Chemical Structure of Poly(β-cyclodextrin-*co*-citric acid)

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Received 28 October 2009; accepted 26 June 2010
DOI 10.1002/app.33002
Published online 29 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: We synthesized water-insoluble polymers, poly(β-cyclodextrin-*co*-citric acid)s, by heating a mixture of citric acid, cyclodextrin (CD), and Na_2HPO_4 as a catalyst with a 6 : 1 : 2 molar ratio at 160, 170, and 180°C for 10 and 20 min. The chemical composition of the polyesters was determined by high pressure liquid chromatography (HPLC) analysis of the polymer hydrolysates. The crosslinking mechanisms and thermal degradation of the polymers were also investigated. The polyesters contained 30–35% citric acid, 1–4% unsaturated carboxylic acids (i.e., itaconic, *cis*-aconitic, *trans*-aconitic, and mesaconic acids), and 60–70% CD, whereas about 40% of them were able to form inclusion complexes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3511–3520, 2011

Key words: crosslinking; degradation; high performance liquid chromatography; host–guest systems; polyesters

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of α-1,4-glycosidically linked D-glucose units: 6, 7, and 8 for α-, β-, and γ-CDs, respectively. CDs may be described as truncated cones with relatively hydrophobic cavities that are capable of binding small molecules through host–guest interactions.[1] The formation of inclusion complexes is also a main mechanism of sorption by water-insoluble CDs containing polymers.[2] One method of polymer preparation is the crosslinking of CDs, mainly by epichlorohydrin, diisocyanates, and dicarboxylic acid dihalides.[3] On the other hand, poly(carboxylic acid)s, especially citric acid, have become a popular crosslinking agent; it is able to overcome toxicity and is less costly than the previously mentioned compounds. Citric acid has already been used in the esterification or crosslinking of some polysaccharides, for example, starch[4] or cellulose,[5–7] and polyhydroxy compounds, such as aliphatic diols,[8,9] glycerol,[10] 1,4 : 3,6-dianhydrohexatols,[11] sorbitol,[12] and also CDs.[13–25] Citric acid has also been used as a crosslinking agent for the grafting of CDs onto various materials to enhance their sorption properties. Cationic exchange textiles with unique metal cations and aromatic molecule binding abilities were prepared by the coating of a nonwoven poly(ethylene terephthalate) with poly(β-cyclodextrin-*co*-citric acid) (CDP).[13,14] A vascular poly(ethylene terephthalate) prostheses[15] and a polyamide biomedical woven fabric[16] were functionalized with CDs to obtain a material with slow antibiotic release. A similar method was applied to develop a medical material that could be loaded by antimicrobial agents by the grafting of CDs onto microporous poly(vinylidene difluoride) membranes.[17] Citric acid–CD mixtures have also been used in wool, polyester, and cotton fabric finishing.[18–20] In this case, cotton material was impregnated with a solution of citric acid, CD, and a catalyst; dried; and cured at 170–190°C. At elevated temperatures, the citric acid underwent thermal dehydration to a cyclic anhydride intermediate that readily reacted with the hydroxyl groups of both CD and cellulose.[21] The observed weight gain of the material (ca. 15–20%) was the consequence of cellulose esterification and CDP formation.[18] The properties of CD-grafted materials have been the subject of several studies,[13–20] but none of them focused on the polyesters, even though the polymers are the most important component of the formed coating. Moreover, the number of articles dealing with the chemical structure and properties of CDPs is very limited.[22–24]

In this article, the results of chemical structure investigations of CDPs are reported. The study involved the determination of the chemical composition of the obtained polyesters and the examination

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Contract grant sponsor: Polish State Committee; contract grant number: N507093633.

of the mechanisms of crosslinking and thermal degradation of the polymers.

EXPERIMENTAL

Materials

Sodium phosphate dibasic dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), sodium phosphate monobasic dihydrate ($NaH_2PO_4{\cdot}2H_2O$), phosphoric acid (H_3PO_4, 75%), citric acid monohydrate, methyl orange, hydrochloric acid, and sodium carbonate decahydrate ($Na_2CO_3{\cdot}10H_2O$) were supplied by POCH (Gliwice, Poland). The unsaturated acids (*cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, itaconic, and glutaconic acids) were from Sigma-Aldrich (St Louis, Missouri). CD was purchased from Roquette (Lestrem, France). All of the chemicals were analytical grade and were used as received.

The absorbance of methyl orange solutions was measured on an ultraviolet–visible spectrometer (UVS-2800, Labomed, Culver City, California). Fourier transform infrared (FTIR) spectra were collected on a Bio-Rad STS 165 spectrometer (Philadelphia, Pennsylvania) with the KBr pellet technique. Thermal decomposition was studied in an air or argon atmosphere in a Mettler Toledo 851e thermobalance (Greifensee, Switzerland) connected online to a ThermoStar Balzers T300 quadruple mass spectrometer (Balzers, Liechtenstein). The heating rate was 10°C/min.

Methods

CDP preparation

In a solution of 12 g of citric acid (57 mmol) and 7.2 g of $Na_2HPO_4{\cdot}12H_2O$ (20 mmol) in 20 mL of distilled water, 12 g of CD (9.5 mmol, dry basis) was dissolved, and the obtained solution was dried for 1 h at 100°C. The powdered mixture was transferred into a Petri dish and heated in an drying oven (Binder VD23, Tuttlingen, Germany) at a temperature 160, 170, or 180°C for 10 or 20 min (samples P1–P6), respectively. The crude product was weighed (where the mass was m_0), powdered, and purified by soaking with distilled water and centrifuged until the supernatant was free of unreacted material and the catalyst (checked by appropriate spectrophotometric methods). The insoluble material was dried at 60°C overnight and weighed (where the mass was m_1). The insoluble polymer fraction (gel fraction) was calculated as follows:

$$\text{Insoluble polymer fraction } (\%) = m_1/m_0 \times 100$$

Crosslinking of CDs by unsaturated carboxylic acids

The unsaturated acid (i.e., *cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, itaconic, or glutaconic acid, 6 mmol), $Na_2HPO_4{\cdot}12H_2O$ (2 mmol), and CD (1 mmol) were mixed with 1 mL of distilled water, and the slurry was dried at 100°C for a few minutes and heated at 180°C for 10 min. The procedures of the polymer purification and the determination of the insoluble polymer fraction were similar to those used for CDP (see previous discussion).

