

Polymerization of β -cyclodextrin with succinic anhydride and thermogravimetric study of the polymers

Tomasz Girek · Wojciech Ciesielski

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Abstract The β -cyclodextrin (β -CD) polymers were prepared by crosslinking β -CD with succinic anhydride (SA) in anhydrous *N,N*-dimethylformamide (DMF) in the presence of sodium hydride (NaH). The formed multi-oxoanionic β -CD derivatives can react with more than two anhydride molecules, yielding polymers with butanodioic ester bridges. The weight-average molecular weight (M_w) and the chemical structure of the polymers were described in earlier papers. It was observed that the molecular weight of polymers increased with reaction temperature. The molar ratio of reagents was important for determination of structure and molecular mass of the obtained β -CD polymers. The thermogravimetric (TG) and calorimetric (DSC) studies of polymers also were carried out.

Keywords Cyclodextrin · Polymerization · Succinic anhydride · Thermogravimetric study

Introduction

Cyclodextrins (CDs) are cyclic oligomers composed of six, seven or eight glucopyranosyl units (AGU) (known as α -, β - or γ -CDs, respectively), linked together by α -1,4-bonds. CDs have hollow truncated cone structure; the cavity is hydrophobic and the outer surface is hydrophilic. In a CD molecule, all secondary hydroxyl groups at the C2 and C3 positions of the AGU protrude from the wide rim of the CD molecule, whereas the primary hydroxyl groups at C6 are

situated at the narrow rim [1]. It is known that CDs can form complexes with a variety of organic and inorganic species, confined in their hydrophobic cavities [2–4]. Due to this unique property, CD are applied in food and cosmetic industries, as well as in pharmaceutical industry for drug delivery [5]. Upon polymerization CDs become more stable and less soluble, therefore CD polymers can be used to remove or isolate contaminants from foods or biological matrices [6, 7].

To polymerize CD, two methods are used. In the first one, CD molecules are attached as pendant groups on polymer chains. Polymers with CD pendants are usually prepared by radical polymerization of the functional CD monomers such as acryloyl cyclodextrin (CD-A) and *N*-acryloyl-6-aminocaprocyclodextrin (CD-NAC) [8, 9]. These monomers may also copolymerize with other monomers such as acryl amide or acrylic acid [8, 9]. The second type of polymerization involves the reaction of CD molecules with bifunctional agents serving as crosslinkers. As such agent epichlorohydrin is often used, albeit other epoxy compounds such as ethylene glycol bisepoxy(propyl) ether [10] or butylene glycol bis(epoxypropyl)ether [11] may also be applied. Reactions of CDs with bifunctional agents usually occur under strong alkaline conditions necessary for deprotonation of hydroxyl groups of glucose units.

It should be pointed out that in anhydrous medium such as *N,N*-dimethylformamide, CDs easily react with sodium hydride to achieve deprotonation of hydroxyl groups mainly at the C2-position of AGU molecules, leading to oxoanions [12]. The reaction of such CDs deprotonated in position 2 with CDs deprotonated in position 3 leading to 2,3-CD epoxides is possible [12]. The formed epoxides may react with maleic and octenylsuccinic anhydrides to give CD polymers [13, 14]. In the present study, the β -CD

T. Girek · W. Ciesielski (✉)
Institute of Chemistry and Environmental Protection, Jan
Długosz University, Armii Krajowej Ave., 13/15,
42 201 Częstochowa, Poland
e-mail: w.ciesielski@interia.pl

polymers S1–S5 were obtained by crosslinking β -cyclodextrin with succinic anhydride via the oxoanion or epoxide intermediate formed by sodium hydride.

Experimental

Reagents and solvents

Crystalline β -CD, succinic anhydride (SA), sodium hydride, *N,N*-dimethyl formamide (DMF) and Linde type 4 Å molecular sieves were purchased from Aldrich (Germany). DMF was predried over molecular sieves and distilled under vacuum. The dried DMF was stored in a dark bottle over molecular sieves [15].

