Sorption properties of β-cyclodextrin—citric acid derivatives.

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Keywords

cyclodextrin, citric acid, crosslinking, host-guest systems, sorbents.

Abstract

β-cyclodextrin—citric acid derivatives were synthesized trough heating of mixture of citric acid, cyclodextrin and Na_2HPO_4 as a catalyst. The degree of substitution of the derivatives was estimated by determination of citric acid by HPLC in the samples hydrolysates. Sorption properties of β-cyclodextrin—citric acid derivatives were determined using spectrophotometric method with methyl orange as a model sorbate. Sorption properties of β-cyclodextrin—citric acid derivatives were compared to native β-cyclodextrin.

Introduction

Cyclodextrins (CD) are cyclic oligosaccharides consisting of α-1,4-glycosidically linked D-glucose units (Fig.1). Cyclodextrin molecule has a hydrophobic inner cavity, contrasting with the two hydrophilic openings. A wide range of organic and non-organic molecules form host-guest inclusion complexes with cyclodextrins.[1] Moreover, formation of inclusion complexes is also a main mechanism of sorption by water insoluble CD polymers.[2] Recently, polycarboxylic acids, especially citric acid (CTR), have become a popular crosslinking agent able to

overcome toxicity and costs. CTR has been utilized to esterify or crosslink polysaccharides i.e. starch[3] or cellulose[4-6] as well as polyhydroxy compounds such as CDs[7-17]. The polyester chains create polymeric supramolecular structures with sorption abilities.

