Synthesis and Characterization of Grafting β-Cyclodextrin with Chitosan

Xueyong Zhang, Yuting Wang, Ying Yi

College of Resource and Environmental Science, Wuhan University, 430072 Wuhan, Hubei, Peoples Republic of China

Received 11 September 2003; accepted 25 March 2004
DOI 10.1002/app.20759
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two new adsorbents [β-cyclodextrin–chitosan (β-CD–CTS) and β-cyclodextrin-6–chitosan (β-CD-6-CTS)] were synthesized by the reaction of β-cyclodextrin (β-CD) with epoxy-activated chitosan (CTS) and the sulfonation of the C-6 hydroxyl group of β-cyclodextrin with CTS, respectively. Their structures were confirmed by IR spectral analysis and X-ray diffraction analysis, and their apparent amount of grafting was determined by ultraviolet spectroscopy. The adsorption properties of β-CD-CTS and β-CD-6-CTS for *p*-dihydroxybenzene were studied. The experimental results showed that the two new adsorbents exerted adsorption on the carefully chosen target. The highest saturated capacity of *p*-dihydroxybenzene of β-CD-CTS and β-CD-6-CTS were 51.68 and 46.41 mg/g, respectively. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 860–864, 2004

Key words: chitosan; adsorption; β-Cyclodextrin

INTRODUCTION

Chitosan (CTS) is a polyaminosaccharide, which is normally obtained by the alkaline deacetylation of the natural mucopolysaccharide chitin and contains in its structure glucosamine and acetylglucosamine joined through β-D-(1–4) linkages. The availability of CTS in a variety of useful forms and its unique chemical and biological properties make it a very attractive biomaterial. It is extensively used in many types of applications, including the wastewater treatment,[1,2] adsorbents,[3,4] and drug-delivery systems.[5,6] In these applications, the key properties of CTS are biocompatibility, nontoxicity, and biodegradatibility.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of at least six glucopyranose linked together by 1,4 linkages to form torus-like structures.[7] CDs have received much attention because of their unique ability to form host–guest complexes with various organic compounds.[8] As a result of this unique property, CDs and their derivatives have been widely used in the food, cosmetic, and pharmaceutical industries.

CDs are water-soluble, cyclic oligosaccharides that can include various guest molecules into their hydrophobic cavity. CTS has the merits of adsorption and biocompatibility. Thus, grafting CD molecules into CTS may lead to a molecular carrier exhibiting promising properties because of the cumulative effects of size specificity and the transport properties of CDs.

Correspondence to: Y. Wang (hxxzls@whu.edu.cn).

Journal of Applied Polymer Science, Vol. 94, 860–864 (2004)

EXPERIMENTAL

Materials

CTS, whose degree of deacetylation was calculated to be 81.2% from amino content, was prepared by the *N*-deacetylation of chitin from shrimp shells and was used after passage through a 200-mesh sieve. Reagent-grade *p*-toluenesulfonyl chloride (TsCl) was recrystallized from petroleum ether and dried overnight *in vacuo* at 25°C. Reagent-grade β-CD was recrystallized from water and dried overnight *in vacuo* at 110°C. Reagent-grade pyridine was dried over sodium hydroxide and distilled. All of the solvents, inorganic and organic compounds, were reagent grade and were used without purification.

Measurements

IR spectra was obtained with a Shimadzu FTIR 8000 series spectrophotometer (Torrance, USA). Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera with nickel-filtered Cu Kα radiation produced by a Rigakn (D/MAX, 111A) diffractometer. A UV-9100 ultraviolet–visible (UV) spectrophotometer was used to measure the apparent quantity (Shanghai, China).

Preparation of β-cyclodextrin-6–chitosan (β-CD-6–CTS)

The reaction scheme for the synthesis of β-CD-6–CTS is shown in Figure 1.

Preparation of tosylated C-6β-cyclodextrin (β-CD-6-OTs) was conducted according to a procedure reported previously.[9] The yield of β-CD-6-OTs was 33%.

