonds to the back-bone chitosan-p-t-butylcalix[4]arenes in the amino group or hydroxyl replaced by p-t-butylcalix[4]arenes. X-ray diffraction patterns of chitosan-p-t-butylcalix[4]arenes have similar diffraction patterns, and there has been a shift in the

pattern at 2θ. It indicates that the synthesized compounds have been modified from the initial compounds. Binding reaction of chitosan compounds on p-t-butylcalix[4]arenes can be seen in Figure 5.

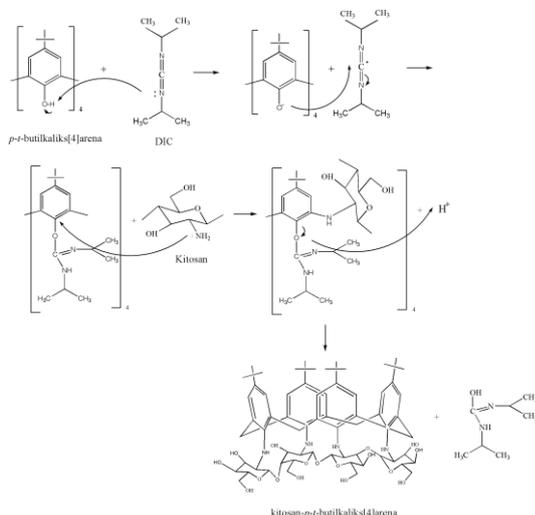


Fig. 5 Reaction formation of chitosan- p-t-butylcalix-[4]arenes

The presence of reactive groups on the chitosan amino groups, primary and secondary of hydroxyl groups causes of chitosan is alkaline, while the p-t-butylcalix[4]arenes are reactive OH groups on the lower rim cause p-t-butylcalix[4]arenes tends to be acidic so it can react by nucleophilic substitution reaction. Reactive groups of chitosan contribute to catch the phenolic groups, ie the proton on the hydroxy group of p-t-butylcalix[4]arenes which are acidic. Hydroxyl group of p-t-butylcalix[4]arenes will react with DIC group coupler agent to form intermediates. Then it reacts with the reactive groups of chitosan to form a secondary amine to remove the DIC cluster.

### 3.1. Characterization of chitosan-p-t-butylcalix-[4]arenes

Character of the compounds synthesized can be determined by physical testing. One of them is by determining the melting point test. Melting point tests performed using the melting point. The melting point of the compounds synthesized chitosan- p-t-butylcalix[4]arenes, p-t-butylcalix[4]arenes and chitosan, respectively, are 238°C, >300°C and 220°C. The melting point modified chitosan- p-t-butylcalix[4]arenes is between the melting point p-t-

butylcalix[4]arenes (over 300°C) and chitosan (220°C) was 238°C.

Specific surface area and pore distribution of the polymer chitosan-p-t-butylcalix[4]arenes were characterized using Surface Area Analyzer (SAA). The method used was BET method (Brunauer, Emmett and Teller) by physical adsorption analysis model using N<sub>2</sub> as adsorbate (molecular weight 28,013 g) at a temperature of 77.350 K and the cross section of 16.200 Å. BET method used is based on adsorption process that takes place in a multilayer. SAA data analysis results are presented in Table 1.

Table 1. Data Analysis SAA Chitosan-pt-butylcalix[4] arenas parameters

parameters	Value
Surface Area	16,352 m <sup>2</sup> /g
Total pore volume	0,5507 cc/g
	(r < 1014,5 Å (radius) P/Po = 0,99046)
Average pore radius	673,6 Å

Specific surface area of the polymer chitosan- p-t-butylcalix[4]arenes larger than the specific surface area of chitosan from the previous research studies (13,5m<sup>2</sup>/g)<sup>12</sup>. The larger the specific surface area will increase the ability of the adsorbent to absorb more adsorbate occurs so that the adsorption more effective. Results p-t-butylcalix[4]arenes compounds linked to the chitosan has a large specific surface area, so the potential both as an adsorbent which has a high adsorption capacity.

The morphology of the polymer synthesized chitosan- p-t-butylcalix[4]arenes characterized using Scanning Electron Microscopy (SEM) as shown in Figure 6.