Thermal degradation of CDP

A few hundred milligrams of polyester P3 was heated in a drying oven at 180°C for 10 min (sample P3a). Another portion of P3 was mixed with $Na_2HPO_4{\cdot}12H_2O$ (10% w/w of the polymer) dissolved in 1 mL of water and heated in the oven at 180°C for 10 min (sample P3b). The obtained samples were analyzed without any purification.

Hydrolysis of CDP

A mixture of 50 mg of CDP with 3 mL of 1*M* Na_2CO_3 was placed in a capped vial and heated at 95°C for 1 h. After saponification, the solution was cooled to room temperature, and 100 μL of the mixture was withdrawn, neutralized by 200 μL of 1*M* HCl, and finally diluted by 1 mL of distilled water. The obtained samples were left for chromatographic analysis.

Chromatographic quantification of the carboxylic acids in hydrolysates

High pressure liquid chromatography (HPLC) analyses were carried out with a system consisting of a pump, a 10-μL injection valve, and a Smartline 2500 UV detector (Knauer, Berlin, Germany). A LiChrospher RP-18 column (Knauer, 250 × 4.0 mm *i.d.*, pore size = 100 Å, particle size = 10 μm) was used in all of the analyses. The chromatographic conditions were as follows: UV detector wavelength = 218 nm, mobile phase = 6 m*M* H_3PO_4 in 50 m*M* NaH_2PO_4, flow rate = 1 mL/min, and column temperature = ambient. The quantities of the carboxylic acids were determined on the basis of calibration curves made separately for each acid.

Cyclodextrin content as determined by the decolorization of methyl orange upon complexation (CD_{MO})

CD_{MO} (mg/g) was determined with a spectrophotometric method based on the decolorization of methyl orange upon complexation by CDs. Mixtures of 0.023 m*M* methyl orange in 0.1*M* HCl [absorbance (A_0) = 0.877 at 508 nm] with different concentrations of CD (in the range 0.2–7mM) were prepared, and the absorbances (A's) at 508 nm were measured against 0.1*M* HCl as a blank sample. A calibration curve was plotted as the $1/(A_0 - A)$ dependency against 1/[CD].

A suspension of 50 mg of CDP in 5 mL of 0.023 m*M* methyl orange in 0.1*M* HCl was prepared. After 30 min, the polymer was centrifuged, and the

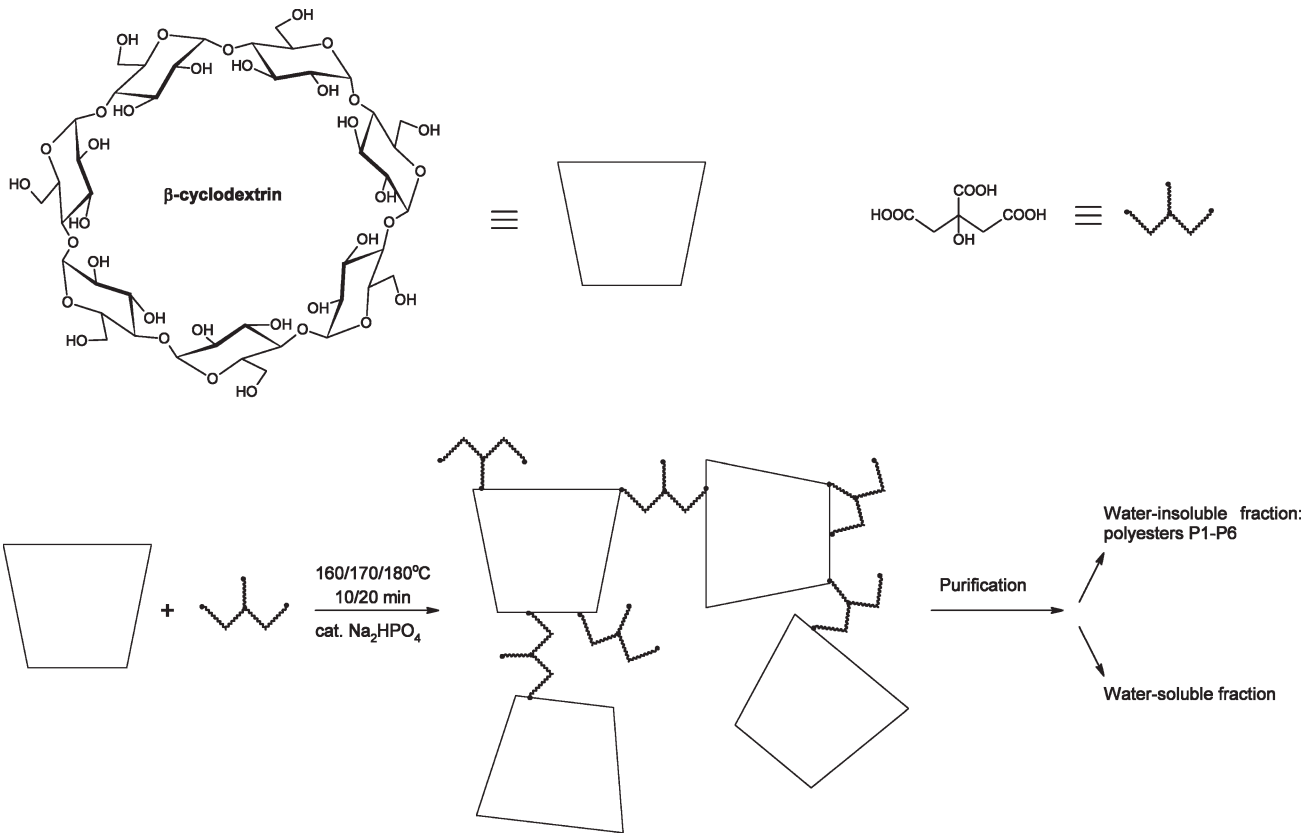

Figure 1 Synthesis of CDP.

absorbance of the supernatant at 508 nm was measured against 0.1*M* HCl as a blank sample. The CD content was calculated on the basis of the calibration curve.

