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Co- and Terpolyesters Based on Isosorbide and Succinic Acid for Coating Applications: Synthesis and Characterization

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Co- and terpolyesters based on succinic acid and isosorbide in combination with other renewable monomers such as 2,3-butanediol, 1,3-propanediol, and citric acid were synthesized and characterized. Linear polyesters were obtained via melt polycondensation of nonactivated dicarboxylic acids with OH functional monomers. Polymer end functionality (i.e., hydroxyl or carboxylic acid) was controlled by adjusting the monomer stoichiometry. The glass transition temperatures of the resulting polyesters could be effectively adjusted by varying the polymer composition and molar mass. By adding polyfunctional monomers such as trimethylolpropane or citric acid, polyesters with enhanced functionality were obtained. These biobased polyesters displayed functionalities and T_g values in the appropriate range for (powder) coating applications. The polyesters were cross-linked using conventional curing agents. Coatings from branched polyesters—hydroxyl as well as acid functional—showed significantly improved mechanical and chemical resistance compared to those formulated from linear polymers. These renewable polyesters proved to be suitable materials for coating applications with respect to solvent resistance, impact resistance, and hardness.

Introduction

The synthesis of polymeric materials based on monomers from renewable feedstock is a steadily growing field of interest. Many of these monomers have unique structures which are not available from conventional sources. Therefore, it is expected that new and interesting material properties can be obtained with regard to thermal and rheological behavior. In addition, the use of renewable feedstock is stimulated by the growing concern for the environment and the rapid depletion of the mineral oil reserves. Renewable monomers with a large functional diversity are already available from a wide range of resources. Improved production processes to obtain various biobased monomers on large scales as well as the development of a sustainable economy should make the use of renewable feedstock even more economically attractive in the future.[1,2]

We are interested in the application of monomers from renewable resources in polyesters from a fundamental point of view as well as with respect to their applicability in technically relevant areas. Among them are polyester resins used in thermosetting powder coatings. These materials are industrially widely used in coating formulations for a broad variety of products, such as metal and wooden furniture, tools, and domestic appliances as well as automotive and engineering applications.[3,4]

Powder coating resins are typically low molecular weight materials with $\overline{M}_n$ values between 2000 and 6000 g/mol. They are synthesized via classical polycondensation of diacids and diols, incorporating small amounts of trifunctional monomers to obtain slightly branched polyesters. In practice, the resin functionality (i.e., carboxylic acid or hydroxyl end groups) is controlled by the monomer stoichiometry. The thermal properties, on the other hand, can be tuned by the choice of different mole percentages of aromatic and aliphatic building blocks. For polyester formulation, carboxylic acid monomers normally include terephthalic acid, isophthalic acid, adipic acid and trimellitic anhydride, while the hydroxyl functional compounds are often aliphatic monomers such as neopentyl glycol, ethylene glycol, and trimethylolpropane. Up to now all commercially used monomers have originated from fossil feedstock. In particular, aromatic monomers have the disadvantage that they are more susceptible to photodegradation,[5−8] leading to yellowing of the coating in time. It is therefore desirable to develop fully aliphatic systems with better UV stability, suitable for outdoor applications. However, due to the high chain flexibility of most aliphatic polymers, these materials generally have a too low glass transition temperature (T_g) for practical powder coating applications. To provide sufficient physical stability of the powder during storage, these polymers must have glass transition temperatures well above room temperature, generally >45 °C. In conventional systems, terephthalic acid usually provides chain rigidity and thus sufficiently high T_g.

1,4:3,6-Dianhydro-D-glucitol (isosorbide) is an interesting renewable monomer for coating applications for environmental as well as for performance reasons. It is obtained from starch[9] and has already been shown to give T_g increasing effects in poly(ethylene terephthalate) (PET).[10] With isosorbide providing enough rigidity to obtain T_g values in the appropriate range, we anticipated that fully aliphatic polyesters can be obtained using this monomer in combination with others, resulting in

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properties sufficient for (powder) coating applications. As diacid components, linear aliphatic diacids such as succinic acid or adipic acid can be used in these polyesters. As succinic acid can also be obtained via fermentation of glucose with yields up to 1.1 kg of succinic acid/kg of glucose (with CO_2 incorporation), the combination of both renewable monomers would ultimately give access to technically applicable polymers based on biobased raw materials.[11]

The use of isosorbide in polymer systems has previously been reported by several authors.[9,12−17] While coating and fiber applications are mentioned,[18,19] the main focus is on biodegradability and optical properties of the chiral polyesters.[20−22] Synthesis of polymers containing isosorbide is often carried out in the melt or in solution, exclusively using activated diacid components such as acid chlorides or anhydrides.