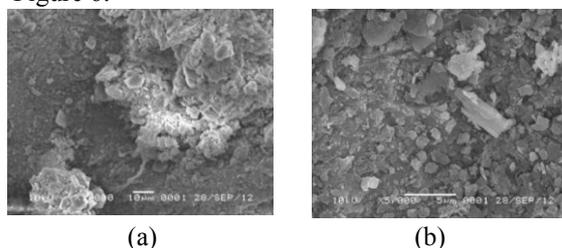


Fig 6. SEM results of Chitosan- p-t-butylcalix[4]arenes (a) Magnification 1000x and (b) Magnification 5000X

The morphology The morphology of the polymer chitosan-p-t-butylcalix[4]arenes as seen on micrographic results showed that the porous polymer, as expected. This is supported by the results of the analysis of SAA in the form of surface area, total pore volume and pore radius which proves that the compound chitosan-p-t-butylcalix[4]arenes are porous.

#### 4. Conclusion

Chitosan-p-t-butylcalix[4]arenes synthesized by nucleophilic substitution reaction between chitosan, p-t-butylcalix[4]arenes and DIC as coupler agents. Modified product form of brownish white powder with a yield of 93.383%. The modified character has a melting point of 238 ° C, the surface area of 16,352 m<sup>2</sup>/g and the material is porous material.

#### 5. Acknowledgement

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#### References

1. Yunizal, 2001. Ekstraksi Khitosan dari Kepala Udang Putih (*Penaeus Merquensis*). *J. Agric*, vol. 21 (3), hal. 113-117
2. Emma R., M. T. Suhartono., Dahrul S. dan Sugiyono, 2004. Karakterisasi Kitosan Hasil Deasetilasi Enzimatis oleh Kitin Deasetilasi Isolat Bacillus Papandayan K29-14
3. Rakhmawati, E., 2007. *Pemanfaata Kitosan Hasil Deasetilasi Kitin Cangkang Bekicot sebagai Adsorben Zat Warna Remazol Yellow*. Skripsi. FMIPA, Universitas SebelasMaret, Surakarta
4. Bhumkar, D. R. dan Varsha, B. P., 2006. Studies on Effect of pH on Cross-linking of Chitosan with Sodium Tripolyphosphate. *AAPS Pharmasci. Tech.* 7(2), 50
5. Mourya, V. K., Nazma, N. I., danAsthutosh T., 2010. Carboxymethyl Chitosan and its Applications. *Adv. Mat. Lett.* 1(1), hal. 11-33
6. Tabakci, M. dan Mustafa, Y., 2008. Synthesis of a Chitosan-linked Calix[4]arene chelating Polymer and its Sorption Ability Toward Heavy Metals and Dichromate Anions. *Bioresource Technol*, hal. 6642-6645. Elsevier
7. Li, H., Yuan-Yin C. dan Shi-Lan L., 2003. Synthesis, Characterization and Metal Ions Adsorption Properties of Chitosan-Calixarene (1). *J. Appl. Polym. Sci.* Vol. 89, Issue 4, hal. 1139-1144. Willey
8. Gutsche, C. D., 1998. *Calixarene Revisited*. Monograph in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge
9. Handayani, D. S., 2011. *Sintesis Poli-5-Allilkaliks[4]arena dan Turunan Ester Serta Asam Karboksilatnya Sebagai Adsorben dan Antidotum Keracunan Logam Berat*. Disertasi. Universitas Gajah Mada. Yogyakarta
10. Solomon, T. W. G. dan Craig B. F., 2011. *Organic Chemistry*. Tenth Edition. John Willey & Sons, Inc
11. Khan, T. A., Kok, K. P. dan Hung S. C., 2002. Reporting Degree of Deacetylation Value of Chitosan: The Influence of Analytical Methods. *J. Pharm. Sci.* Vol. 5(3), hal. 205-212
12. No, H. K., Lee, Shin H. L., Na Y. P., and Samuel P.M. 2000. Correlation Between Physicochemical Characteristics and Binding Capacities of Chitosan Products. *J. Food Sci.* Vol. 65, No.7, pp. 1134-1137