Enhancing the Functionality of Biobased Polyester Coating Resins through Modification with Citric Acid

Bart A. J. Noordover,[†] Robbert Duchateau,[†] Rolf A. T. M. van Benthem,[‡] Weihua Ming,[‡] and Cor E. Koning*,[†]

Laboratory of Polymer Chemistry and Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, Den Dolech 2, 5600 MB Eindhoven, The Netherlands

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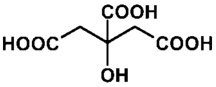
Citric acid (CA) was evaluated as a functionality-enhancing monomer in biobased polyesters suitable for coating applications. Model reactions of CA with several primary and secondary alcohols and diols, including the 1,4:3,6-dianhydrohexitols, revealed that titanium(IV) *n*-butoxide catalyzed esterification reactions involving these compounds proceed at relatively low temperatures, often via anhydride intermediates. Interestingly, the facile anhydride formation from CA at temperatures around CA's melting temperature (T_m = 153 °C) proved to be crucial in modifying sterically hindered secondary hydroxyl end groups. OH-functional polyesters were reacted with CA in the melt between 150 and 165 °C, yielding slightly branched carboxylic acid functional materials with strongly enhanced functionality. The acid/epoxy curing reaction of the acid-functional polymers was simulated with a monofunctional glycidyl ether. Finally, the CA-modified polyesters were applied as coatings, using conventional cross-linking agents. The formulations showed rapid curing, resulting in chemically and mechanically stable coatings. These results demonstrate that citric acid can be applied in a new way, making use of its anhydride formation to functionalize OH-functional polyesters, which is an important new step toward fully biobased coating systems.

Introduction

Various monomers with a rigid structure, which are suitable for polycondensation chemistry, are available from renewable resources.[1,2] With rigid biobased starting materials such as isosorbide, aliphatic polymer resins with high T_g values can be synthesized that can replace traditional terephthalic acid based polyesters. In this way, sustainable polymers are designed by replacing conventional monomers from fossil resources by biobased alternatives. In addition, the new polymers might have improved properties. For example, aromatic polyesters are prone to yellowing when exposed to UV light.[3–5] Fully aliphatic systems are expected to perform better in this respect. One of the main goals of our research is to formulate, synthesize, and characterize fully renewable polyesters that are designed to be suitable for, for example, thermoset coating applications. An important class of coating systems are thermoset powder coatings. Such systems often contain polyesters of moderate molecular weight as binder resins. These resins are coextruded with curing agents and additives (such as flow agents, degassing agents, and catalysts) and are subsequently ground to fine powders. Electrostatic application of the powder onto the substrate is followed by thermally induced flow and curing, occurring simultaneously in a curing oven. Conventional polyesters for such applications are based on bifunctional monomers such as terephthalic acid, isophthalic acid, adipic acid, neopentyl glycol, and ethylene glycol. In order to obtain a fully cured network, these polymers are designed to have at least two functional groups per chain. To increase the functionality of the polyester, polyfunctional monomers are added, such as trimellitic anhydride, trimethylolpropane, or pentaerythritol.[6]

Scheme 1. Chemical Structure of Citric Acid (or 2-Hydroxy-1,2,3-propanetricarboxylic Acid)



In a recent paper we describe aliphatic co- and terpolyesters based on isosorbide and succinic acid.[7] Said materials have properties that meet the requirements for the type of systems described above. When an attempt was made to synthesize carboxylic acid functional materials, some difficulties were encountered. The limited reactivity of the isosorbide end groups restricts conversion into acid-functionalized polyesters. However, we have observed that modifying linear OH-terminal polyesters with citric acid (CA) does yield acid-functional polyesters with significantly enhanced functionality that, after curing with conventional, multifunctional epoxy curing agents and β-hydroxyalkylamides, afforded coatings with good chemical and mechanical stability. These promising preliminary results indicate that CA might be a very useful polyfunctional monomer, which can be seen as an aliphatic and sustainable alternative for trimellitic anhydride.

Citric acid (CA) is produced commercially via fermentation, with an approximate annual production of 7 × 10^5 tons.[8] CA (Scheme 1) has two primary and one tertiary carboxylic acid groups, the latter obviously being less reactive than the primary acid groups. In addition, it contains a sterically hindered tertiary hydroxyl group.[9] This low cost monomer is a solid at room temperature and has a melting temperature of 153 °C.

CA has been utilized by different authors to esterify or cross-link starch, cellulose fibers, or corn fibers.[10–16] Several publications describe the synthesis of biodegradable polyester networks based on CA, in combination with polyol moieties such as glycerol, gluconolactone, sorbitol, linear aliphatic alcohols, and

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* To whom correspondence should be addressed. E-mail: c.e.koning@tue.nl. Phone: +31-40-2475353. Fax: +31-40-2463966.

[†] Laboratory of Polymer Chemistry.

[‡] Laboratory of Materials and Interface Chemistry.

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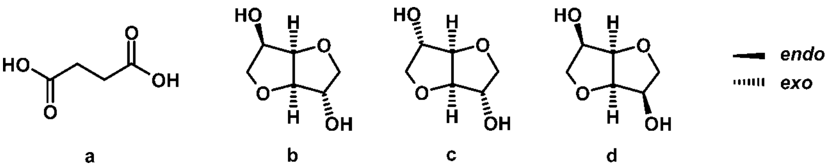
Scheme 2. Chemical Structures of (a) Succinic Acid (SA), (b) Isosorbide (IS), (c) Isoidide (II), and (d) Isomannide (IM)



poly(ethylene glycol)s.[9,17–22] Reaction temperatures vary but are usually in the range between 120 and 180 °C. Acid-functional, water-soluble polyester resins based on citric acid and alkylene oxides (e.g., propylene oxide) have been synthesized at 150 °C. These polyesters were cured with melamine resins.[23] Low T_g copolyesters of succinic acid and 1,4-butanediol combined with CA, present as a comonomer during the polycondensation carried out at 170–200 °C, were described.[24]

As opposed to many of the papers described above, we do not aim to use CA itself as a cross-linking agent but rather as a polyfunctional modifier to transform polyesters with OH functionalities of moderate reactivity into novel, reactive, acid-functional polymers. By doing so, carboxylic acid functional, fully biobased polyesters can be made, with the proper characteristics for thermoset coating applications. Ideally, by reacting with only one of its carboxylic acid groups, CA would be introduced at the polyester chains ends. This new method of modification with CA should not lead to cross-linking and the polyester resin should have appropriate flow properties at T_{cure} as well as sufficient functionality as well as reactivity to contribute to the network formation upon curing. The remaining two carboxylic acid groups of CA are to react with the curing agent during the final step of the powder coating process, to form the completely cross-linked network. Due to the high reaction temperatures (up to 230 °C) and the limited thermal stability of CA, we cannot introduce CA during the initial synthesis of the OH-functional polyester. In addition, solvents are not to be used in the preparation of powder coatings resins, so modification in solution is not an option either.

In this paper, citric acid is evaluated as a functionality-increasing agent for biobased polyesters, used in coating applications. First of all, the thermal stability of CA during polyester modification and curing was assessed. Reactions of CA with several primary alcohols and secondary diols were investigated using NMR and FTIR spectroscopy with the aim to gain more insight into the mechanism of the chemical modification of OH-functional polyesters with CA in the melt. In addition, the subsequent curing reaction of the CA-modified polymers with epoxy cross-linkers was studied in detail, followed by coating evaluation.

Experimental Section

Materials. Isosorbide (polymer grade Polysorb P, 98.5+ %) and isoidide (99.8%) were obtained as gifts from Roquette Freres. Isomannide (97+ %) was a gift from Agrotechnology and Food Innovations. Citric acid (anhydrous, 99+%), citric acid-*1,5*-$^{13}C_2$, citric acid-*2,4*-$^{13}C_2$, *cis*-aconitic anhydride, trimethyl citrate, 1-butanol, *tert*-butyl glycidyl ether, and triglycidyl isocyanurate (TGIC) were purchased from Aldrich. Succinic acid and titanium(IV) *n*-butoxide were bought from Acros Organics. 1,4-Butanediol was obtained from Merck. DMSO-d_6 was bought from Campro Scientific. *N,N,N′,N′*-Tetrakis(2-hydroxyethyl)adipamide (trade name Primid XL-552) was obtained as a gift from EMS Chemie. Araldite PT912 (a mixture of triglycidyl trimellitate and diglycidyl terephthalate) was bought from Huntsman. Irganox HP2921, a mixture of phenolic and phosphonic antioxidants,[25] was a gift from Ciba Specialty Chemicals. All chemicals were used as received.