Cyclodextrin content as determined by the material balance (CD_A)

CD_A (mg/g) was estimated on the basis of the material balance:

$$CD_A = 1000 - TA$$

where TA (mg/g) is the total amount of carboxylic acids determined by HPLC.

RESULTS AND DISCUSSION

Preparation of the CDPs

We prepared the polyesters by heating the mixture of citric acid, CD, and $Na_2HPO_4 \cdot 12H_2O$ with a 6 : 1 : 2 molar ratio under solvent-free conditions at 160–180°C for 10 or 20 min (Fig. 1, Table I). The amount of the insoluble polymer fraction depended on the process conditions and was established in the range 13–69%. Synthesis at temperatures above 160°C with a molar ratio of citric acid to CD greater than 4 and a reaction time longer than 10 min favored the formation of a water-insoluble polymer.[23] At lower temperatures and with a lower excess of citric acid, water-soluble citric esters of CD were formed, and a decrease in the amount of the insoluble polymer fraction was observed.[23,26]

CDP chemical composition

Samples of the polyesters were hydrolyzed in 1*M* Na_2CO_3 at 95°C for 1 h. In our preliminary experiments, the possibility of the decomposition/rearrangement of the acids (citric, *cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, itaconic, and glutaconic acids) in the hot alkaline solution was studied. In agreement with previous findings,[27,28] we proved, using HPLC, that in such conditions, all of the acids

TABLE I
Polymerization Conditions and the Insoluble Polymer Fractions of the CDPs

Polyester	Temperature (°C)	Time (min)	Insoluble polymer fraction (%)
P1	160	10	13
P2	170	10	53
P3	180	10	60
P4	160	20	49
P5	170	20	69
P6	180	20	57

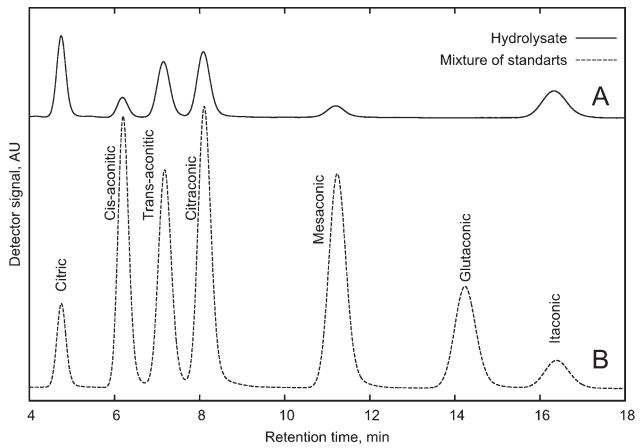

Figure 2 Results of HPLC separation: (A) a typical chromatogram of a hydrolysate of CDP and (B) an example of separation of the organic acids standards (concentration of citric acid = 0.5 mg/mL, concentration of the other acids = 0.02 mg/mL).

were stable and did not undergo any transformations. Additionally, in tentative experiments, at appropriate time intervals, the carboxylic acid concentrations in the hydrolysate were determined. We found that saponification was finished after 60 min. An increase in the reaction time did not influence the acid concentrations because CDP was hydrolyzed completely.

The chemical composition of CDP was estimated on the basis of the HPLC analysis of the polymer hydrolysates. A different approach to those described in the literature[27,29,30] was applied. With 6m*M* H_3PO_4 in 50m*M* NaH_2PO_4, an excellent separation of citric, *cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, glutaconic, and itaconic acids was achieved with a C18 column at ambient temperature (Fig. 2). The carboxylic acid content in samples P1–P6 was determined, and the results are shown in Figure 3. The obtained polyesters contained approximately 30–35% citric acid, 1–4% unsaturated carboxylic acids, and 60–70% CD (on the basis of material balance). Among all of the investigated acids, the amount of citric acid was the highest (1.6–1.9 mmol/g), but a significant quantity of itaconic acid (0.04–0.19 mmol/g) was also detected. *Trans*-aconitic and citraconic acids were present in lower concentration, estimated as 0.01–0.04 mmol/g; however, the amounts of *cis*-aconitic and mesaconic acids were less than 0.01 mmol/g in most of the samples. Glutaconic acid, a possible product of citric acid thermal decomposition, was not detected at all (Fig. 2). The maximal amount of citric acid was obtained when polymerization at 160°C for 20 min (sample P4) was carried out, and at higher temperatures, a decrease in the acid content was observed (samples P5 and P6). The unsaturated carboxylic acid content increased with increasing reaction time and temperature, and the trend was especially significant for itaconic acid.

The heating of citric acid above its melting point (153°C) caused its dehydration to the anhydride and thermal decomposition (dehydration and decarboxylation) to unsaturated acids/anhydrides: *cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, itaconic,