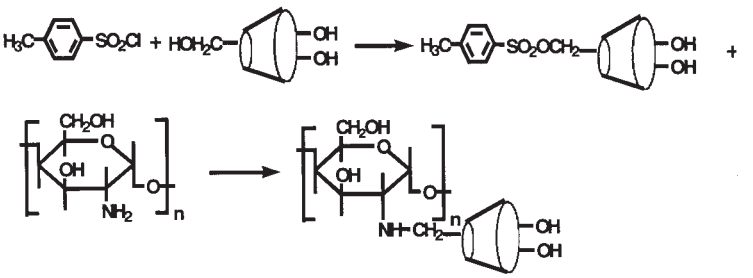

Figure 1 Reaction scheme for the synthesis of β-CD-6-CTS.

The experimental results showed that the structure of β-CD-6-OTs was as reported.

Powdered CTS was swelled in *N,N*-dimethylformamide; then, the β-CD-6-OTs was dissolved in DMF and slowly dropped into the CTS solution. The mixture was stirred for 48 h at 50°C, filtered, washed with water, and dried to give yellow β-CD-6–CTS. The apparent amount of grafting was 46.72 μmol/g.

Preparation of β-cyclodextrin–chitosan (β-CD–CTS)

The reaction scheme for the synthesis of β-CD–CTS is shown in Figure 2.

Preparation of schiff base epoxy-activated chitosan SBCTS was conducted according to the procedure reported previously.[10] The experimental results showed that the structure of the intermediate was as reported.

Epoxy-activated chitosan (EACTS) (1.5 g) was swelled in 80 mL of NaOH (0.1 mol/L); then, β-CD (2.0 g) was dissolved in 20 mL of NaOH (0.1 mol/L) and was slowly dropped into the intermediate solution. The mixture was stirred for 4 h at 60°C, filtered, washed with water, and dried to give yellow, solid β-CD-CTS. The apparent amount of grafting was 25.8 μmol/g.

Measurement of the apparent amount of grafting

Preparation of standard curve was conducted according to a procedure reported previously.[11] The method of measurement was conducted as follows: CTS grafting with β-CD (25 mg) was hydrolyzed in 15 mL of sulfuric acid (0.5 $molL^{-1}$) and stirred for 10 h at 100°C. The hydrolysate was gradually transferred to a measuring flask and diluted to 50 ml. The concentration of glucosyl was determined with a spectrometer at 490 nm and transformed to the apparent amount of grafting. The apparent amount of grafting (Q) was calculated as follows:

$$Q = \frac{C \times 50 \times 1000}{180 \times 7 \times W}$$

where C is the concentration of glucose (μg/mL), and W is the weight of β-CD-CTS or β-CD-6-CTS (mg).

Adsorption procedure for β-CD-6-CTS, β-CD-CTS, and CTS with *p*-dihydroxybenzene

The adsorption of *p*-dihydroxybenzene was performed by the immersion of a precisely weighed amount of CTS, β-CD-6-CTS, and β-CD-CTS in a *p*-

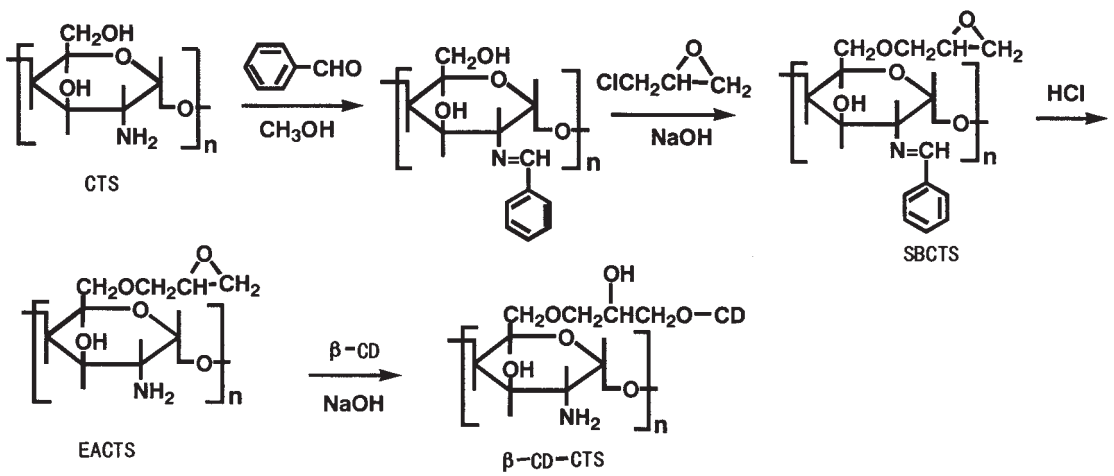

Figure 2 Reaction scheme for the synthesis of β-CD-CTS.