Reactions of CA with 1-Butanol or Several Diols. CA was reacted with 1-butanol and several diols according to the following procedure, described for isoidide: Citric acid (15.93 g, 83 mmol), isoidide (6.06 g, 41 mmol), $Ti(OBu)_4$ (0.02 mol % relative to isoidide), and Irganox HP2921 (0.16 g) were weighed into a 50 mL three-neck round-bottom flask. The flask was fitted with a Vigreux column and a Dean–Stark type condenser to collect the condensation product. An inert atmosphere was created by repeated vacuum/inert gas flushing cycles. Afterward, the system was left open under a continuous inert gas flux, avoiding contact with oxygen. While being stirred magnetically, the reaction mixture was heated by means of an oil bath to the required reaction temperature. Reaction times were measured from the moment a clear, homogeneous melt was obtained ($t = 0$). The maximum reaction temperature was 160 °C.

CA Modification of Hydroxyl Functional Polyesters. Previously synthesized linear OH-functional polyesters,[7] based on isosorbide and succinic acid, were reacted with CA to obtain polyesters with carboxylic acid end groups. A typical example was performed as follows: 52.9 g of an OH-functional polymer ($\overline{M}_n = 2200$ g/mol, acid value = 1.5 mg of KOH/g, hydroxyl value = 65.0 mg of KOH/g) and 1.1 molar excess of CA (calculated relative to the amount of OH groups per gram of polyester sample, determined by titration) were charged to the reactor. The temperature was increased slowly up to 170 °C ($T_{\max}$), leading to a clear melt. After the reaction mixture was stirred under inert gas flush for 2.5 h, processing was continued in vacuo for 3 h. Subsequently, the clear melt was discharged from the reactor and allowed to cool. For NMR characterization, some experiments were performed on a small scale, using the following ^{13}C-labeled CA compounds: citric acid-*1,5*-$^{13}C_2$ or citric acid-*2,4*-$^{13}C_2$.

Curing of Carboxylic Acid Functional Polyesters. Carboxylic acid functional polyesters were cured with triglycidyl isocyanurate (TGIC), *N,N,N′,N′*-tetrakis(2-hydroxyethyl)adipamide (Primid XL-552) or a mixture of diglycidyl terephthalate (60 wt %) and triglycidyl trimellitate (40 wt %). Curing from solution proceeds as described in the following example: a solution of 0.3–0.5 g of polyester and 1.05 mol equiv of the cross-linker (calculated from COOH value, determined by titration) in 1 mL *N*-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto the aluminum substrate. The film was left to dry at room temperature, followed by curing at 180 °C during 10 min under nitrogen. Coatings were also applied through a powder-coating process, which typically proceeds as follows: A CA-modified polyester was coextruded with the curing agents in a 1 to 1 ratio at approximately 90 °C, using a twin-screw miniextruder. In addition, 1.5 wt % flow agent (Resiflow PV5) and 0.75 wt % degassing agent (benzoin) were added to the formulation. The obtained extrudate was ground to particles smaller than 90 μm and powder coated onto an aluminum gradient panel using corona spraying, followed by curing in a gradient oven at temperatures ranging from 100 to 250 °C.

Measurements. Size exclusion chromatography (SEC) analysis was carried out using a setup equipped with a Shimadzu LC-10AD pump and a Waters 2414 differential refraction index detector (at 35 °C). Injections were done by a MIDAS autoinjector, the injection volume being 50 μL. PSS (2* PFG-lin-XL, 7 μm, 8 × 300 mm, 40 °C) columns were used. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was used as eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR (proton decoupled) spectra were obtained using a

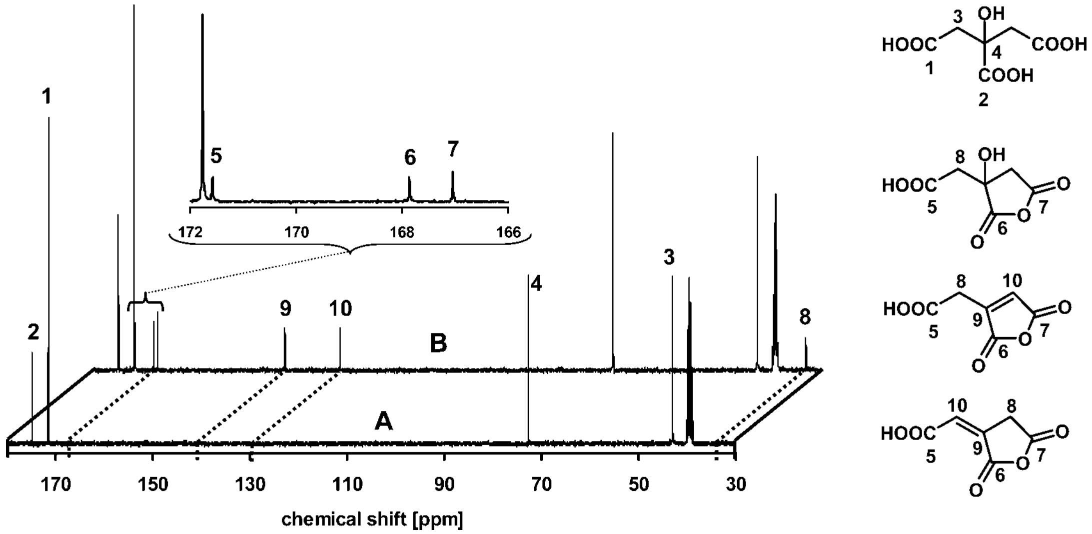


Figure 1. ^{13}C NMR spectra of (A) citric acid and (B) citric acid and degradation products after heat treatment of CA during 2 h at 180 °C including possible structures and peak attributions.

Varian Mercury Vx (400 MHz) spectrometer, DMSO-d_6 was used as the solvent (unless stated otherwise). Signal assignments of CA anhydride derivatives were partly determined by comparison with the ^{13}C NMR spectrum of *cis*-aconitic anhydride (obtained commercially), which also contains peaks caused by *trans*-aconitic anhydride, due to the spontaneous isomerization of *cis*-aconitic anhydride.[26,27] Differential scanning calorimetry measurements were carried out with a DSC Q100 from TA Instruments. Potentiometric titrations, used to determine acid and hydroxyl values, were carried out as reported in a previous publication.[7] Attenuated total reflection Fourier-transform infrared spectrometry (ATR-FTIR) was performed on a Bio-Rad Excalibur FTS3000MX spectrophotometer. A golden gate setup was used, equipped with a diamond ATR crystal. The resolution was 4 cm^{-1}. Cross-linking and coating performance at room temperature were evaluated using several characterization methods: acetone rub test (solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs, the coating has good acetone resistance), reverse impact test (a rapid deformation test, performed by dropping a certain weight (in kg) on the back of a coated panel from a certain height (in cm), described in ASTM D 2794), and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained cured coatings were measured using a magnetic induction coating thickness meter (Twin-Check by List-Magnetik GmbH).