Synthesis of five β -CD polymers S1–S5 crosslinked with succinic anhydride

The β -CD polymers crosslinked by SA were obtained as reported previously [15, 17]. In this procedure β -CD (1.135 g, 0.001 mol) was dissolved in DMF (25 mL), and then solid NaH (0.001–0.007 mol) was slowly added with vigorous stirring to give manno-2,3-epoxy- β -cyclodextrin [13]. The obtained β -CD oxoanion or epoxide solution was slowly treated with solid MA (0.001–0.011 mol). The reaction mixture was continuously stirred in a sealed round bottom flask on an oil bath at a controlled 25–130 °C temperature during 24 h. The reaction product was precipitated and washed with a large quantity of acetone, and finally dried in a vacuum desiccator at room temperature. For investigation only polymers obtained at 60 and 100 °C were taken into account.

of 99.99% purity. Samples of approximately 0.020 g were heated in corundum crucibles with non-hermetic lids. Corundum (SINGLE *R) was the standard. The heating was performed under static conditions in the air in the range of 20–500 °C with the 5 K min⁻¹ temperature rate. The measurements were duplicated. They provided the ± 0.5 °C precision in temperature reading. Recorded thermograms were analyzed with the NETZSCH-TA-ANALYSIS and NETZSCH SEPARATION OF PEAKS programs.

Results and discussion

Basing on the analysis of TG/DTG/DSC curves, two types of polymers may be differentiated: anhydrous polymeric systems comprising S1–S3 polymers and hydrated polymeric systems comprising S4 and S5 polymers.

Anhydrous polymeric systems:

S1 obtained at 60 °C, at ratio of starting materials (CD:NaH:SA) 1:4:7, then denoted as R (Fig. 1).

S2 obtained at 60 °C, at R = 1:7:7 (Fig. 2).

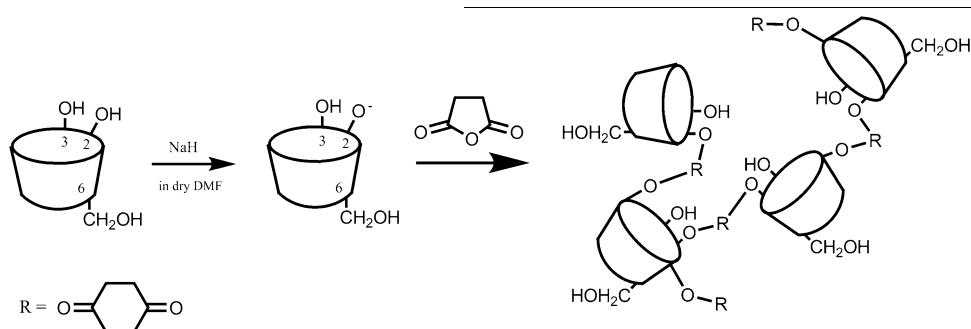
S3 obtained at 100 °C, at R = 1:7:7 (Fig. 3).

Hydrated polymeric systems:

S4 obtained at 60 °C, at R = 1:4:4 (Fig. 4).

S5 obtained at 60 °C, at R = 1:7:4 (Fig. 5).

In investigation of anhydrous polymers S1–S3 (Figs. 1–3) we have observed that they undergo decomposition beginning at temperature by ca 120 °C lower than that of hydrated polymers. For S1 and S3, after a very fast decomposition ($tg\alpha$ values equal to 4.85 and 5.85, respectively) a monotonous,