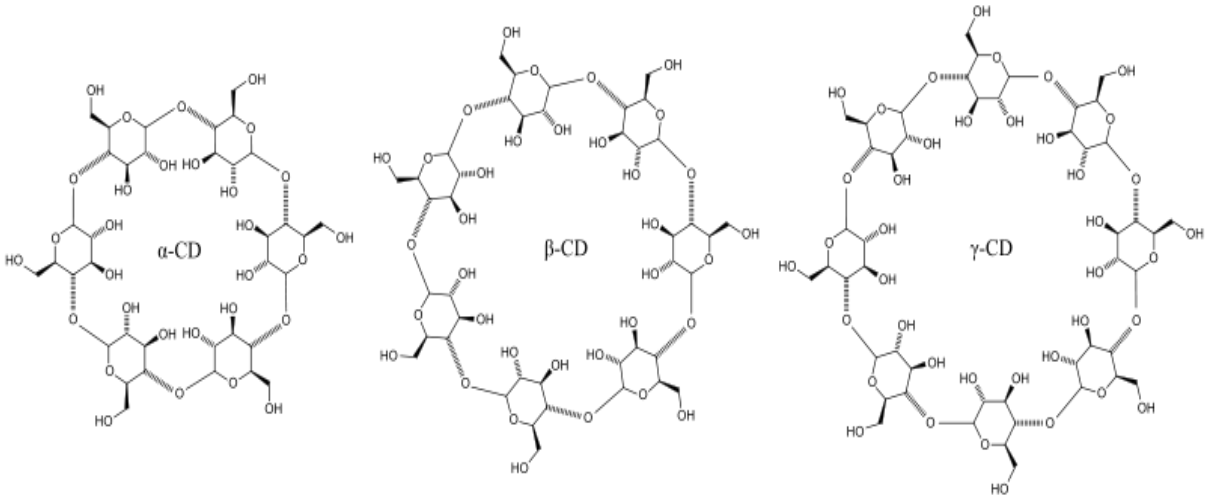
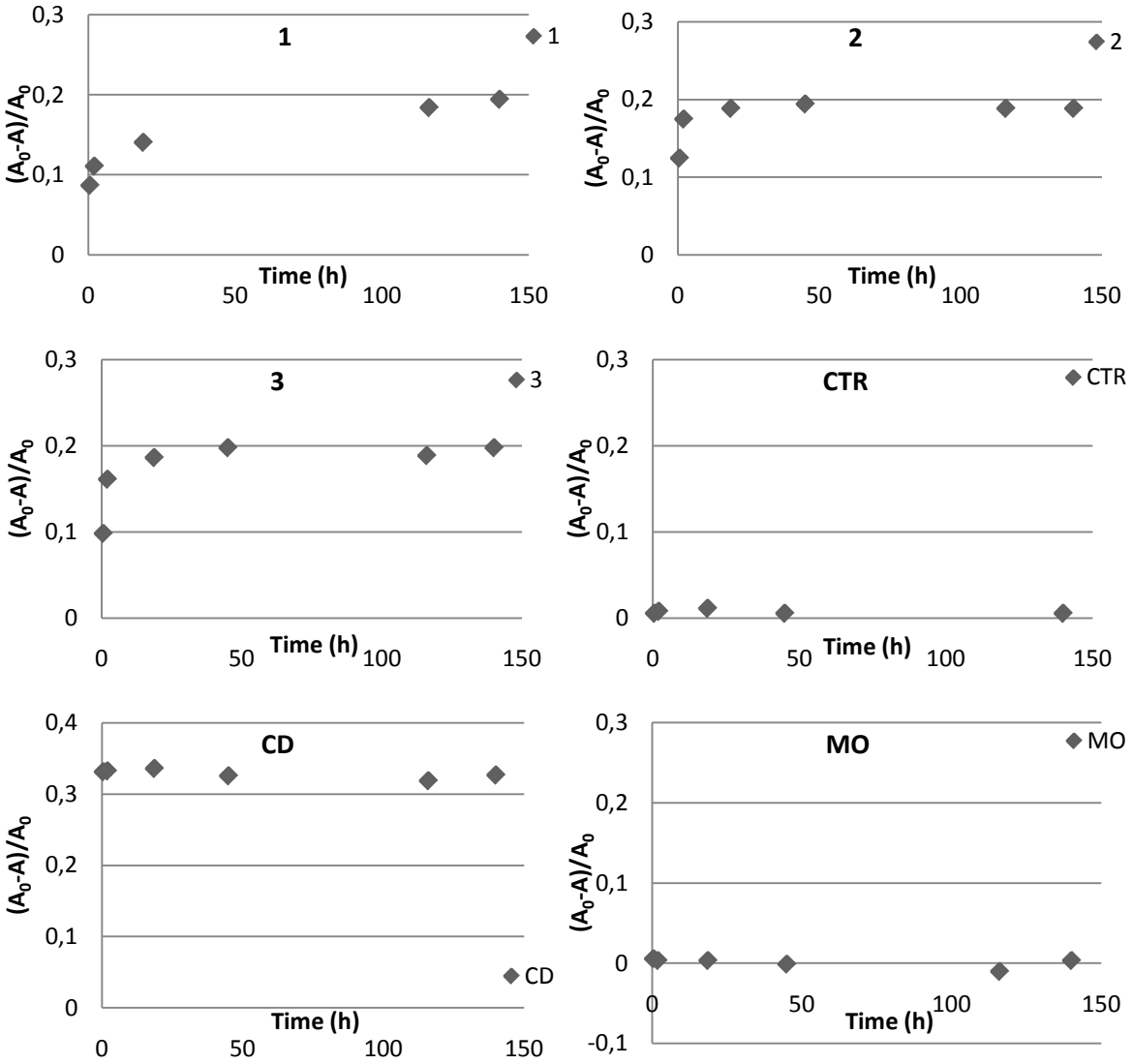


Figure 1 Chemical structure of the three main types of cyclodextrins.[18]

Results & discussion

Spectrophotometric method CD_{ANT} proved that the degree of substitution in most samples of investigated derivatives was around 4, which means that 4 CTR molecules react with 1 molecule of CD. As a matter of fact, the addition of NaOH to a mixture of substrates don't significantly influence the degree of substitution. However, the amount of a product was decreasing within increasing amount of NaOH added to the mixture of substrates. Probably it was caused by formation of water-soluble (less crosslinked) products.



Time dependency of the absorbance of methyl orange solutions in the presence of CD-CTR samples (K1,K3,K4), citric acid solution (CTR), cyclodextrin solution (CD) and blank sample (MO).

Analysis of sorption properties confirmed that CD molecules, present in investigated derivatives, preserved their ability to form inclusion complexes. However, CD-CTR samples complexed MO from its solution much slower than native CD molecules. Moreover, the CD content in CD-CTR samples was around 60% (CD_{ANT}), and 50% of the CDs were able to form inclusion complexes (CD_{MO}). The limited accessibility of the CD cavity in the polyester may have been the result of the relative overcrowding of the CD molecules and the presence of CD esters with sterically hindered cavities. Furthermore, in all samples an aggregate of CTR and CD content was around 95% instead of 100%. Probably residual ~5% refers to presence

of secondary reaction products like unsaturated carboxylic acids. Presence of those acids could be a result of heating of citric acid above its melting point (153°C) cousing its dehydration and thermal decomposition. Unsaturated carboxylic acids can also take place in esterification of CD's[20]. Finally, it was noticed that absorbance of MO solutions in presence of CD and CTR samples was constant against time.