Results and Discussion

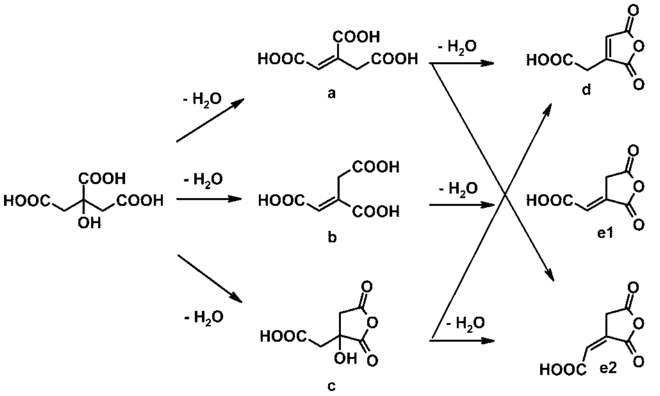
The polymers used for this study are fully renewable aliphatic polyesters based on succinic acid combined with the 1,4:3,6-dianhydrohexitols (1,4:3,6-dianhydro-D-glucitol or isosorbide, 1,4:3,6-dianhydro-L-iditol or isoidide, and 1,4:3,6-dianhydro-D-mannitol or isomannide), derived from starch (Scheme 2). The big advantage of IS, II, and IM is their rigid structure, which affords high T_g polymers,[28–32] even for the relatively low molecular weights typically required for coating resins. Their hydroxyl groups have either the endo or the exo orientation, which causes differences in reactivity due to steric effects and internal hydrogen bonding. In general, the exo-oriented OH groups are more reactive in esterification reactions.[33–35]

These polyesters mainly have secondary hydroxyl end groups, since they are synthesized using an excess of the 1,4:3,6-dianhydrohexitols, relative to the diacid used. We have previously shown that it is not possible to make purely COOH functional linear polyesters just by adding an excess of succinic acid during resin synthesis.[7] Especially the endo-oriented hydroxyl groups of isosorbide and isomannide prove difficult to esterify at high conversions (and low acid concentrations). Only with activated diacid species, such as succinic anhydride or succinyl chloride, it has been possible to synthesize polyester chains with predominantly carboxylic acid end groups. However, the maximum functionality F_n obtainable by this method is $F_n = 2$.

Thermal Stability and Reactivity of Citric Acid. For conventional, nonrenewable polyesters, trimellitic anhydride, an aromatic, trifunctional carboxylic acid compound, is often used as a branching agent. This monomer can be directly added during resin synthesis and can withstand the high temperatures (i.e., temperatures up to 250 °C) reached during the production process. CA, however, generally cannot be added directly during polycondensation due to its limited thermal stability as CA is prone to dehydration and decarboxylation at elevated temperatures. These side reactions start to take place at an appreciable rate above 180 °C. One could think of using trimethyl citrate in the polycondensation or modification reaction, since this compound has a higher thermal stability (analogous to using dimethyl terephthalate in conventional polyester synthesis).[36] However, the aim is to make a polymer with free carboxylic acid groups at the chain end, which will not be obtained when using the trimethyl ester of CA.

Figure 1 shows the ^{13}C NMR spectra of CA before and after a heat treatment of 2 h at 180 °C in bulk under a slight argon purge. During this treatment, formation of water as well as of CO_2 (the gas flux was bubbled through an aqueous solution of calcium hydroxide) was observed, suggesting that both dehydration and decarboxylation took place. In the ^{13}C NMR spectrum of the thermal degradation product(s), a new aliphatic carbon signal appears at 33.2 ppm (C8). In addition, peaks at 129.3 ppm (C10) and 140.7 ppm (C9) can be assigned to olefinic carbon atoms. Finally, a signal attributed to carboxylic acid carbonyls is observed at 171.6 ppm (C5) and resonances corresponding to anhydride carbonyls are visible at 167.0 ppm (C7) and 167.9 ppm (C6) (see inset Figure 1). The first steps in the thermal degradation of CA are the formation of citric acid anhydride (Scheme 3, structure c) or the dehydration of the β-hydroxyl group to form *cis*- or *trans*-aconitic acid (structures a and b). Subsequently, these compounds can lose a second

Scheme 3. Initial steps in the thermal degradation of citric acid, with (a) *cis*-aconitic acid, (b) *trans*-aconitic acid, (c) citric acid anhydride, (d) *cis*-aconitic anhydride, and (e1/e2) *trans*-aconitic anhydrides, *E*/*Z* configuration[37,38]



molecule of water, affording *cis*- or *trans*-aconitic (*E*/*Z* configurations) anhydrides (structures d and e1/e2). For a more extensive degradation scheme, see the Supporting Information (Scheme S1).[13,18,37–39]

Structures a, b, d, and e correspond especially well to the observed signals in Figure 1, plot B, that is, the three new carbonyl peaks, the two olefinic signals, and the new aliphatic carbon signal. In Figure 1, these four structures are displayed with possible peak assignments. Peaks 6 and 7 show shifts which can correspond to carboxylic acids, anhydrides, or ester carbonyls. Since only CA was used during the experiment, ester formation could only occur through the reaction of a CA moiety with the tertiary OH of another CA molecule. This is unlikely to occur at an appreciable rate.[40] It is therefore most probable that these signals are caused by acid and/or anhydride species formed from CA by dehydration.

The amounts of *cis*-aconitic acid/anhydride (11%) and *trans*-aconitic acid/anhydrides (12%) present in the sample upon thermal degradation were similar, as determined from ^{1}H NMR data. Other identified degradation products such as itaconic acid (~4%), citraconic acid (~3%), and 3-hydroxyglutaric acid (~2%) or the corresponding anhydrides confirmed that decarboxylation had also taken place, but to a lesser extent than dehydration (see Supporting Information, Figure S1). It should be noted that the aconitic derivatives, formed through dehydration, all contain three carboxylic acid equivalents (either as the free acid or as an anhydride), while the other degradation products formed through decarboxylation have two acid equivalents per molecule. Hence, partial thermal degradation of CA will only result in a somewhat lower functionality of the final resin (minimum: $F_n = 2$) but will never lead to deactivated chains.

To confirm the formation of anhydrides, ATR-FTIR spectra were recorded as a function of time at isothermal heating (170 °C). In Figure 2, the spectra of the measurements at $t = 0$, $t = 2$ min, $t = 10$ min, and $t = 25$ min are given.

At $t = 0$ (A), there is a strong absorbance at 1710 cm^{-1}, due to the hydrogen-bonded CA carboxylic acid carbonyls. In time, the peak maximum shifts to 1735 cm^{-1}, attributed to free carboxylic acid carbonyls. Simultaneously, the development of two bands at 1855 and 1770 cm^{-1} is observed, which are characteristic for the symmetric and the asymmetric stretching vibrations of cyclic anhydrides, respectively.[41,42] At the same time, two bands appear at 984 and 892 cm^{-1}, caused by the stretching modes of the C–O–C linkages of the anhydrides. After approximately 25 min at 170 °C, the anhydride band at 1770 cm^{-1} (Figure 2D) has become the strongest band in the spectrum, indicating that large amounts of anhydrides had been formed. In addition, broad absorption bands appear between 1650 and 1550 cm^{-1}, which indicates the formation of unsaturated structures. These results support the proposed mechanisms of citric acid anhydride and aconitic anhydride formation (Scheme 3).