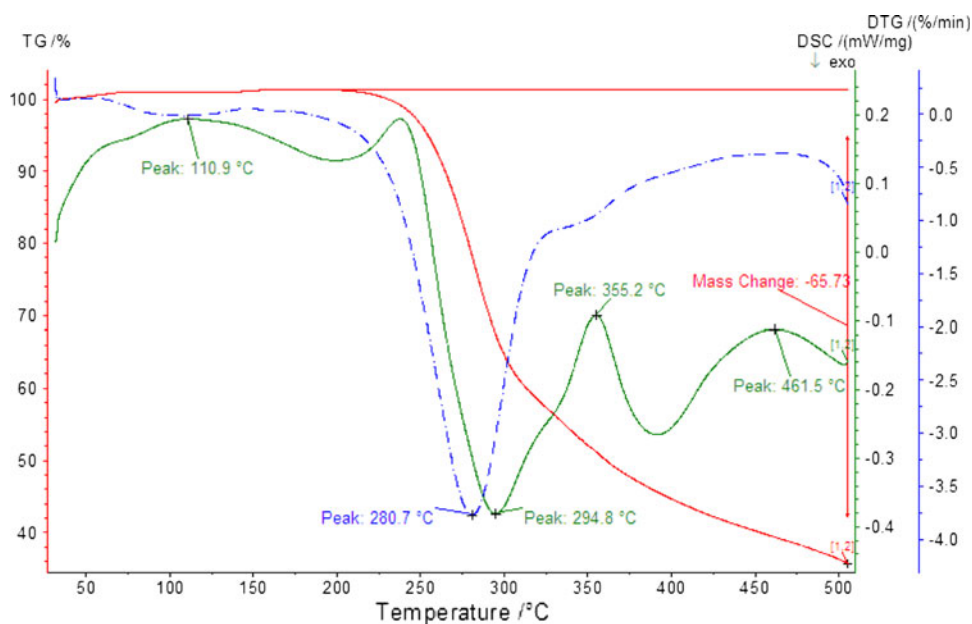
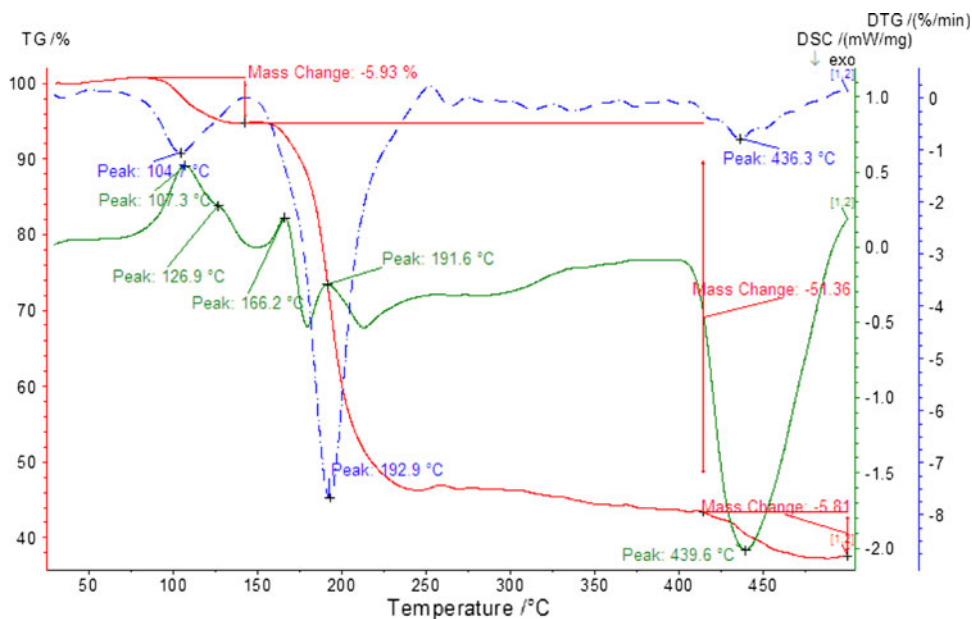


Thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) of β -CD polymers S1–S5

The thermal DSC-TG-DTG analysis was carried out with the NETZSCH STA-409 simultaneous thermal analyzer calibrated with standard indium, tin, zinc, and aluminium

slow decomposition occurs up to 500 °C, resulting in the 61% mass loss of the polymer (Figs. 1, 3).