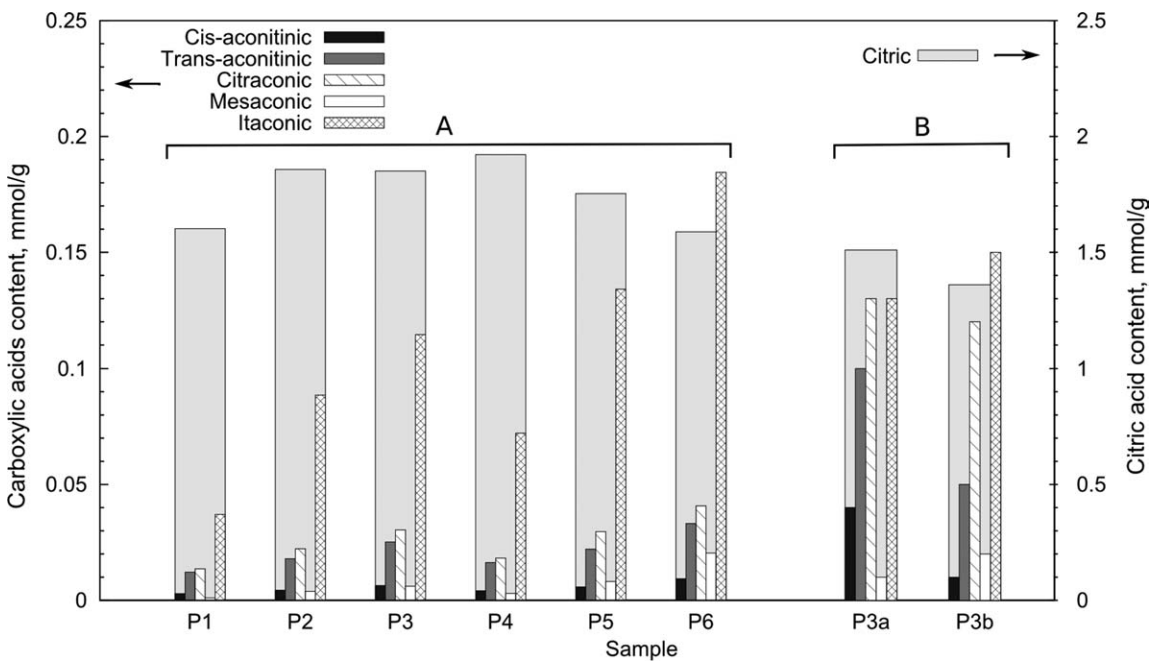

Figure 3 Results of carboxylic acid determination: (A) CDP samples and (B) thermally decomposed samples of the polyester P3.

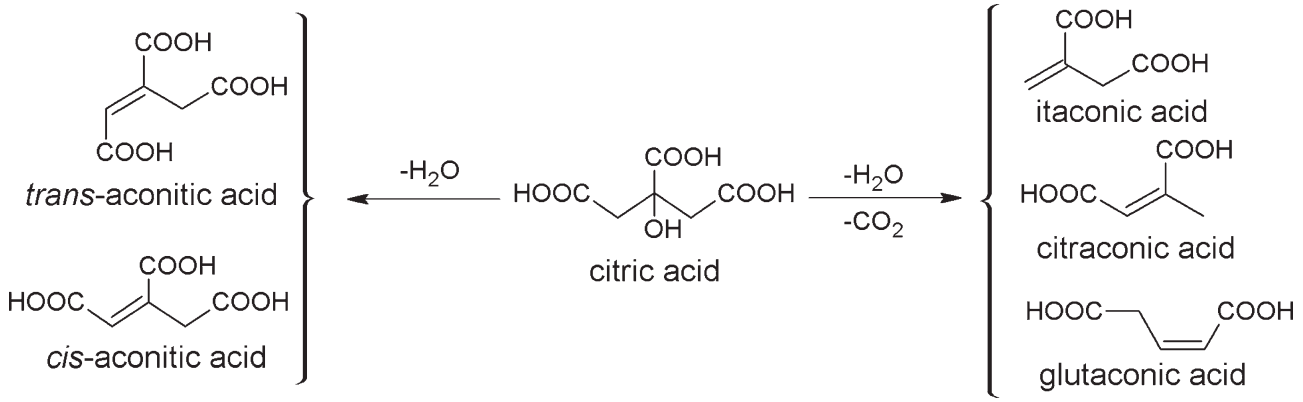

Figure 4 Simplified scheme of the degradation pathways of citric acid at elevated temperatures. For more details, see ref. 11.

and glutaconic (Fig. 4).[11] Anhydrides are more reactive than the acids, and when a hydroxyl group is present (e.g., CD), esterification can occur. Not only did the carboxylic acid content in the CDPs depend on the anhydride concentration (their formation rate and volatility), but also, the reactivity and thermal stability of the formed CD esters had to be taken into consideration. Additionally, the anhydrides, that is, *cis*-aconitic, *trans*-aconitic, and also citraconic and itaconic anhydrides, or their esters were rearrangement-sensitive; this could have influenced the reagent concentration.[11,28,31]

The citric acid content in the investigated polyesters was a result of two competitive processes: transformation of citric acid into citric anhydride followed by the esterification of CD and thermal decomposition of the anhydride and also citric esters that formed. Citric acid can form mono-CD and di-CD esters (Fig. 5). The formation of the triester seemed to be less probable because of steric hindrance. The thermal dehydration and decarboxylation of the esters could yield esters of citraconic, itaconic, and glutaconic acids. On the other hand, glutaconic acid was not detected in the CDP hydrolysates. This suggests that the decarboxylation of the carboxylic group at the C_2 of citric ester [Fig. 5 (A,D,E)] was much slower or did not occur at all. However, small amounts of mesaconic acid (an