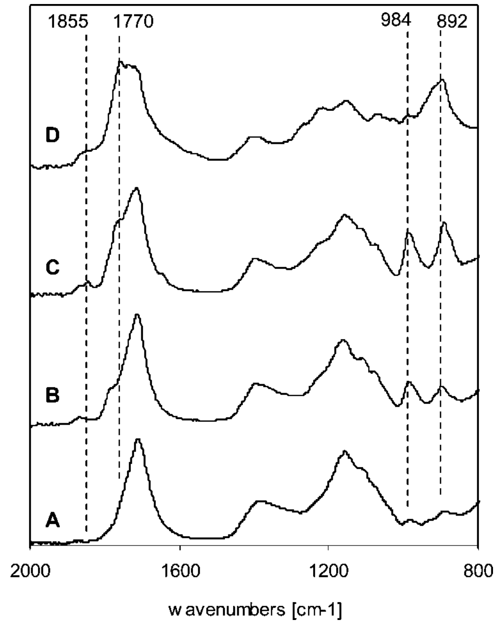


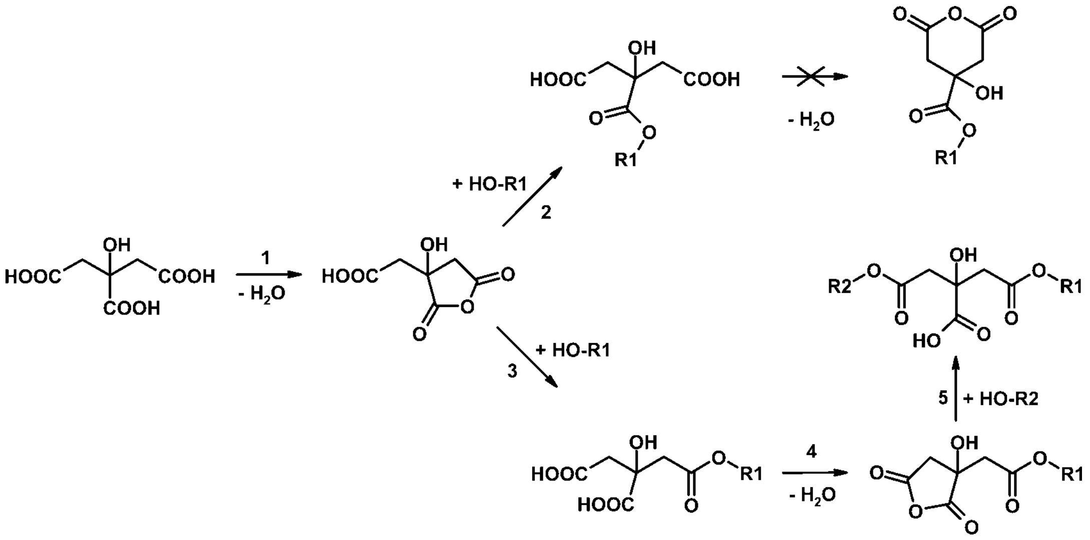
Figure 2. FTIR spectra of CA heated isothermally at 170 °C at (A) $t = 0$, (B) $t = 2$ min, (C) $t = 10$ min, and (D) $t = 25$ min.

Although thermal degradation seems detrimental for polymer functionalization, this is not necessarily the case. The anhydrides formed during CA degradation are more reactive than CA itself and react even with deactivated, sterically hindered secondary alcohols. Ironically, the thermal instability of CA facilitates its use at relatively low temperatures: high enough to form reactive anhydrides but low enough to prevent extensive formation of unsaturated structures. CA-derived anhydrides are already formed at temperatures between 140 and 160 °C. At such temperatures, the SA/IS-based polyester systems under investigation form a melt with sufficiently low viscosity, so that CA can be added and incorporated into the polymer melt without using solvents. In the ideal case, only citric acid anhydride is formed through the dehydration of CA. The formation of this asymmetric cyclic anhydride and its subsequent esterification are shown in Scheme 4. The citrate end group resulting from reaction 3 can again form a cyclic anhydride and react once more (reactions 4 and 5).

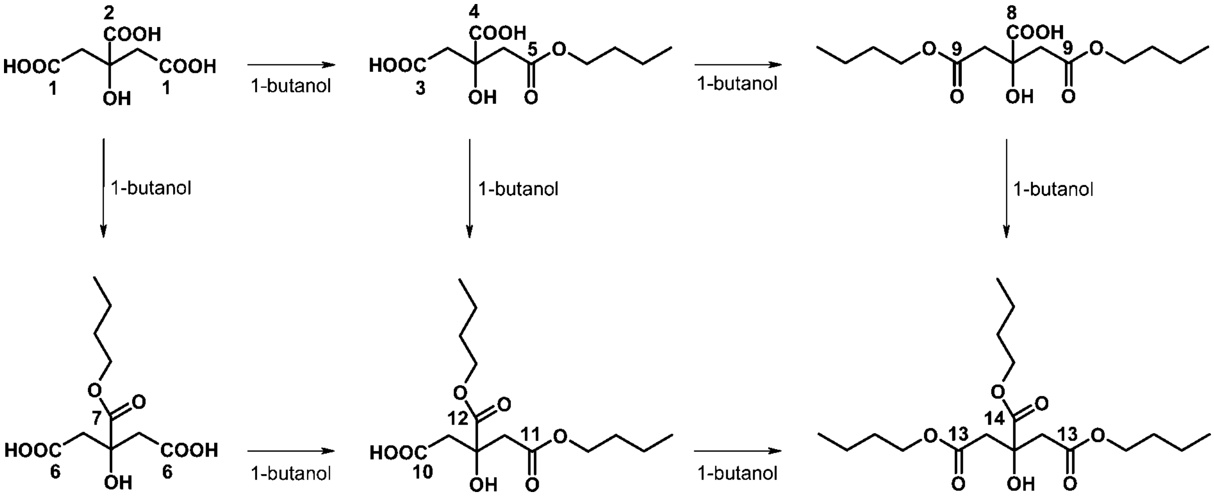
The formation of a symmetric six-membered cyclic anhydride[43] from CA (other than the degradation product glutaconic anhydride, see Supporting Information, Scheme S1, structure k) upon heating is not described in literature and we have no indications that a similar compound is formed after esterification of the tertiary carboxylic acid group of CA (reaction 2). This means that such a six-membered anhydride is either not formed or very reactive and therefore not observed. If a six-membered anhydride is not formed after reaction 2 has taken place, subsequent ester formation of the two remaining primary carboxylic acids might be more difficult.[15]

Model reactions of citric acid with different diols. Since we want to use CA to end-cap linear 1,4:3,6-dianhydrohexitol-based polyesters, it was necessary to determine if the secondary OH groups of the 1,4:3,6-dianhydrohexitols are sufficiently

Scheme 4. Citric Acid Anhydride Formation, followed by its Esterification[13]



Scheme 5. Reaction of CA with Butanol via Esterification[a]



[a] Intermediate anhydride formation as well as possible reactions of the tertiary hydroxyl functionality of CA have been omitted for clarity.

reactive toward esterification with CA or its anhydrides at temperatures between 150 and 170 °C. In addition, it was important to establish how readily more than one acid functionality of a single CA moiety would react. If one CA molecule reacts with two or even three polyester hydroxyl end groups, chain extension, branching or even cross-linking might occur. Model reactions between CA and 1-butanol as well as the diols IS, II, and IM and 1,4-butanediol (BD) were carried out to monitor ester formation and conversion in time. Due to the volatility of some of the monomers, water could not be actively removed from the reaction mixture by applying vacuum. However, the reactions were performed in open systems under a slight inert gas flux, allowing for some water to evaporate from the reactor. Before we elaborate on the differences in reactivity between the several diol compounds, the less complex ^{13}C NMR spectrum of the reaction between 1-butanol and CA will be discussed in more detail.

^{13}C NMR shifts of carbonyls are highly sensitive to even small changes in the molecule and form a very useful probe to monitor anhydride formation, esterification, and/or degradation of CA. As already mentioned, CA gives two resonances in the carbonyl region of the ^{13}C NMR spectrum: one assigned to the primary carbonyls at the 1 and 5 positions (Scheme 5, No. **1**) and one assigned to the tertiary carbonyl carbon atom (Scheme 5, no. 2). When one of the carboxylic acid groups of CA has been esterified (in this case with the OH group of 1-butanol), the chemical shifts of the two remaining carboxylic acid carbonyl signals are affected noticeably. The same can be said for the resulting ester carbonyl signals. The various possible carbonyl species depicted in Scheme 5 can therefore be found to cause separate signals in the NMR spectrum, as demonstrated in Figure 3. The signals are clustered in four groups of either carboxylic acid or ester carbonyl carbon atoms, as already described by others.[19,22] A 3-fold molar excess of 1-butanol (relative to CA, so the overall 1-butanol/COOH molar ratio is 1:1) was added, to make sure that even (part of) the least reactive tertiary acid groups of CA would react. This was necessary to visualize and identify all the 14 different possible carbonyl resonances which might occur in the ^{13}C NMR spectra for the reaction performed (Scheme 5 and Figure 3). The intensities of the observed signals support the peak assignments. No olefinic signals characteristic for aconitic acids/anhydrides were found, indicating that these species were not formed at 150 °C. Anhydride signals assigned to citric acid anhydride were absent as well, suggesting either that this reactive anhydride species was not formed or that it was rapidly converted to esters by reaction with the primary OH groups of 1-butanol. To see if anhydrides are formed at 150 °C, CA was isothermally heat