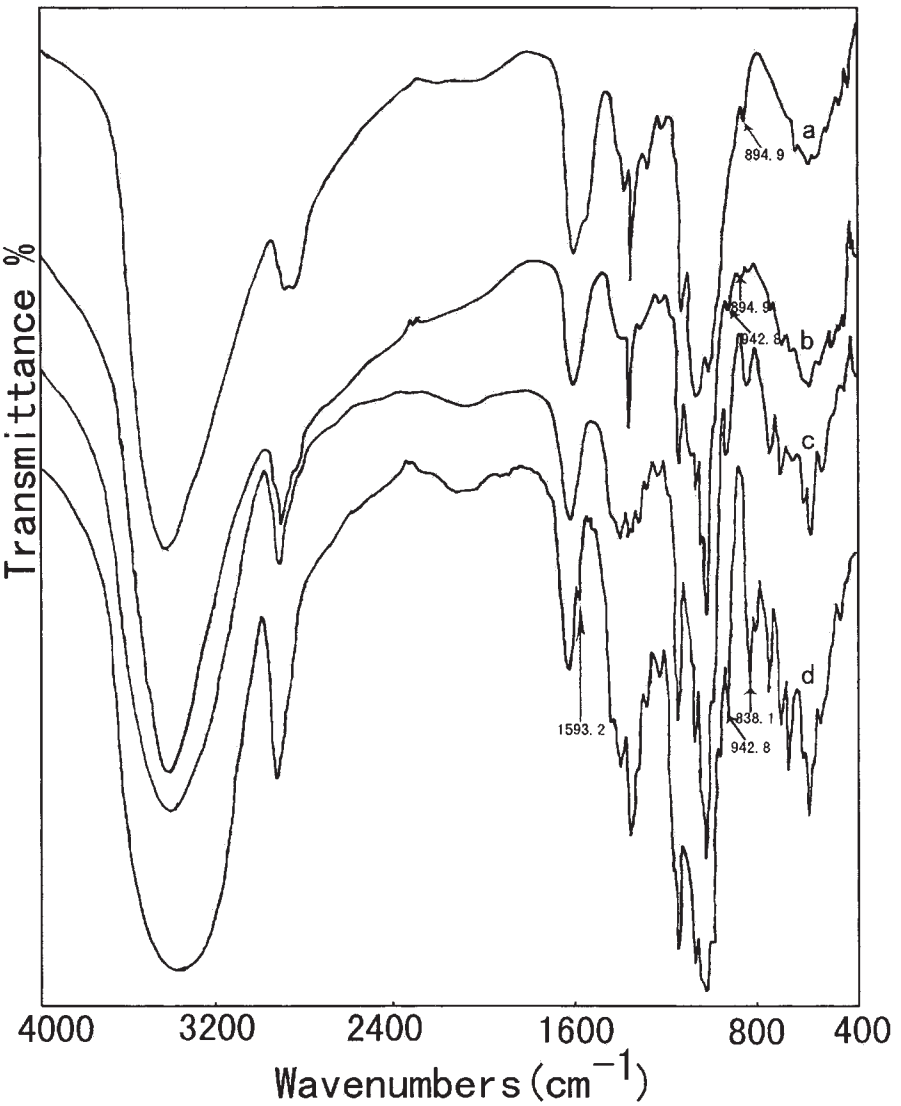

Figure 3 IR spectra of (a) CTS, (b) β-CD-6-CTS, (c) β-CD, and (d) β-CD-6-OTs.

dihydroxybenzene solution, which was shaken at 37°C. The concentration of the *p*-dihydroxybenzene solution at different times was determined at 288 nm. The adsorbed *p*-dihydroxybenzene by CTS, β-CD-6-CTS, or β-CD-CTS was calculated as follows:

$$Q = \frac{V(C_0 - C_1)}{W}$$

where V is the volume of the *p*-dihydroxybenzene solution (mL), C_0 is the initial concentration of *p*-dihydroxybenzene (mg/mL), C_1 is the the concentration of *p*-dihydroxybenzene solution after absorption (mg/mL), W is the weight of the adsorbent or CTS (mg), and Q the adsorbed *p*-dihydroxybenzene by the adsorbent or CTS (mg/g).