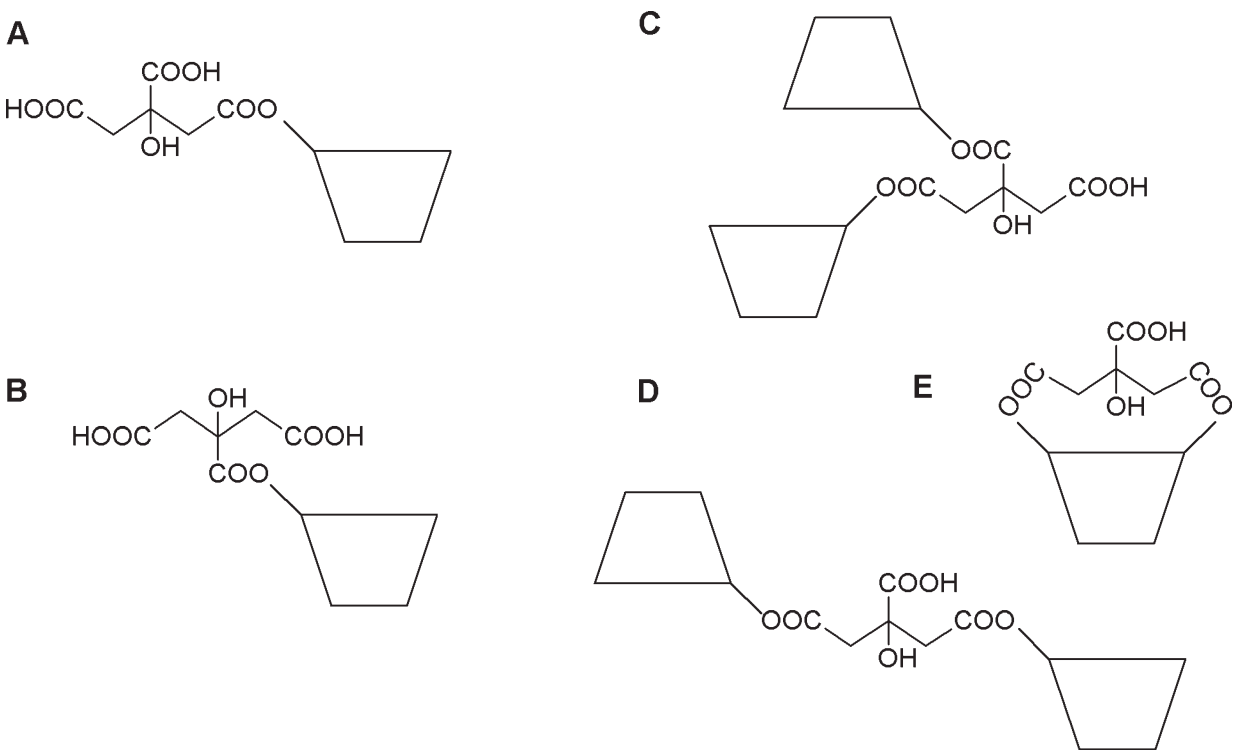

Figure 5 Schematic structures of (A,B) monoesters and (C,D,E) diesters of citric acid and CDs.

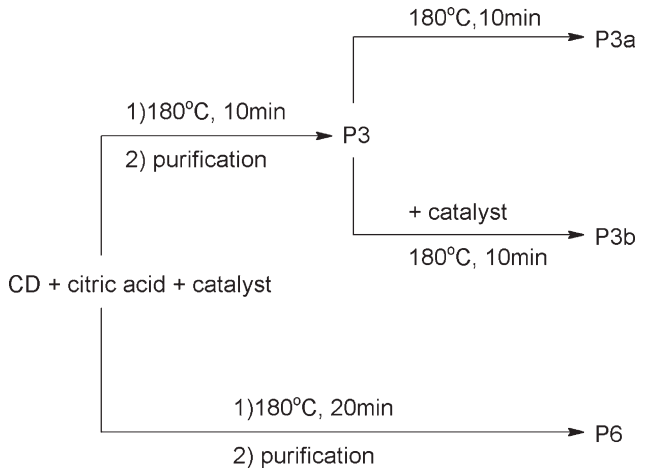

Figure 6 Overview of the thermal degradation of the CDP experiments.

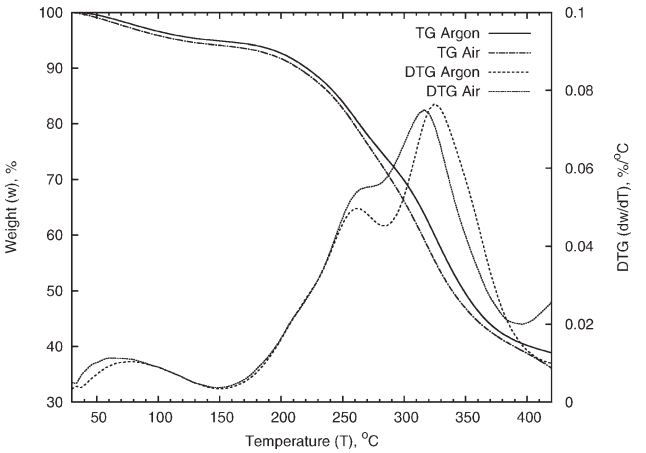

Figure 7 TG/differential TG curves of the polyester P3 in inert and oxidative atmospheres.

indirect product of the thermal decomposition of citric acid) detected in CDP might have been the result of citraconic and itaconic acids or the rearrangements of their esters.[28]

The relatively high amount of itaconic acid determined in the CDP samples may have been the consequence of a high concentration of itaconic anhydride in the reaction mixture or its high reactivity in the CD esterification reaction. Moreover, the CD esters could decompose (citric, *cis*-aconitic and *trans*-aconitic) or rearrange (citraconic) to itaconic derivatives.[11,28,31] The increase in both the reaction time and temperature may have been responsible for the acceleration of these processes.

Thermal decomposition of CDP

CDP chemical composition studies indicated a complex mechanism of polyester formation. The mechanism can be simplified to a few dependent paths: (1) the dehydration of citric acid to the anhydride followed by the esterification of CD, (2) the decomposition of citric acid to unsaturated acids and the esterification of CD by the formed derivatives, and (3) the thermal degradation of CD esters. The processes of the thermal degradation of CDP (path 3) were investigated by thermal analysis coupled with mass spectrometry (MS), and additionally, the chemical composition of the degraded samples of CDP was determined. An overview of the degradation experiments is shown in Figure 6.