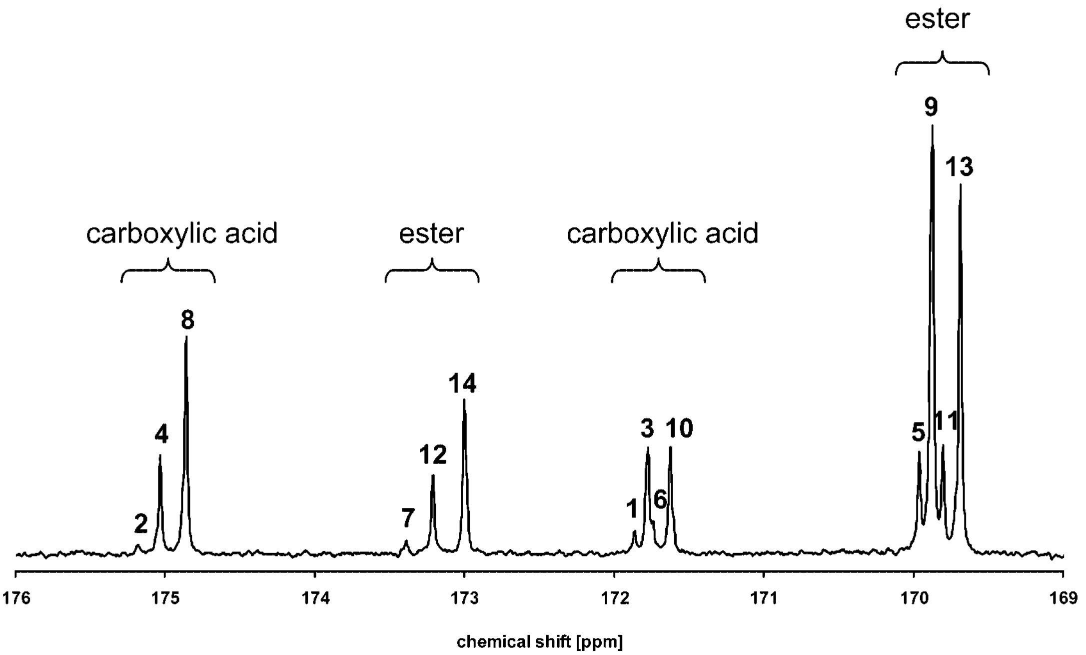


Figure 3. Carbonyl region of the ^{13}C NMR spectrum of the product of the reaction between CA and 1-butanol (ratio CA:1-butanol = 1:3, T_{max} = 150 °C, t = 450 min). Peak labels in Figure 3 refer to the structures in Scheme 5.

at this temperature while measuring FTIR spectra as a function of time. Although significantly slower than at 170 °C, the formation of anhydrides was observed in a similar way as demonstrated before. The absence of anhydride peaks in the NMR spectrum suggests that the reaction of these in situ generated anhydrides with 1-butanol is fast and complete. At the same time, the absence of olefinic signals suggests that no or hardly any aconitic derivatives or other unsaturated species are formed at these temperatures. This is beneficial, since unsaturated species can lead to UV instability (and therefore yellowing) of the final coatings.

Conversion of the carboxylic acid groups was estimated by integration of the clusters of acid and ester peaks. The tertiary acids showed a lower conversion (~43%) than the primary acid groups (~80%), which was in line with the expectations. This means that in total approximately 68% of the carboxylic acid groups have reacted with 1-butanol. From ^{1}H NMR, the conversion of 1-butanol was determined to be 76%. The slight discrepancy between the determined COOH and OH conversions can be explained by the underestimation of ester formation from the ^{13}C NMR spectrum, caused by the inaccuracy of the integration of such spectra.

Reactions between CA and several diols were subsequently carried out. To mimic the ratio used to modify a linear polymer chain with 2 hydroxyl end groups, the molar ratio CA:diol was 2:1. The reactions were performed following a standard procedure (see Experimental Section) at a maximum temperature of 160 °C, in order to minimize thermal degradation of CA. Diol conversions were determined from ^{1}H NMR spectra. The results obtained after 170 min at 160 °C are given in Table 1. Conversion values for the differently oriented OH groups of the 1,4:3,6-dianhydrohexitols are specified as well.

There is a significant difference between the conversions of the endo and exo hydroxyl groups. After 170 min of reaction, the exo-oriented OH-functionalities show conversions that are approximately 10% higher than for their endo counterparts. Such differences were also observed in polymerization reactions between the different 1,4:3,6-dianhydrohexitols and succinic acid. This means that the (nearly) complete CA modification of IM- or IS-based polyesters will require longer processing times than the modification of II-based polyesters. Also, from the relatively low conversions we can conclude that vacuum processing is required to actively remove water from the reaction mixture. As expected, the primary OH groups of 1,4-butanediol react faster, showing a conversion of 91% after 170 min at 160 °C.

Table 1. Conversion Values for the OH Groups of IS, II, IM, and 1,4-Butanediol (BD) after 170 min of Reaction with CA at 160 °C

		OH conversion (%)		
experiment	feed composition	endo	exo	total OH conv (%)
A	CA:IS 2:1	73	81	77
B	CA:II 2:1		84	84
C	CA:IM 2:1	72		72
D	CA:BD 2:1			91

The carbonyl regions of the ^{13}C NMR spectra of reactions A−D again encompass four distinct clusters of resonances, attributed to either carboxylic acid or ester carbonyl carbon atoms (see Supporting Information, Figure S2). It is clear that the carboxylic acid peaks are more intense than the ester peaks, indicating that significant amounts of free carboxylic acid groups are still present after 170 min of reaction. With the ratio carboxylic acid:hydroxyl being 3:1, the conversion of the carboxylic acid groups was expected to be approximately 33% at full OH conversion. The following values for carboxylic acid conversions were estimated from the ^{13}C NMR spectra of the experiments A−D: A, 25%; B, 26%; C, 17%; D, 26%. Again, these values are lower than those expected based on the OH conversion in Table 1, but they are within the right order of magnitude.

Interestingly, signals of citric acid anhydride and/or aconitic acid/anhydride were observed in the ^{13}C NMR and ^{1}H NMR spectra of reactions A–D (in the presence of diol) after 170 min at 160 °C, amounting to approximately 3–6% of the initial amount of CA (determined from the ^{1}H NMR spectra). When heating CA at 180 °C without adding diol monomers, we observed approximately 22% of anhydride. The fact that we

Table 2. Characteristics of CA-Modified Polymers

polyester	feed composition	composition (NMR)	T_g (°C)	$\overline{M}_n$ [b](g/mol)	PDI	av (mg of KOH/g)	OHV (mg of KOH/g)
I	SA/IS [1:1.14]	SA/IS [1:1.09]	56.5	3000	2.0	1.5	65.0
II	OH: CA [1:1.1][a]	SA/IS/CA [1:1.11:0.2]	68.7	3500	2.3	108.3	65.2
III	OH: CA-*1,5*-$^{13}C_2$ [1:1.1][a]	SA/IS/CA-*1,5*-$^{13}C_2$ [1:1.11:0.19]	64.6	3800	2.3	n.d.[c]	n.d.[c]
IV[d]	SA/IS/CA [1:1.13:0.29]	SA/IS/CA [1:1.09:0.2]	59.0	2200	2.7	101.8	65.2

[a] The amount of citric acid added to the OH-functional polyesters was based on OHV data of these polymers. [b] Determined by SEC in HFIP, calibrated with PMMA standards. [c] Not determined, since not enough material was available to carry out titration experiments. [d] Synthesized on a 300 g scale. The CA modification was performed directly upon synthesis of the OH-functional precursor; the latter intermediate was therefore not isolated.