In this paper we describe the synthesis of isosorbide-based polyesters for coating applications. Monomers such as isosorbide, 1,3-propanediol, 2,3-butanediol, and succinic acid were used in the polymer synthesis. The emphasis is on a systematic investigation of a synthetic protocol for the melt polymerization of nonactivated monomers, the evaluation of the polymer properties, and first application tests. To the best of our knowledge, the melt polymerization of isosorbide for powder coating applications has not been described.

Experimental Section

Materials. Isosorbide (IS) was obtained as a gift from Agrotechnology and Food Innovations (98+% pure) as well as from Roquette Freres (98.5+% pure). Succinic acid (SA), 2,3-butanediol (BD), neopentyl glycol (NPG), trimethylolpropane (TMP), titanium(IV) *n*-butoxide, 4-(dimethylamino)pyridine, and acetic anhydride were purchased from Acros Organics. Normalized solutions of KOH in methanol, 1,3-propanediol (PD), triglycidyl isocyanurate (TGIC), dibutyltin dilaurate (DBTL), and 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene (antioxidant) were obtained from Aldrich. Citric acid (CA) was purchased from Merck. Vestagon B1530 was a gift from Degussa, and Desmodur N3600 and Desmodur BL3272 were gifts from Bayer AG. Primid XL-552 was received as a gift from EMS Chemie. All chemicals were used as received.

Polymerization of Renewable Monomers To Form Copolyesters. A typical polymerization was carried out according to the following procedure. Succinic acid (44.9 g, 0.38 mol) and isosorbide (63.4 g, 0.43 mol) were weighed into a 250 mL round-bottom glass flange reactor. The reactor was fitted with a Vigreux column and a Dean−Stark-type condenser to collect the condensation product. During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate transport of water vapor. While being stirred, the mixture was heated to 180 °C using a heating mantle. Titanium(IV) *n*-butoxide (0.02 mol % relative to succinic acid), dissolved in toluene, was added to the melt. Subsequently, the reaction temperature was increased stepwise to maintain distillation of the formed water. The maximum reaction temperature was 250 °C. After 4 h, vacuum processing was started at 230−250 °C, with typical pressures ranging from 1 to 5 mbar. Vacuum was applied for 4 h, after which the polymer was discharged from the reactor and left to cool and solidify.

Reaction of Hydroxyl Functional Polyesters with Citric Acid Moieties. Synthesis of polyesters with acid functionalities was started from previously synthesized linear OH functional polyester: 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 citric acid were charged to the reactor. The temperature was increased slowly to 170 °C, leading to a clear melt. After the solution was stirred under an inert gas flush for 2.5 h, processing was continued in vacuo for 3 h. Subsequently, the clear melt was discharged and left to cool.

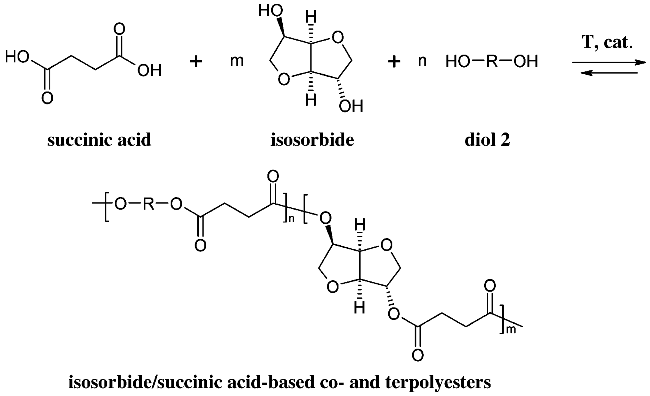
Curing of Hydroxyl Functional Polyesters. Hydroxyl functional polyesters were cured using (1) conventional polyisocyanate curing agent, Vestagon B1530, an ϵ-caprolactam-blocked trimer of isophorone diisocyanate (NCO equivalent weight 275 g/mol), (2) Desmodur N3600, a trimer of hexamethylene diisocyanate (NCO equivalent weight 183 g/mol), or (3) Desmodur BL3272, an ϵ-caprolactam-blocked trimer of hexamethylene diisocyanate (NCO equivalent weight 410 g/mol).

For (1) and (3), a solution of 0.3−0.5 g of polyester, 1.05 mol equiv of the cross-linker (calculated from the OH value, determined by titration) and 0.5 wt % (relative to solid resin) dibutyltin dilaurate in 1 mL of *N*-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a film of approximately 250 μm thickness was applied onto an aluminum panel, using a doctor blade. The film was left to dry at room temperature, followed by curing at 200 °C for 30 min under nitrogen. For (2), a solution of 0.3−0.5 g of polyester in 0.7 mL of NMP was prepared, as well as a separate solution of Desmodur N3600 (1.05 mol equiv, calculated from titration data) in 0.3 mL of NMP. The two solutions were mixed and applied directly to the aluminum substrate as a wet film with a thickness of 250 μm. After being dried at room temperature, the film was cured at 180 °C under N_2 for 20 min.