Polymer S2 undergoes a two-step decomposition. This polymer, similarly as both S1 and S3 does not have the water adsorbed on its surface, but, contrary to S1 and S3, contains the coordinated water molecules. In the first step of heating (up to 100 °C) no mass loss nor thermal effects

Fig. 1 TG/DTG/DSC curves of polymer **S1** (60 °C; R = 1:4:7)**Fig. 2** TG/DTG/DSC curves of polymer **S2** (60 °C; 1:7:7)

connected with the removal of water bound on the polymer surface are observed. Then the small (6%), slow ($tg\alpha = 0.43$) mass loss begins, and peaks resulting from removal of coordinated water appear.

The shape of corresponding parts of DSC diagrams of **S2** confirms the different than for **S1** and **S3** status and kind of water coordination mode, as well as three steps of its removal, indicated by presence of small peaks at ca 105 and 127 °C, and a more intense peak at ca 166 °C. After the water removal at ca 190 °C, the very fast ($tg\alpha = 6.85$) decomposition begins, followed by a slow decomposition resulting in ca 60% mass loss (Fig. 2).

In investigation of hydrated polymers **S4** and **S5** (Figs. 4, 5) we have observed that after removal of 14–15% of water ($tg\alpha = 0.46$ and 0.69, respectively), accompanied by the endothermic effect in the low temperature part of DSC diagrams (69 and 73 °C, respectively), on the TG line a plateau appears. Then, from the point of plateau breakdown, the fast mass loss begins ($tg\alpha = 3.75$ and 4.16, respectively). This point indicates the start of the polymer decomposition.

Next, the sharp monotonous lowering of the TG line occurs, connected with the fast mass loss. The mass loss in **S4** and **S5** is accompanied by two endothermic effects for

Fig. 3 TG/DTG/DSC curves of polymer **S3** (100 °C; 1:7:7)

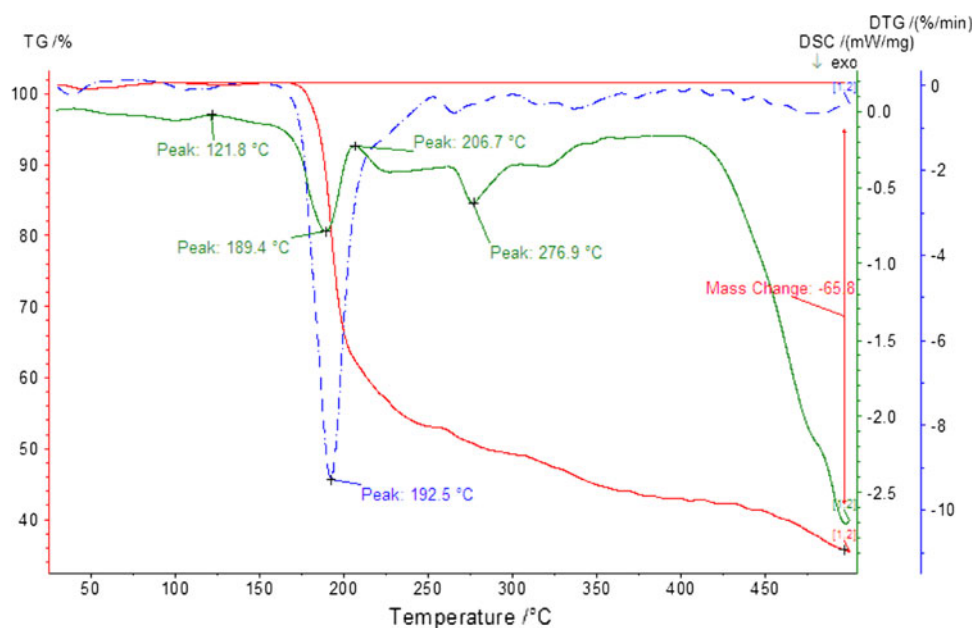
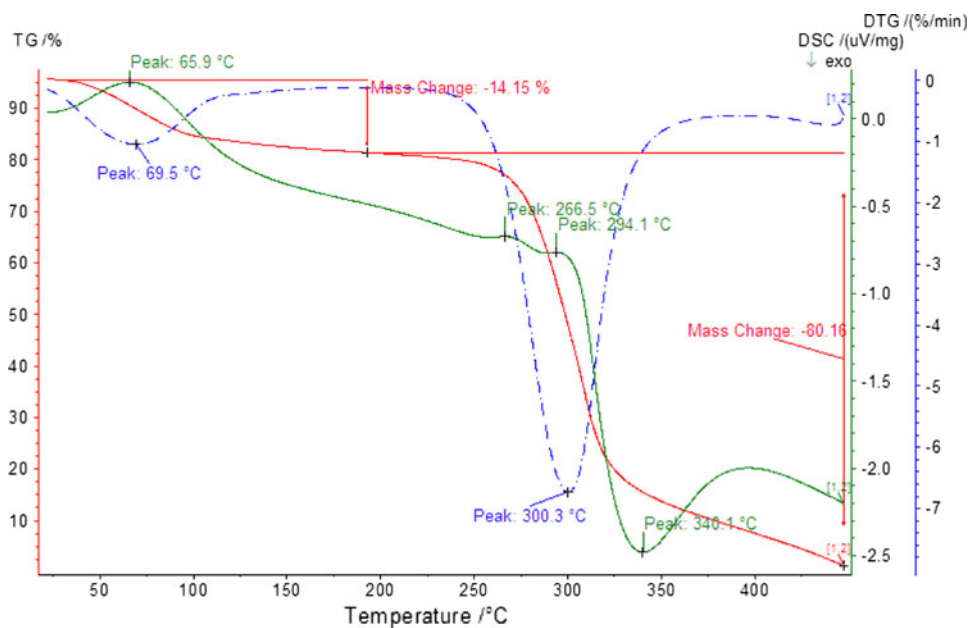