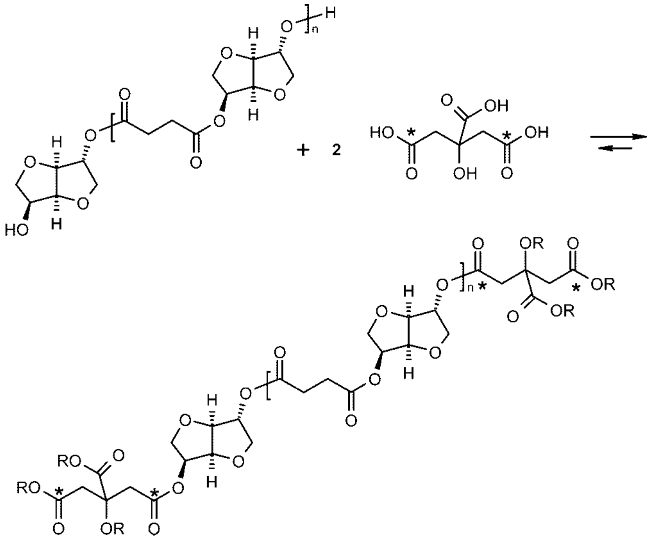
observe much lower levels of anhydrides when heating CA with diols present suggests that the anhydride esterifies rapidly. In order to verify this observation, FTIR model experiments were carried out, in which 2 equiv of CA was reacted with 1 equiv of isoidide, to monitor anhydride levels as well as ester formation and disappearance of OH groups. Anhydride bands appear at 1855 and 1770 cm^{-1} (symmetric and asymmetric stretching of cyclic anhydride carbonyls) as well as at 981 and 892 cm^{-1} (C−O−C stretching). After having reached a certain level, the amount of anhydrides seems to stay constant. At the same time, the carboxylic acid bands show a shift from 1712 cm^{-1} (H-bonded carboxylic acid carbonyl) to 1734 cm^{-1} (free carboxylic acid carbonyl). The carboxylic acid and the ester carbonyl bands overlap at approximately 1720 cm^{-1}.[42] The esters also have a strong band at 1171 cm^{-1}. However, here there is overlap with the aliphatic ethers present in isoidide. When the same experiment is performed with a CA:II ratio of 1:3, only low levels of anhydride formation are observed and the anhydride absorption bands disappear at high conversion, indicating that the anhydrides have esterified with isoidide. This also becomes clear from the strong increase of the intensity of the ester bands at 1171 and 1720 cm^{-1} (for plots, see Supporting Information, Figure S3).

Citric Acid Modification of 1,4:3,6-Dianhydrohexitol-Based OH-Functional Polyesters. Since CA should be incorporated into the polyester at relatively low temperatures, linear OH-functional polyester was first synthesized at 180–230 °C, followed by a CA-modification step at 150–160 °C. For ^{13}C NMR analysis, the OH-functional succinic acid/isosorbide copolyester (entry I in Table 2) was reacted with ^{13}C-labeled CA (i.e., citric acid-*1,5*-$^{13}C_2$, referred to as CA-*1,5*-$^{13}C_2$) (Scheme 6). The ratio of OH groups (determined by titration) to CA-*1,5*-$^{13}C_2$ was 1:1.1, which corresponds to approximately 20 wt % of CA-*1,5*-$^{13}C_2$.

During the reaction, samples were taken to monitor the development of molecular weight, polydispersity, and conversion of the OH groups of the polyester resin (^1H NMR) as well as the carboxylic acid groups of CA (^{13}C NMR). Figure 4 shows the SEC data for this reaction.

In this plot, we can see a slight drop in $\overline{M}_n$ between $t = 0$ and $t = 150$ min (which corresponds to the atmospheric processing step), suggesting that, at the beginning of the reaction, polyester chains are broken up through interchange (acidolysis) reactions with CA to some extent. However, when the reaction proceeds under vacuum, the molecular weight is built up again. In addition, the polydispersity index increases from 2.0 to 2.3, implying branching of the polyester by incorporation of CA into the polymer chains. SEC data do not indicate extensive cross-linking of the polymer sample, since the weight-average molecular mass of the polyester does not increase exponentially and virtually all CA-modified polymer remains soluble. In Table 2, the characteristics for the starting OH-functional polyester (entry I) as well as the polymers obtained after two separate CA-modification experiments (entry II with CA, entry III with CA-*1,5*-$^{13}C_2$) are summarized. In addition, a CA-modified polyester (entry IV) was synthesized on a larger scale, to facilitate, for example, powder coating experiments.

Scheme 6. Reaction between OH-Functional SA/IS Copolyester with Citric Acid-*1,5*-$^{13}C_2$[a]



[a] R = H or R = oligo- or polyester if ester interchange occurs.

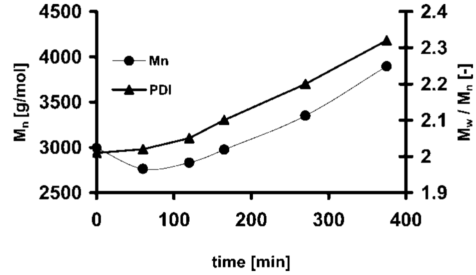
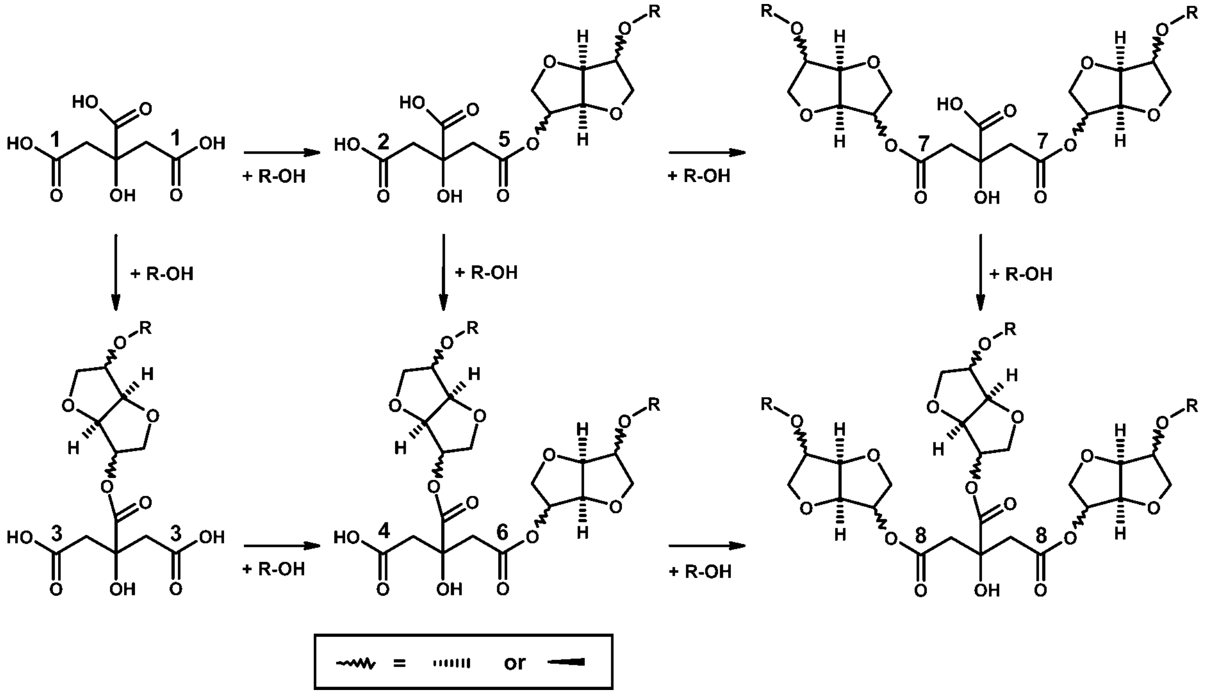


Figure 4. $\overline{M}_n$ and polydispersity index as a function of reaction time for the CA modification of polyester I (Table 2) with citric acid-*1,5*-$^{13}C_2$.

The molecular weights of the polymers listed in Table 2 are determined by SEC, making use of PMMA standards. It should be noted that these data give approximations rather than absolute values. Apart from the chemical differences between PMMA and the polymer samples under investigation here, the SEC results can be strongly influenced by the hydrodynamic volume and the type(s) of end groups of such low molecular weight species. To confirm the order of magnitude of the molecular weight mentioned in Table 2, the absolute molecular weight of polyester II was determined from SEC measurements, combining light scattering and concentration detection, without using PMMA calibration. In this case, the following results were obtained: $\overline{M}_n = 3100$ g/mol, $\overline{M}_w = 6100$ g/mol, PDI = 2.0.

The ^1H NMR spectra of polyesters I and II show the decrease in isosorbide end groups upon CA modification of the OH-functional starting material (see Supporting Information, Figure

Scheme 7. Possible Reaction Products Resulting from CA Modification of OH-Functional Polyester[a]



[a] Note: only the labeled carbonyls are numbered, the tertiary carboxylic acid and ester carbonyls are not visible in the ^{13}C NMR spectrum presented in Figure 5.