sample code	Feed ratio (mol)				Amount of insoluble product (g)	CD_{OM} (%)	CD_{ANT} (%)	CTR_{HPLC} (%)	mol CTR/ 1mol CD
	CD	CTR	NaOH	$Na_2HPO_4*12H_2O$					
1	1	6	0	2	11,2	29	56	35,0	4,1
2	1	6	0,5	2	7,4	29	68	32,3	3,2
3	1	6	1,9	2	4,2	28	62	33,5	3,7

Conclusion

CD's content in obtained β-cyclodextrin—citric acid derivatives was 56-68% (CD_{ANT}) whereof about 50% were able to form inclusion complexes (CD_{OM}). Concluding, guest molecules have limited access to CD's cavities, it might be caused by blocking those cavities by CTR moieties or by small distances between CD molecules in CD-CTR samples. Moreover, an amount of obtained insoluble product decreased within increasing addition of NaOH to a mixture of substrates. On the other hand, it probably does not affect any changes in chemical structure of CD-CTR samples.

Experimental

Materials

Sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), methyl orange, citric acid monohydrate and hydrochloric acid were supplied by POCH (Poland). CD was purchased from Roquette (France). All of the chemicals were analytical grade and were used as received.

Methods

Water insoluble polymers - poly(β-cyclodextrin-*co*-citric acid) (CD-CTR) (Fig.3) were synthesized through heating of mixture of CTR,CD and Na_2HPO_4 as a catalyst with 6:1:2 molar ratios at 170^{o}C for 20 minutes (Fig.2). The crude product was powdered and purified by soaking with distilled water and centrifuged until supernatant was free of unreacted material and the catalyst. CD content was determined using standard anthrone protocol[19] (CD_{ANT}) and a spectrophotometric method based on decolorization of methyl orange (MO) upon complexation by CDs (CD_{MO}). Mixtures of 0.023 mM MO in 0.1 M HCl with different concentrations of CD were prepared and absorbance (A) at 508 nm were measured against 0.1M HCl as a blank sample. Calibration curve was plotted as a dependency of $1/(A_0-A)$ against 1/[CD]. A suspension of 100 mg of CD-CTR in 10 ml of 0.023 mM MO in 0.1M HCl was prepared. Absorbance measurements were conducted in specific periods of time and suspensions were centrifuged before every measurement. An absorbance of supernatant at 508 nm was measured against 0.1M HCl as a blank sample. The CD content was calculated based on the calibration curve.

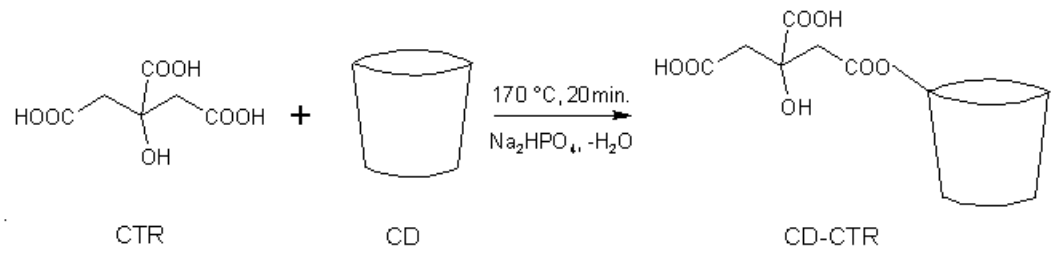


Figure 2 Synthesis of β-cyclodextrin—citric acid derivatives.

The degree of substitution of the derivatives was determined by HPLC analysis of citric acid contained in the samples hydrolysates. Those analyses were carried out using a system consisted of pump (Knauer), injection valve 10 µl and UV detector (Knauer). A LiChrospher RP-18 column (Knauer) 250x4.0 mm i.d. with a pore size of 100Å and particle size 10µm was used in the analyses. Chromatographic conditions were as follows: UV detector wavelength 218 nm; mobile phase: 6 mM H_3PO_4 in 50 mM NaH_2PO_4; flow rate 1 ml min^{-1}; column temperature: ambient. Quantities of the carboxylic acids were determined based on calibration curves made for each acid.