RESULTS AND DISCUSSION

IR spectral analysis of β-CD-6-CTS

The IR spectra of β-CD, CTS, β-CD-6-OTs, and β-CD-6-CTS are shown together in Figure 3.

In the IR spectra of β-CD-6-OTs, the characteristic peak of the α-pyranyl vibration of β-CD was at 942.8 cm^{-1}, the characteristic peak of the benzene ring vibration appeared at 1593.2 cm^{-1}, and the bending vibration of the benzene ring appeared at 838.1 and 814.8 cm^{-1}. This evidence indicated that β-CD had reacted with TsCl.

As both β-CD and CTS were carbohydrates, they had some similar groups. When β-CD grafted with CTS, the IR spectral peaks of most groups of β-CD were covered by the similar groups of CTS. So, the IR spectra of β-CD-6-CTS was similar to that of CTS.

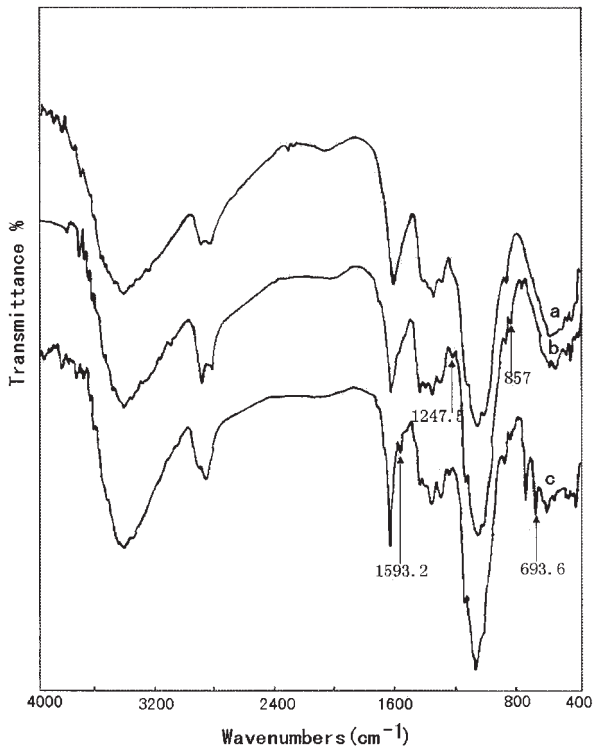

Figure 4 IR spectra of (a) β-CD-CTS, (b) EACTS, and (c) SBCTS.

However, the characteristic peak of the β-pyranyl vibration of CTS at 894.9 cm^{-1} and the characteristic peak of the α-pyranyl vibration of β-CD at 942.8 cm^{-1} both appeared in the IR spectra of β-CD-6-CTS. Further, the characteristic peak of the benzene ring backbone vibration (Ts groups of β-CD-6-OTs) at 1593.2 cm^{-1} and the bending vibration of the benzene ring (Ts groups of β-CD-6-OTs) at 838.1 cm^{-1} disappeared in the IR spectra of β-CD-6-CTS because the Ts groups removed by β-CD-6-OTs when β-CD-6-OTs was reacted with CTS. These data supported β-CD grafting with CTS.

IR spectral analysis of β-CD-CTS

The IR spectra of SBCTS, EACTS, and β-CD-CTS are shown together in Figure 4.

In the IR spectra of SBCTS, the characteristic peak of the benzene ring backbone vibration at 1593.2 cm^{-1} and the bending vibration of the benzene ring at 693.6 cm^{-1} disappeared in the IR spectra of EACTS, showing that phenyl aldehyde left SBCTS and formed EACTS.

In the IR spectra of EACTS, the characteristic peaks of the epoxy group were at 857 and 1247.5 cm^{-1}. These peaks disappeared in the IR spectra of β-CD-CTS because the epoxy group of EACTS reacted with β-CD. Furthermore, the peaks were strengthened from 2882 to 3388 cm^{-1}. These data supported β-CD grafting with EACTS.