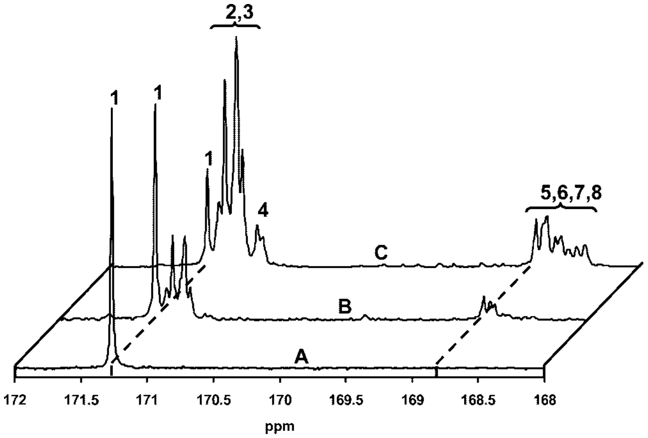


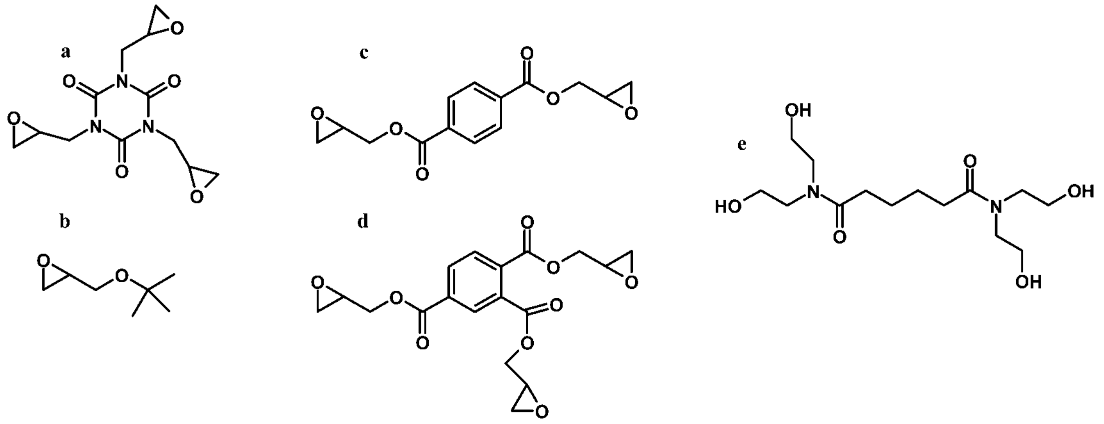
Figure 5. Carbonyl region of the ^{13}C NMR spectrum of (A) citric acid-*1,5*-$^{13}C_2$ and of the CA modification of a SA/IS copolyester at (B) $t = 170$ min and (C) $t = 375$ min (this particular reaction was performed at $T = 155–160$ °C). Note: the different spectra are not scaled relative to each other, so they can only be compared qualitatively.

S4). ^{13}C NMR spectroscopy yielded information concerning the reaction between polyester I and CA-*1,5*-$^{13}C_2$. In Scheme 7, the various types of free carboxylic acids and esters that can be formed during this reaction are given. The NMR spectrum (Figure 5) is more complex than the spectrum shown in Figure 3 due to the effect of endo- and exo-oriented OH groups of isosorbide, resulting in an increase of the number of possible signals.

Note that in Figure 5, the carboxylic acid and ester carbonyl signals of the unlabeled tertiary carbonyl carbon atoms are not visible due to their low concentrations. The ^{13}C-labeled carbonyl carbon atoms, on the other hand, are clearly visible in the ^{13}C NMR spectrum of the modified polyester. The spectrum contains separate clusters of acid and ester carbonyls. A strong signal is observed at 171.3 ppm in spectrum A, caused by the two unreacted labeled carbons of CA-*1,5*-$^{13}C_2$ (Scheme 7, carbonyl 1). After 170 min of reaction (spectrum B), peaks are present between 170.8 and 171.3 ppm. These signals result partly from the succinate ester carbonyls of the original SA/IS copolyester. However, they are mainly attributed to the labeled carboxylic acid carbonyls (Scheme 7, carbonyls **2** and **3**), which have shifted slightly upon reaction of one (or two) of the other carboxylic acid functionalities. As the reaction proceeds, ester signals become visible between 168.4 and 169.1 ppm. These signals are significantly lower in intensity than the acid signals. At $t = 170$ min, approximately 50% of the polyester hydroxyl end groups have reacted with CA-*1,5*-$^{13}C_2$, as determined from ^1H NMR spectra. After 375 min, high-intensity carbonyl signals are visible in the area between 170.8 and 171.3 ppm. All these peaks are attributed to carboxylic acid carbonyls. The conversion of the polyester hydroxyl end groups does not seem to be complete. To reach full conversion of the OH end groups, significantly longer reaction times might be necessary, since conversion is hampered by the less reactive endo-oriented OH groups of isosorbide. Due to vacuum processing, the conversion of the hydroxyl end groups of the polyester had increased to 75%, and the conversion of the carboxylic acid groups of CA was approximately 27%. The maximum theoretical functionality F_n which could be obtained upon modification with CA was $F_n = 4$ (at 100% OH and 33% COOH conversion, respectively). On average, the functionality per chain at 75% OH conversion is approximately $F_n = 3$. When comparing the intensities of signals 2 and 3 (i.e., CA has reacted with only one of its acid functionalities) with the intensity of signal 4 (i.e., CA has reacted with two of its acid groups), we can conclude that 80–85% of the CA present at the polyester chain end has esterified with only one of its carboxylic acid functionalities.

It is important to determine whether the degradation of CA would take place to a significant and possibly detrimental extent during the modification of OH-functional polyesters with CA. Formation of aconitic acids and their anhydrides takes place at a significant rate at temperatures of 180 °C and above, whereas no unsaturated structures were found when performing a reacti

Scheme 8. Chemical Structures of (a) Triglycidyl Isocyanurate (TGIC), (b) *tert*-Butyl Glycidyl Ether (TBGE), (c) Diglycidyl Terephthalate (DGT), (d) Triglycidyl Trimellitate (TGT), and (e) *N,N,N′,N′*-Tetrakis(2-hydroxyethyl)adipamide



between CA and 1-butanol at 150 °C (vide supra). To study the formation of unsaturated structures from CA during the modification of a polyester at 150–160 °C, a reaction between citric acid-*2,4*-$^{13}C_2$ (referred to as CA-*2,4*-^{13}C) and an OH-functional linear resin was carried out. The labeled carbon atoms at the 2 and 4 positions were clearly visible in the ^{13}C NMR spectra. If unsaturated structures are formed, signals should appear at a chemical shift between 125 and 145 ppm, as these unsaturated structures would always include one of the labeled carbon atoms. No clear signals were observed in the mentioned region, not even after prolonged heating at 155 °C, indicating that formation of unsaturated structures did not take place to a significant degree (see Supporting Information, Figure S5). The ^{1}H NMR spectrum of the same reaction only showed very faint traces of aconitic acid or anhydride. The total amount of degradation products is estimated to be 2–3% of the original amount of CA-*2,4*-^{13}C. It is not expected that these low levels of side products are detrimental to the final properties of the polyester resin. As already mentioned, these degradation products all have at least two acid functionalities. Therefore, if these molecules would react with a hydroxyl end group of a polymer, this would still lead to a carboxylic acid functional chain end, which can take part in cross-linking reactions.

In order to investigate whether CA can be built into the polyester chain by means of ester interchange reactions (specifically acidolysis), an OH-functional polyester was fully end-capped with benzoyl chloride following a procedure described by Kollodge at al.[44] After end-capping, no residual OH end groups were present in the polymer sample as verified by ^{1}H NMR and MALDI-ToF-MS (see Supporting Information, Figures S6 and S7). The end-capped polyester was reacted with CA-*1,5*-$^{13}C_2$ at 155 °C for 3.5 h. Since there were no OH end groups to be esterified, incorporation of CA-*1,5*-$^{13}C_2$ could only occur by acidolysis of ester links by the acid groups of CA-*1,5*-$^{13}C_2$. The ^{1}H NMR spectrum of the resulting polymer was not different from that of the starting material, except the appearance of a new multiplet caused by the presence of CA-*1,5*-$^{13}C_2$ at 2.95 ppm. In the ^{13}C NMR spectrum (see Supporting Information, Figure S8), new signals of higher intensity were present at 169.7 and 171.6 ppm. These peaks were assigned to anhydride species formed by dehydration of CA-*1,5*-$^{13}C_2$ and amounted to approximately 21% of the initial amount of CA-*1,5*-$^{13}C_2$. Although the spectrum showed no clear CA-*1,5*-$^{13}C_2$ ester signals (in the area between 168 and 169 ppm), some low-intensity carboxylic acid carbonyl signals (between 171.0 and 171.2 ppm) indicated that the labeled CA was built into the polyester chains through acidolysis to some extent (approximately 5%). So the incorporation of CA into the polyester chain through acidolysis proceeds, albeit to a much lower extent than through the normal esterification reaction with hydroxyl end groups. These results may explain the initial drop in polymer molecular weight during CA modification, as demonstrated in Figure 4.