A typical thermogram of polyester P3 in inert and oxidative atmospheres is shown in Figure 7. The thermal degradation had three main stages. The first one was below 140°C and was due to the loss of adsorbed water (~ 5%). The second and the third stages were at 150–280°C (20%) and 280–400°C (~ 40%), respectively, and indicated the degradation of the polyester. It was found that in an inert atmosphere, the temperature of CD degradation is 314°C;[32] this corresponds well to the location of the maxima of the third peak found for CDP. Therefore, this stage may have been result of the thermal degradation of CD units. The second weight loss could have been an effect of the following processes: the decarboxylation of the residual carboxylic groups, the formation of anhydrides from monoesters [Fig. 5(A)], and esterification reactions. The described course of the thermal degradation of CDP was also confirmed by the results of the thermogravimetry (TG)/MS experiments. As shown in Figure 8, during all of the decomposition stages, H_2O was released as a side product, and additionally, above 180°C, the formation of CO_2 was affirmed. On the basis of the course of the TG curves in air and inert atmospheres (Fig. 7), it was found that CDP was thermally stable up to 150°C, and above 250°C, the rate of the oxidative degradation processes became significant.

To examine the thermal degradation processes, a sample of polymer P3 was heated in air at 180°C for

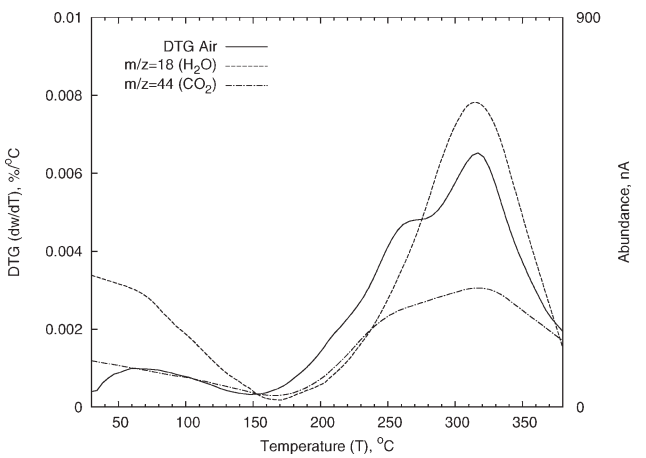

Figure 8 Differential TG/MS curves of the polyester P3 heated in an oxidative atmosphere.

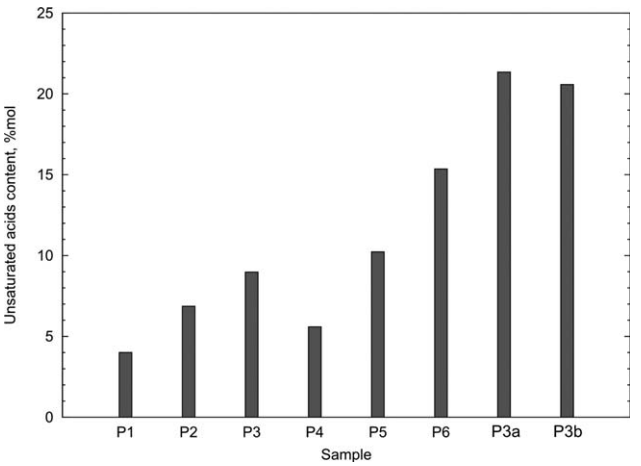

Figure 9 Unsaturated acid content as an indicator of the thermal degradation of CDPs. The content was calculated relatively to the total molar acid amount (a sum of citric and unsaturated acids).

10 min (sample P3a), and the chemical composition of the degraded CDP was determined [Fig. 3(B)]. Remarkable differences were observed in the carboxylic acid content of sample P3a compared with those of samples P3 and P6 [Fig. 3(A,B)]. The citric acid concentration was decreased, and a significant increase in citraconic acid was affirmed. Additionally, a small increase in the itaconic acid content was noticed. The amounts of *cis*-aconitic and *trans*-aconitic acids increased, too. In a manner similar to those of samples P1–P6, the formation of glutaconic derivatives during the thermal degradation of CDP was not observed. The heating of CDP caused a decrease in the citric acid concentration and the formation of unsaturated acids, especially citraconic acid. The *cis*-aconitic and *trans*-aconitic acids may have been produced by the dehydration of citric esters of CD; however, citraconic acid may have been formed by the decarboxylation of *cis*-aconitic and *trans*-aconitic esters or via the thermal rearrangement of itaconic esters.[11,28,31]

During the heating of the reagents mixture at 180°C for 20 min (polymer P6), *cis*-aconitic, *trans*-aconitic, and citraconic acid formation was less significant than during the heating of polymer P3. During the preparation of CDP, itaconic acid was a main byproduct; however, the heating of the polyester led to an increase in the *cis*-aconitic, *trans*-aconitic, and citraconic acid concentrations. This effect may have been caused by the presence of a catalyst in the reaction mixture, which was not present in the purified samples of the polyesters (e.g., P3). To examine the phenomenon, the chemical composition of sample P3 with the addition of the catalyst heated at 180°C for 10 min (sample P3b) was determined [Fig. 3(B)]. The carboxylic acid content was similar to that of polymer P3a, but significantly smaller amounts of *cis*-aconitic and *trans*-aconitic acids, and somewhat higher amounts of itaconic and mesaconic acids were affirmed. The citraconic acid content was also higher than that found in polymer P6. It seemed that the role of the catalyst (Na_2HPO_4) was to accelerate formation of cyclic anhydrides from the corresponding poly(carboxylic acid)s at the lower temperature.[33] For that reason, the catalyst may have inhibited the dehydration of tertiary hydroxyl groups in the citric monoesters; thus, decreases in the *cis*-aconitic and *trans*-aconitic acid contents in polyester P3b were observed. However, the catalyst seemed to have no influence on the formation of citraconic acid. It was not clear why the acid was produced in significantly higher amounts during the thermal degradation of CDP than during polymerization (the synthesis of CDP). The polymerization required the heating of the reagents above the melting point of citric acid; thus, the acid in the melted state was considered a reaction solvent. In this medium, the decomposition of the acid esters proceeded with different rates or via other mechanisms compared to the degradation of the pure polymer. This could explain the differences in the chemical compositions of polyesters P3a/P3b and P6.