Fig. 4 TG/DTG/DSC curves of polymer **S4** (60 °C; R = 1:4:4)



each polymer, at ca 260 and ca 295 °C. The fast mass loss of the polymer finishes at ca 350 °C. The shape of the TG line suggests the one-stop mass loss of the sample, and the corresponding DTG peak is observed at 300 °C (for **S4**) and at 286 °C (for **S5**). The peaks of DTG curves are symmetric and sharp, this fact confirming one-step, fast decomposition of the polymer. Then the decomposition becomes slower and occurs up to 500 °C, leaving ca 10% of starting mass of the polymer (Figs. 4, 5).

Analysis of thermal properties of β -CD polymers **S1–S5** with succinic anhydride enables the following suggestions concerning the structure of formed polymers. Temperature

of the main peak of decomposition (corresponding to oxidation of polymer) for anhydrous **S1–S3** is considerably higher than in the case of hydrated **S4** and **S5**. According to Table 1 and data concerning molecular masses [17], the formation of the polymer results in the shift of this exothermic peak toward higher temperatures as compared with noncoordinated β -CD.

The residue at 500 °C for anhydrous polymers is also much more higher (40%) than for hydrated polymers (10%). These two observations prove that structures of anhydrous polymers are more densely crosslinked and thermally more stable than those of hydrated polymers.

Fig. 5 TG/DTG/DSC curves of polymer **S5** (60 °C; 1:7:4)