Curing of CA-Modified Biobased Polyesters. As was previously determined, the CA modification of the hydroxyl end groups of the polyester resin was not complete. However, since acid functionalities of the obtained products were quite high (see Table 2), curing experiments were carried out to see if a conversion of ~75% and an approximate functionality $F_n = 3$ would suffice. In industry, polyesters with carboxylic acid functionality are cured with epoxy- or β-hydroxyalkylamide curing agents. At the moment, triglycidyl isocyanurate (TGIC, Scheme 8) is one of the most common epoxy curing agents for acid-functional resins, even though it is classified as a category 2 mutagen.[45] Other commercial epoxy curing agents include mixtures of diglycidyl terephthalate (DGT, Scheme 8) and triglycidyl trimellitate (TGT, Scheme 8). Curing of the conventional systems takes place at elevated temperatures (180–200 °C), during approximately 10–15 min. We studied the reaction of CA end groups with *tert*-butyl glycidyl ether (TBGE, Scheme 8), as a model for epoxy cross-linkers. In this way, we could estimate the extent to which the CA end groups (i.e., primary and tertiary carboxylic acids) will react with an epoxy curing agent to form a network.

Polyester III (Table 2), synthesized by reacting polyester I with CA-*1,5*-$^{13}C_2$, was selected for the reaction with TBGE. Its labeled CA end groups are clearly visible in ^{13}C NMR, facilitating the analysis upon reaction with the glycidyl ether. For polyester III, the ratio of carboxylic acid/ester in the carbonyl region of the ^{13}C NMR spectrum was 73:27. This means that, of all the carboxylic acid groups of CA-*1,5*-$^{13}C_2$ initially present in the reaction mixture, approximately 27% had reacted with the hydroxyl end groups of the starting polyester I. The subsequent reaction of polyester III with TBGE (Scheme 8, structure b) was performed in solution at 150 °C at an carboxylic acid/epoxy ratio of approximately 1:1. After 80 min of reaction, the ^{13}C NMR spectrum shows a strong decrease in the ratio carboxylic acid/ester, to approximately 15:85. This indicates that an additional $85 - 27 = 58\%$ of the total amount of carboxylic acid groups had reacted with the glycidyl ether. This corresponds to almost 80% of the remaining free carboxylic acid groups, present in polyester III. With an average chain functionality of $F_n = 3$, this extent of conversion is more th

Table 3. Coatings Based on Carboxylic Acid Functional Polyesters, Applied from NMP Solution

film	polyester[a]	curing agent[b]	T_{cure} (°C)	t_{cure} (min)	acetone resistance	impact test (1 kg, 100 cm)
F1	II	a	180	10	+	+
F2	II	e	200	10	+	+/−
F3	IV	a	180	20	+	+
F4	IV	e	180	20	+	+

[a] See Table 2. [b] See Scheme 8.

sufficient to obtain a well-cured polymer network when using a trifunctional curing agent (in theory, gelation occurs already at 50% conversion). Unfortunately, there is some overlap between the signals caused by the carboxylic acid carbonyls of CA-*1*,*5*-$^{13}C_2$ and those caused by the ester carbonyls of the SA/IS copolyester, so the mentioned numbers are estimates.

To determine if esterified CA is stable enough to withstand curing cycles at high temperatures, a degradation experiment was performed, in which trimethyl citrate was heated to 180–190 °C for 2 h. The trimethyl ester of CA remained colorless and the ^{13}C as well as the ^{1}H NMR spectra, recorded after heating, were identical to those of the starting material. From this experiment, we conclude that a curing cycle of 15 min at 180 °C should not pose a problem with respect to degradation of the polyester. In addition, TGA measurements were performed to investigate the thermal stability of polyester resins I and II (Table 2). The results (Supporting Information, Figure S9) show that no significant weight loss occurs up to 250 °C for polymer I. For the CA-modified polyester II, weight loss is observed to start at approximately 210 °C. This difference between I and II is thought to be due to the occurrence of dehydration and/or decarboxylation of the citric acid residues at the polyester chain ends. Still, the thermal stability of the polyesters containing CA is more than sufficient for their application as thermosetting coatings.

Coatings from CA-Modified Biobased Polyesters. Several coating formulations were prepared, based on CA-modified resins II and IV. These polyesters (Table 2) were cured with TGIC and *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)adipamide (Scheme 8, structures a and e, respectively) and the coatings were applied from NMP solution. The properties of the solvent cast coatings are summarized in Table 3. Average dry film thicknesses were between 35 and 40 μm for all coatings, and all coatings had König hardnesses around 200–220 s. The T_g values of the cured systems were significantly higher than of the polyester resin, as expected. For example, coating F3 has a T_g of 77.6 °C, while resin IV has a T_g of only 59.0 °C.

As displayed in Table 3, curing of acid functional polyesters results in coatings with good to excellent solvent resistance. The impact resistance of F1 is good, while some slight cracking is observed in F2. In general, it was observed that coatings cured with curing agent a perform better than those cured with curing agent e, with respect to mechanical performance and film appearance. CA-modified polyester IV was also tested as a binder resin in powder paint formulations. In these systems, the resin was cured with 60:40 mixture of DGT and TGT. Rapid curing was observed, also at relatively mild curing cycles ($T =$ 150 °C, $t = 15$ min). Transparent, glossy coatings were obtained with excellent solvent and impact resistance. These results show that the obtained levels of carboxylic acid functionality resulting from CA-modification of biobased polyesters are more than sufficient for thermoset coating purposes.

Conclusion

The possibilities of using citric acid as a functionality-enhancing compound in polyester synthesis were studied. NMR and FTIR studies showed that CA forms a reactive anhydride intermediate above its melting temperature, which seems to react rapidly with OH groups to form ester bonds. Actually, the tendency of CA to lose a molecule of water upon heating proves to be highly beneficial as it results in a more reactive anhydride intermediate. Hence, although its thermal stability would suggest otherwise, CA can be applied in polymer modification even in the melt at temperatures up to 160 °C. Model reactions between CA and several mono- and bifunctional alcohol species showed that reaction occurred to a sufficient extent at relatively low temperatures. In addition, it was demonstrated that CA reacts faster with primary OH groups than with secondary OH groups, as expected. Interestingly, the model reactions also confirm previous observations that the exo-oriented OH groups present in isosorbide and isoidide are more reactive than their endo-oriented counterparts present in isosorbide and isomannide. Linear polyesters, having hydroxyl end groups of limited reactivity could be effectively modified with CA at moderate temperatures (i.e., between 150 and 160 °C), yielding novel, slightly branched polymers with high acid functionalities. The presence of carboxylic acid end groups was confirmed by ^{13}C NMR spectroscopy applied to polyesters modified with ^{13}C-labeled CA. Only low levels of unsaturated structures were formed. Curing of the system was simulated by reacting the product with *tert*-butyl glycidyl ether. Finally, the modified biobased polyesters were cured using several curing agents, leading to chemically and mechanically stable coatings, applied from solvent as well as through powder coating application. The systems could be cured at relatively low temperatures, around 150 °C. We can therefore conclude that CA is a very useful monomer for enhancing polyester functionality. CA can be seen as a cheap, aliphatic and biobased alternative for, for example, trimellitic anhydride.

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Supporting Information Available. CA degradation schemes, ^{1}H NMR spectra of CA and its degradation products, of a benzoyl chloride end-capped poly(isosorbide succinate), and of CA-modified polyesters, ^{13}C NMR spectra of products of model reactions and of CA-modified polyesters, FTIR spectra of model reactions, and TGA data for biobased polyesters. This material is available free of charge via the Internet at http://pubs.acs.org.

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