Figure 9 shows the unsaturated acid content in CDP. It easy to see that the relative concentrations of this compounds increased with the polymerization temperature and time. The polyesters decomposed at temperatures above 150°C. For example, the heating of CDP at 180°C for 10 min led to an essential increase in the unsaturated acid concentration from 9 to 21% mol/mol for polyesters P3 and P3a, respectively. The amount of unsaturated acids became essential compared to that of citric acid, and the presence of the acids may change the physicochemical properties of the polyesters.

Mechanism of the crosslinking of CDP

CDP is a polyester containing citric and, in smaller amounts, *cis*-aconitic, *trans*-aconitic, citraconic, mesaconic, and itaconic acids. The acids can form diesters

TABLE II
Insoluble Polymer Fractions of the Polyesters Prepared from CD and Selected Carboxylic Acids

Carboxylic acid	Insoluble polymer fraction (%)
Citric acid	60
cis-Aconitic acid	11
trans-Aconitic acid	0
Citraconic acid	0
Mesaconic acid	0
Itaconic acid	4

Reactions conditions: temperature = 180°C, time = 10 min, molar feed composition = CD/acid/catalyst = 1 : 6 : 2.

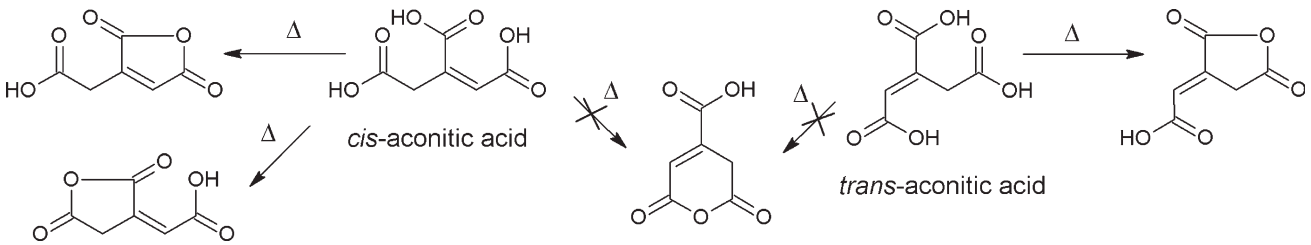

Figure 10 Thermal dehydration of *cis*- and *trans*-aconitic acids: the formation of five-membered cyclic anhydrides.[35]

and monoesters (Fig. 5), but only diesters are responsible for the crosslinking of the polymer. The ability of the carboxylic acids to form crosslinked polyesters with CD was investigated (Table II). The highest amount of water-insoluble polymer was obtained for citric acid, but also, *cis*-aconitic acid acted as a crosslinking agent. The reaction with *trans*-aconitic acid did not yield insoluble polyester. Dicarboxylic acids, except, unexpectedly, itaconic acid, were also not able to form water-insoluble polymers.

Citric acid has three carboxylic groups, and it can form two different anhydride five-membered rings, and therefore, two ester linkages may be formed.[34,35] For that reason, citric acid is an effective crosslinking agent for polyhydroxy compounds (e.g., CDs). Bifunctional carboxylic acids (e.g., citraconic, mesaconic, itaconic) are not able to form five-membered cyclic anhydride intermediates once their first carboxylic acid group esterifies;[35] therefore, crosslinking is not possible. *Cis*-aconitic and *trans*-aconitic acids are tricarboxylic acids and theoretically may form two five-membered anhydrides, similarly to citric acid. However, detailed study has shown that in opposition to *trans*-aconitic acid, only *cis*-aconitic acid has an appropriate geometry that permits the formation of two different cyclic anhydrides,[35] as shown in Figure 10. From this reason, we supposed that *cis*-aconitic acid was the crosslinking agents but *trans*-aconitic acid was not.

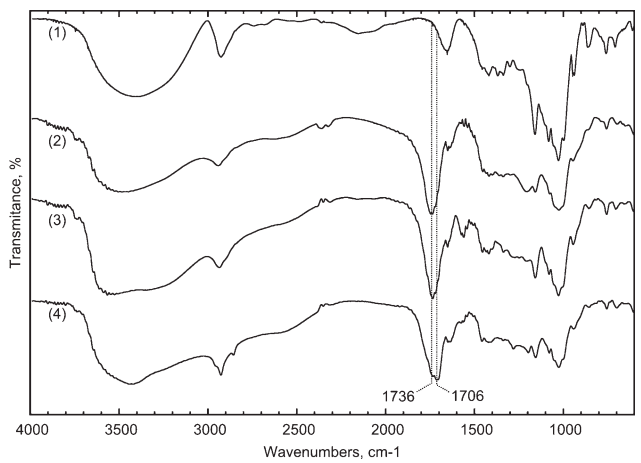

Figure 11 FTIR spectra of (1) CD and water-insoluble CD polyesters of the acids: (2) citric, (3) *cis*-aconitic, and (4) itaconic acids.

The crosslinking of CD by itaconic acid may have occurred by a radical ionic mechanism. Itaconic acid (or anhydride) could have undergone free-radical polymerization, and the carboxylic groups of the formed oligomer (polymer) served as linkers and may have esterified the CDs through a cyclic anhydride intermediate. The proposed mechanism was already used to explain the crosslinking of cellulose by itaconic acid and poly(itaconic acid).[36] On the other hand, it is well known that itaconic acid does not polymerize under the free-radical conditions commonly used for vinyl monomers. Homopolymerization requires a large amount of initiator (e.g., $K_2S_2O_8$) and takes a few dozen hours.[31,37–39] The phenomenon may explain the low yield of the CD–itaconic acid insoluble polymer (Table II). The FTIR spectra of the insoluble CD–carboxylic acid polyesters (Fig. 11) showed two strong peaks at 3550–3450 cm^{-1}, corresponding to O—H stretching vibrations of free hydroxyl groups in CD, and a sharp peak at 1736 cm^{-1}, indicating the formation of ester groups. Additionally, a band at 1706 cm^{-1} appearing in the FTIR spectra of the itaconic polyester suggested the presence of significant amounts of free carboxylic groups, probably from a poly(itaconic acid) linker.