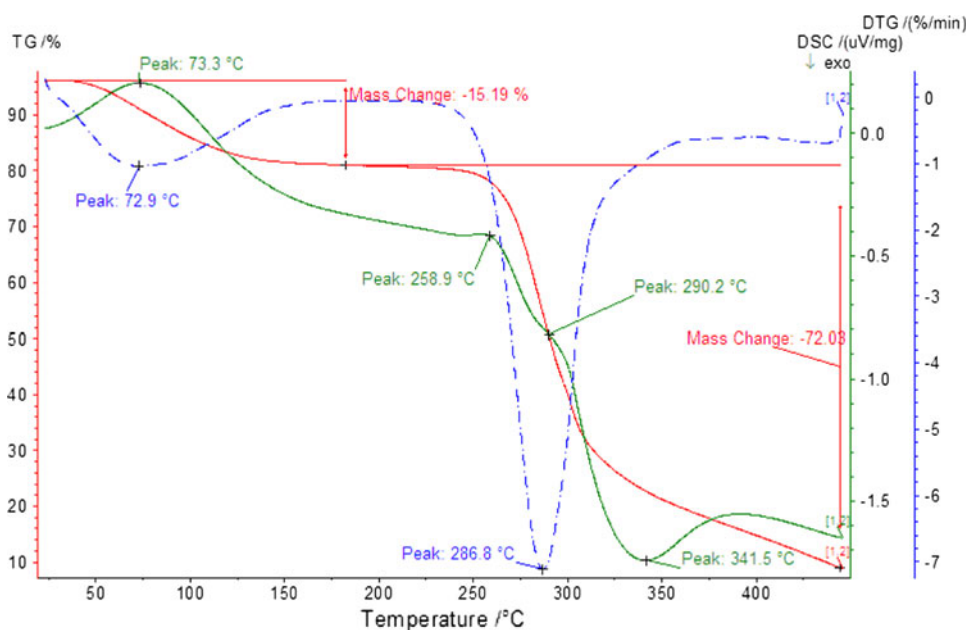


Table 1 Thermal properties of β -CD polymers S1–S5 with succinic anhydride

TGA			DTG ^a	DSC	
Temperature range (°C)	Weight loss ^b (%)	Slope (tg α)	Complex (°C)	Temperature (°C)	ΔH^c (J g ⁻¹)
Temp. 60 °C, 1:4:7 (S1)					
25–225	–	0.03		110.9	–112.6
225–500	66	4.85	280.7	294.8	+307.3
				355.2	–129.2
				461.5	–97.8
Temp. 60 °C, 1:7:7 (S2)					
25–100	6	0.01	104.7	107.3	–68.3
				126.9	–7.4
100–200	57	0.43	192.9	166.2	–73.4
				191.6	–27.8
200–500	63	6.85	436.3	439.6	+396.3
Temp. 100 °C, 1:7:7 (S3)					
25–175	–	0.69		121.8	–9.4
175–500	66	5.85	192.5	189.4	+28.3
				206.7	–21.8
				276.9	+22.4
Temp. 60 °C, 1:4:4 (S4)					
25–200	14	0.46	69.5	65.9	–67.3
200–500	94	3.75	300.3	266.5	–10.7
				294.1	–9.2
				340.1	+197.9
Temp. 60 °C, 1:7:4 (S5)					
25–175	15	0.69	72.9	73.3	–78.4
175–500	87	4.16	286.8	258.9	–29.2
				290.2	–9.3
				341.5	+247.8

The analysis of TG/DTG/DSC data for polymers **S1**, **S4** and **S5** obtained for different R values, i.e. ratios of starting materials CD: NaH: SA (1:4:7; 1:4:4 and 1:7:4, respectively) indicates that the temperature of 60 °C is optimal for their preparation. It was observed that temperature strongly influences the formation of these (**S1**, **S4** and **S5**) polymers.

The analysis of TG/DTG/DSC data for polymers **S2** and **S3**, obtained at R = 1:7:7, indicates that for **S2** optimal is temperature 60 °C, while for **S3** optimal is 100 °C, since **S3** obtained at 100 °C is more densely crosslinked and more stable than **S2**. These properties of **S3** are manifested by a large residue at 500 °C (ca 40%) and a shift of temperature of the main peak to above 500 °C.

Conclusions

β -Cyclodextrin (β -CD) polymers were prepared by cross-linking β -CD with succinic anhydride (SA) in anhydrous *N,N*-dimethyl formamide (DMF) in the presence of NaH. The thermal properties of the polymers were determined using thermogravimetric and calorimetric studies. For ratios 1:4:4; 1:4:7 and 1:7:4 of the starting materials the temperature 60 °C showed to be optimal for preparation of polymers. Only in the case of ratio 1:7:7 the optimal temperature for preparation of polymer was equal to 100 °C.

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