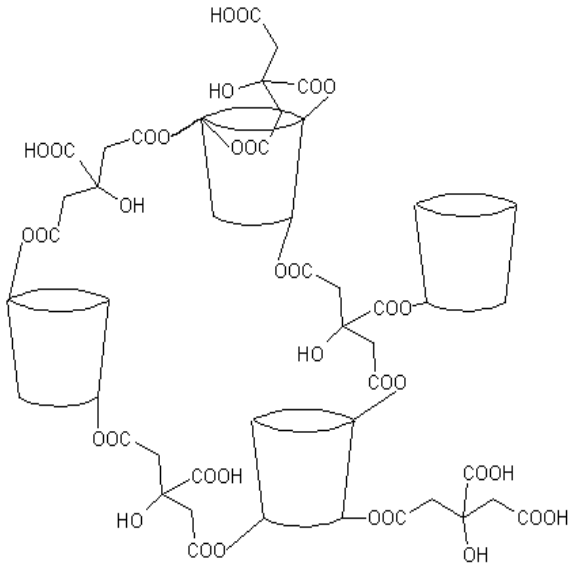


Figure 3 Poly(β-cyclodextrin-co-citric acid)

References

1) Dodziuk, H. Cyclodextrins and Their Complexes: Chemistry, Analytical Methods, Applications, Wiley-VCH, 1. edn., 2006.
2) Crini, G. Bioresour. Technol. 2003, 90, 193.
3) Wing, R. E. Starch 1996, 48, 275.
4) Demitri, C.; Sole, R. D.; Scalera, F.; Sannino, A.; Vasapollo, G.; Maffezzoli, A.; Ambrosio, L.; Nicolais, L. J Appl Polym Sci 2008, 110, 2453.
5) Abo-Shosha, M. H.; Ibrahim, N. A.; Elnagdy, E. I.; Gaffar, M. A. Polym Plast Technol Eng 2002, 41, 963
6) Wang, C.; Chen, C. J Appl Polym Sci 2005, 97, 2450.
7) Ducoroy, L.; Bacquet, M.; Martel, B.; Morcellet, M. React Funct Polym 2008, 68, 594.

8) Ducoroy, L.; Martel, B.; Bacquet, M.; Morcellet, M. J Appl Polym Sci 2007, 103, 3730.
9) Blanchemain, N.; Haulon, S.; Boschin, F.; Marcon-Bachari, E.; Traisnel, M.; Morcellet, M.; Hildebrand, H. F.; Martel, B. Biomol Eng 2007, 24, 149.
10) El Ghoul, Y.; Blanchemain, N.; Laurent, T.; Campagne, C.; El Achari, A.; Roudesli, S.; Morcellet, M.; Martel, B.; Hildebrand, H. F. Acta Biomater 2008, 4, 1392.
11) Boschin, F.; Blanchemain, N.; Bria, M.; Delcourt-Debruyne, E.; Morcellet, M.; Hildebrand, H.; Martel, B. J Biomed Mater Res Part A 2006, 79, 78.
12) Martel, B.; Weltrowski, M.; Ruffin, D.; Morcellet, M. J Appl Polym Sci 2002, 83, 1449.
13) Martel, B.; Morcellet, M.; Ruffin, D.; Vinet, F.; Weltrowski, M. J. Inclusion Phenom 2002, 44, 439.
14) Bednarz, S.; Mazela, W.; Pajda, M.; Lukasiewicz, M. Text Rev (Przeglad Wlokienniczy) 2008, 62, 58 (in Polish).
15) Yang, C.; Wang, X.; Kang, I. Text Res J 1997, 67, 334.
16) Zhao, D.; Zhao, L.; Zhu, C.; Huang, W.; Hu, J. J. Inclusion Phenom Macrocyclic Chem 2009, 63, 195.
17) Martel, B.; Ruffin, D.; Weltrowski, M.; Lekchiri, Y.; Morcellet, M. J Appl Polym Sci 2005, 97, 433.
18) Cyclodextrin http://en.wikipedia.org/wiki/Cyclodextrin (read 25.10.2010)
19) Morris D L. Quantitative determination of carbohydrates with Dreywood's anthrone reagent. Science 107:254-5, 1948.
20) Szczepan Bednarz, Marcin Lukasiewicz, Wojciech Mazela, Michal Pajda, Wiktor Kasprzyk Chemical Structure of Poly(b-cyclodextrin-co-citric acid) J Appl Polym Sci 2011, 10.1002/app.33002