X-ray diffraction pattern analysis of β-CD-6-CTS and β-CD-CTS

The X-ray diffraction patterns of β-CD-CTS and β-CD-6-CTS are shown together with that of CTS in Figure 5.

The WAXD pattern of CTS showed characteristic peaks at 2θ = 10, 20, and 28°. The peaks at 2θ = 10° and 28° disappeared, and the peak at 2θ = 20° decreased greatly in β-CD-6-CTS and β-CD-CTS. We thought that the decrease in the crystallinity of β-CD-6-CTS and β-CD-CTS was due to the deformation of the strong hydrogen bonds in the CTS backbone as the amino group reacted with the active group in β-CD-6-OTs or the epoxy group in the crosslinked CTS reacted with active hydroxyl in β-CD. Both derivatives gave low crystallinity, indicating that they were considerably more amorphous than CTS.

Inclusion or adsorption ability of β-CD-6-CTS or β-CD-CTS with *p*-dihydroxybenzene

Adsorption capacities of β-CD-CTS and β-CD-6-CTS

The highest saturated capacities of *p*-dihydroxybenzene of β-CD-CTS, CTS, and β-CD-6-CTS were 51.68, 31.64, and 46.41 mg/g, respectively.

The two graftings of CD molecules onto CTS resulted in higher adsorption capacities for *p*-dihydroxybenzene than that of CTS. This was due to the presence of β-cyclodextrin molecules, which allowed the inclusion of various guest molecules into their hydrophobic cavity, as compared to CTS.

Influence of the adsorption time on the adsorption capacity for *p*-dihydroxybenzene

The adsorption experimental results of β-CD-CTS and β-CD-6-CTS for *p*-dihydroxybenzene are shown together with that of CTS in Figure 6.

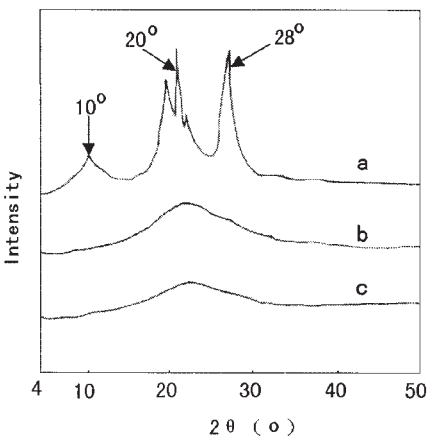

Figure 5 X-ray diffraction patterns and of (a) CTS, (b) β-CD-6-CTS, and (c) β-CD-CTS.

The adsorption velocities of β-CD-CTS and β-CD-6-CTS were the fastest within 2 h. The adsorption equilibria for *p*-dihydroxybenzene by β-CD-CTS and β-CD-6-CTS were 8 h, whereas the adsorption equilibrium for *p*-dihydroxybenzene by CTS was 4 h.

As also shown in Figure 6, the adsorption capacities of β-CD-CTS and β-CD-6-CTS had a maximum. The reason for this abnormal phenomena was that the adsorbent could adsorb solute and solvent in the solid–liquid phase. At the beginning, the concentration of solute decreased rapidly because adsorbent adsorbed solute at a greater velocity than it adsorbed solvent, which led to a dramatic increase the adsorption capacity.

When the adsorption of solute was approaching saturation, the adsorption velocity of solvent got much greater. Therefore, the concentration of solute increased comparatively in the solution, leading to a decrease in the adsorption capacity. When both the velocities equated, the concentration remained constant. That is, the adsorption capacity reached equilibrium.

Effect of the concentration of *p*-dihydroxybenzene

The experimental results indicated that the adsorption of *p*-dihydroxybenzene by polymeric adsorbents such as β-CD-CTS and β-CD-6-CTS were greatly affected by the increase in *p*-dihydroxybenzene concentration.

As shown in Figure 7, the adsorption capacity of *p*-dihydroxybenzene increased at the beginning with the *p*-dihydroxybenzene concentration. However, after the *p*-dihydroxybenzene concentration reached 200 mg/L, the adsorption capacity decreased. This was because the higher *p*-dihydroxybenzene concentration inhibited the diffusion of *p*-dihydroxybenzene into the adsorbent.