Curing of Carboxylic Acid Functional Polyesters. Carboxylic acid functional polyesters were cured with (1) TGIC or (2) *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)adipamide (Primid XL-552). A solution of 0.3−0.5 g of polyester and 1.05 mol equiv of the cross-linker (calculated from the COOH value, determined by titration) in 1 mL of NMP was prepared. Subsequently, a film of approximately 250 μm thickness was applied to the aluminum substrate. The film was left to dry at room temperature, followed by curing at 180 °C for 10 min under nitrogen.

Measurements. SEC analysis was carried out using a Waters GPC equipped with a Waters 510 pump and a Waters 410 refractive index detector (at 40 °C). Injections were done by a Waters WISP 712 autoinjector; the injection volume was 50 μL. Two linear columns, mixed C, Polymer Laboratories, 30 cm, 40 °C, were used. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using polystyrene standards (Polymer Laboratories, $M = 580$ g/mol to $M = 7.1 \times 10^6$ g/mol). Data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, and deuterated chloroform was used as the solvent (unless stated otherwise). The thermal stabilities of the polymer samples were determined using a Perkin-Elmer Pyris 6 TGA apparatus. Approximately 10 mg of polymer was heated from 40 to 700 °C at a heating rate of 10 °C/min under a N_2 flow of 20 mL/min. Results were analyzed using Pyris 4.01 software. DSC measurements were carried out with a DSC Q100 from TA Instruments. MALDI-TOF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Da, and the mass resolution was approximately *m*/*z* 12000. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as the matrix. Potassium trifluoroacetate (Aldrich, >99%) was used as the cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL), and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with a Ag titrode. The carboxylic acid functionality was measured by titration with a normalized 0.1 N methanolic KOH solution. The acid value (AV) is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin. Hydroxyl end groups were acetylated with acetic anhydride at room temperature (4-(dimethylamino)pyridine was used as the catalyst), followed by titration of the resulting acetic acid with normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (OHV) is

Scheme 1. Renewable Co- and Terpolyesters Based on Isosorbide and Succinic Acid and Optionally 2,3-Butanediol or 1,3-Propanediol (with $0 < m \leq 1$ and $0 \leq n < 1$, Respectively)



the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material. All titrations were carried out in duplo. Curing reactions were followed using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) 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 150−200 rubs, the coating has good acetone resistance), rapid deformation test (reverse impact test, ASTM D 2794), and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained coatings were measured using a magnetic induction coating thickness meter (Twin-Check by List-Magnetik GmbH).

Results and Discussion

Synthesis and Characterization of Co- and Terpolyesters Based on Succinic Acid and Isosorbide. In this study, several series of isosorbide-based polyesters were synthesized. All polyesters were obtained from dicarboxylic acid and diol monomers (Scheme 1) in bulk. The functional polymer end groups were used in a subsequent curing process for coating formation. For the synthesis of the polyesters we followed two parallel approaches: (1) synthesis of isosorbide/succinic acid copolymers using isosorbide as the only diol component; (2) systematic partial replacement in these copolymers of isosorbide by, for example, 2,3-butanediol or 1,3-propanediol, leading to terpolymers. In the first approach, the goal was the optimization of the reaction conditions, while the second approach was aimed at obtaining insight into detailed structure−property relationships.

Succinic Acid/Isosorbide Copolyesters. A series of polymerization experiments were conducted with succinic acid and isosorbide in bulk. It was noted that the reaction proceeds without the addition of a catalyst up to a conversion of 60% at 180 °C. A strong discoloration of the polyester was observed during the course of the reaction. The discoloration was prevented to a large extent by polymerization under an inert gas and optimization of the reaction time, leading to yellow polymers. Furthermore, significant improvements with respect to polyester color were obtained using a special polymer grade of isosorbide (Polysorb P, Roquette, 98.5+%), which yielded a colorless polymer.

A reaction of isosorbide with succinic acid, carried out at 180 °C, was monitored in detail. A hydroxyl functional polymer with a molecular weight of 2500 g/mol was targeted. A convenient way to follow the progress of the reaction is end group titration. As can be seen in Figure 1, the titrated acid and hydroxyl values (AV and OHV, respectively) decrease during the course of the reaction due to the esterification reaction, as expected. However, the theoretical OHV of 38 mg of KOH/g (AV = 0 mg of KOH/g), corresponding to the target molecular weight, was not reached, not even at an extended reaction time (Table 1, polyester **A**). This suggests that the reaction stops at a certain conversion under these reaction conditions. This was confirmed by SEC results obtained from samples withdrawn during the reaction (see the Supporting Information). The number average molecular weight ($\overline{M}_n$) of the final sample is between 2000 and 2500 g/mol (polystyrene calibration). The titration data suggest that the molecular weight obtained from SEC is overestimated. This is probably caused by differences in hydrodynamic volume between polyesters and the polystyrene chains used for the calibration.[23−25] Considering the low molecular weight of the material, it is surprising that still a T_g of 43 °C is obtained.