Another possible mechanism of CDP crosslinking was a polycondensation process, which led to citric polyester formation, where the acid esterified itself through a tertiary hydroxyl group.[6,21,40,41] However, the hydrolysis of the polyester and chromatographic analysis of the products did not allow us to distinguish between the acid molecules that formed CD esters and those that were linked with the citric hydroxyl group. Therefore, the mechanism described previously could not be accepted or rejected.

Sorption properties of CDP

The CD content in CDP was estimated by two indirect methods based on methyl orange sorption and material balance. To decrease the interactions between the dye and free residual carboxylic groups of CDP, sorption measurements were carried out at pH 1. Additionally, to simplify the interpretation of the results, only host–guest interactions between methyl orange and CD were considered.

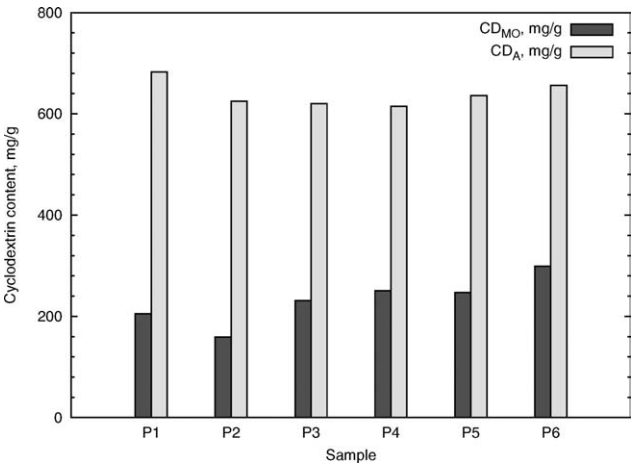

Figure 12 Comparison of CD_{MO} and CD_A for CDPs.

The sorption results are shown in Figure 12. CD_A and CD_{MO} varied in the 615–690 and 160–300 mg/g ranges, respectively. Changes in CD_A were negligible. The CD_{MO} values increased with elongation of the polymerization time at the same process temperature. The average values of CD_A and CD_{MO} were 650 and 250 mg/g, respectively. The reason for the significant difference probably lay in the limited accessibility of the CD cavity in the polyesters and the density of the polymer network.[42]

As it is known, CDs and citric acid can form 1 : 1 complexes with a binding constant of about 15.[43,44] The preparation of CDP required the dissolution of CD in the carboxylic acid solution. Under an excess of citric acid, almost all of CDs formed complexes with the acid. In other words, the polyester was prepared by the heating of the mixture of free citric acid and the CD–citric acid complex. The structure of the complex is not fully understood.[43,45] The CD–citric acid interaction probably relies on the ability of the tertiary hydroxyl group of the acid to modify the intramolecular and intermolecular hydrogen-bond system of CD.[43] The interactions occur, most likely, on the CD molecule surface; that is, citric acid might be coordinated in the outer sphere of CD.[45] Regardless of the details of the complex structure, the carboxylic group of citric acid molecule coordinated by CD could be close to the hydroxyl groups of CD. At elevated temperatures, it may favor the esterification of two near hydroxyl groups of CD by only one citric acid molecule [Fig. 5(E)], and thus, the formation of esters with sterically hindered CD cavities may occur. The resulting esters are not able to bind guest molecules.

The density of crosslinking, that is, the ratio of the size of the crosslinking agent molecule to the degree of CD substitution, is another key factor responsible for the sorption properties of CD polymers.[46] Recently, water-soluble CD polyesters prepared by polycondensation between difunctionalized poly(ethylene glycol) (PEG; number-average molecular weight $\approx$ 600 g/mol, length of the linker $\approx$ 13 ethylene oxide units) and CD were synthesized.[47] The polyesters contained 30–50% CD (the PEG/CD molar ratio = 2–4.5 : 1) and had binding properties as good as free CDs. The polymerization of CD with citric acid yielded a much denser polymer network, and the distance between CD molecules was estimated to be a length of one citric acid molecule. CDP contained about 70% CD and 30% citric acid (citric acid/CD molar ratio = 3 : 1). The ratio was similar to the PEG–CD polyester, but the sorption capacity of CDP was much lower than that of the PEG–CD polymer. This suggested that the length of crosslinking agent molecules had a bigger influence on the sorption properties of the CD polymers than the degree of CD substitution.

CONCLUSIONS

The chemical structure of CD crosslinked by citric acid was studied. The hydrolysis of the polyesters and chromatographic analysis of the hydrolysates gave quantitative information about the chemical composition of the polymers. The polyesters contained about 30–35% citric acid and 1–4% unsaturated carboxylic acids (i.e., itaconic, *cis*-aconitic, *trans*-aconitic, and mesaconic acids). The unsaturated acids were produced in the thermal decomposition of citric acid and the thermal decomposition of the citric esters of CD and esterified the CDs through anhydride intermediates. Only acids that formed two five-membered-ring anhydrides were effective crosslinking agents. Citric acid was responsible for the formation of a water-insoluble polyester, and also, to a negligible extent, *cis*-aconitic anhydride may have acted as a crosslinking agent. Itaconic acid was not able to form a five-membered cyclic anhydride intermediate once its first carboxylic acid group was esterified, but under the reaction conditions, it could polymerize through a radical mechanism that resulted in a crosslinked polyester.

The CD content in CDP was 60–70%, and 40% of the CDs were able to form inclusion complexes. 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.

CDPs start to decompose at 150°C in air and easily undergo hydrolysis in alkaline solutions. These two properties are major limitations to the use of CDP in, for example, textile applications. However, the improvement of the thermal and hydrolytic resistances of CDP will lead to promising, biobased polyesters with interesting properties.

The authors thank Dorota Majda from the Regional Laboratory for Physicochemical Analyses and Structural Research, Jagiellonian University (Poland), for thermogravimetric analysis.

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