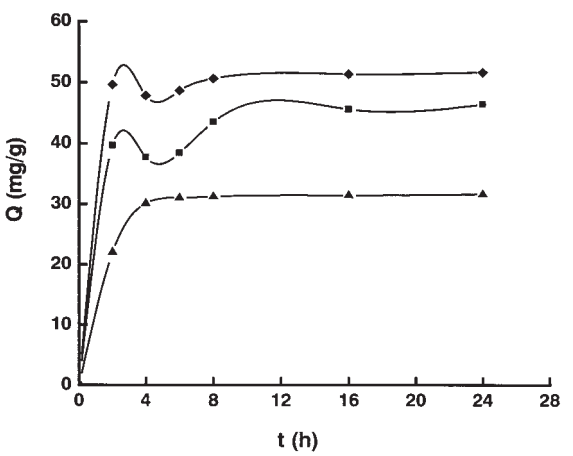

Figure 6 Influence of the adsorption time (*t*) on the adsorption capacity for *p*-dihydroxybenzene: (◆) β-CD-CTS, (■) β-CD-6-CTS, and (▲) CTS. Adsorption conditions: temperature = 37°C, *p*-dihydroxybenzeneconcentration = 0.2 mg/mL, time = 24 h, adsorption solution = 25 mL, and weight of dry adsorbent-50 mg.

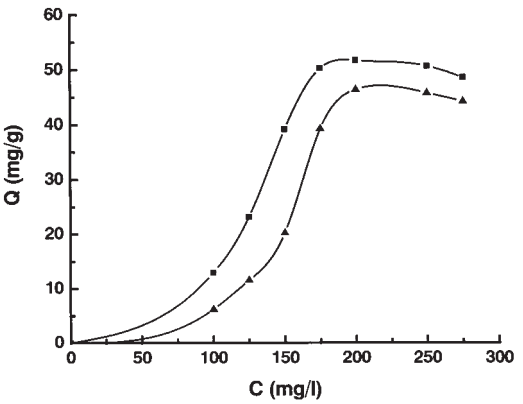

Figure 7 Influence of the concentration of *p*-dihydroxybenzene on the adsorption capacity for *p*-dihydroxybenzene: (■) β-CD-CTS and (▲) β-CD-6-CTS. Adsorption conditions: temperature = 37°C, time = 24 h; adsorption solution = 25 mL, and weight of dry adsorbent = 50 mg.

CONCLUSIONS

β-CD-CTS and β-CD-6-CTS were synthesized by the reaction of β-CD with EACTS and β-CD-6-OTs with CTS Structures were confirmed by IR spectral analysis and X-ray diffraction analysis. The apparent amount of grafting of them was determined by UV spectroscopy, and the experimental loadings were 46.72, 25.8 μmol/g, respectively. Because of the presence of β-cyclodextrin in crosslinked CTS and CTS, their adsorption capacities for *p*-dihydroxybenzene were higher than that of CTS. Therefore, we predicts that they could be applied in wastewater treatment.

References

1. Chang-Hong, P.; Yu-Ting, W.; Yu-Rong, T. Environ Chem 1998, 17, 349.
2. Nishiki, M.; Tojima, T.; Nishi, N. Carbohydr Lett 2000, 4, 61.
3. Sreenivasam, K. J Appl Polym Sci 1998, 69, 1031.
4. Yi-Hua, Y.; Bing-Lin, H. React Funct Polym 1999, 41, 191.
5. Lorenzo-Lamosa, M. L.; Remunan-Lopez, C J Controlled Release 1998, 52, 109.
6. Shanthe, K. L.; Harding, D. R. K. Int J Pharm 2000, 207, 65.
7. Christopher, J. E.; Stephen, F. L. Modified Cyclodextrins: Scaffolds and Templates for Supramolecular Chemistry; Imperial College Press: London, 1999.
8. Fujiwara, T.; Tanaka, M. N.; Kobayashi, S. Chem Lett 1990, 221, 739.
9. Raffaele, P. B.; Vincenzo C. Inorg Chem 1991, 30, 2708.
10. Chang-Hong, P.; Yu-Ting, W.; Yu-Rong, T. J Appl Polym Sci 1998, 70, 501.
11. Michel, D.; Gilles, K. A. Anal Chem 1956, 28, 350.