A similar molecular weight limit was observed in all reactions. One explanation for this phenomenon could be found in the structure of isosorbide, which is a chiral bicyclic ether having two secondary hydroxyl groups. However, these two functionalities have different reactivities, since they differ in orientation. One is in the *endo* position and is involved in intramolecular hydrogen bonding,[26,27] while the other is in the *exo* position. The latter is more reactive in polycondensation reactions, since it does not participate in internal hydrogen bonding and is less sterically hindered.[28] The *endo*-oriented OH probably causes the conversion limitation under these reaction conditions.

Further information about the end group structure was obtained from MALDI-TOF-MS analysis. It has to be noted that this technique does not afford quantitative data. Moreover, one has to be aware that ionization efficiencies can be significantly different for acid and hydroxyl end groups.[25,29] Nevertheless, MALDI gives information concerning the types of end groups present in a polymer sample and the monomer residues present in the individual polyester chains. MALDI spectra for succinic acid/isosorbide copolyesters show individual molecular peaks between 600 and 2500 g/mol, separated by the mass of one repeating unit (228 Da). The polymer chains are almost exclusively hydroxyl functionalized with only small amounts of cyclic structures or acid end groups.

The situation is different when acid-functionalized polymers are targeted. Even after using an excess of succinic acid, a combination of all possible end groups can be identified in the MALDI spectrum (Figure 2). Although the majority of polyester chains are acid functionalized, significant amounts of hydroxyl end groups are present in the polymers. This observation can only be explained by a reduced reactivity of the secondary hydroxyl groups in the chain growth steps in particular at chain ends when additional sterical constraints are present (i.e., *endo* orientation of the OH group). Therefore, the synthesis of fully acid functional linear isosorbide polymers cannot be achieved under these reaction conditions.

To increase the conversion and, as a result, the molecular weight, the synthetic procedure was modified by raising the reaction temperature (up to 250 °C) and lowering the vacuum (1−5 mbar). In addition, titanium(IV) *n*-butoxide was used as an esterification and transesterification catalyst. The resulting OH functional polymers have slightly higher molecular weights, as determined from SEC data. Titration data confirm this increase: polyesters **1a** and **1b** have significantly lower acid

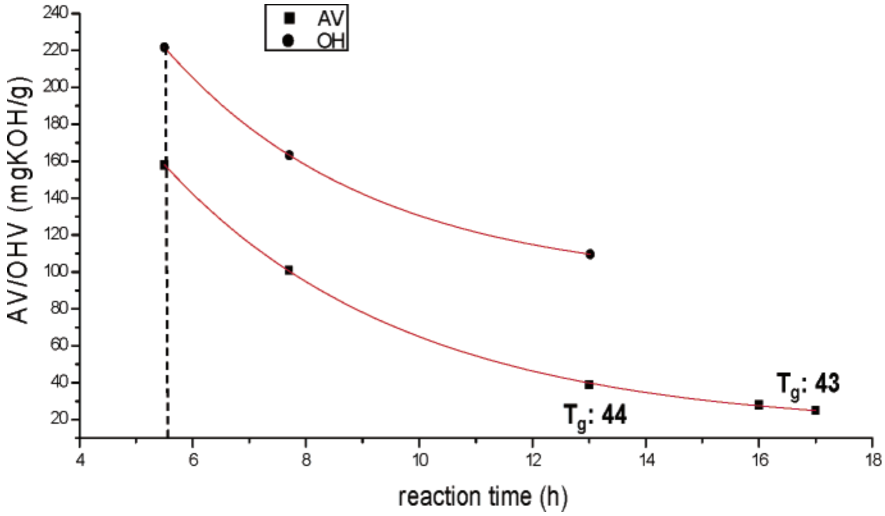


Figure 1. Development of acid value (AV) and hydroxyl value (OHV) as a function of the reaction time of the bulk polymerization of isosorbide with succinic acid. The dotted line indicates the start of the evacuation of the vessel (180 °C, 30 mbar). The initial AV = 402 mg of KOH/g, and the initial OHV = 440 mg of KOH/g.

Table 1. Linear Copolyesters from Succinic Acid and Isosorbide

polyester	feed composition	composition (NMR)[a]	T_g (°C)	M_n (g/mol)	M_w/M_n	AV[b] (mg of KOH/g)	OHV[b] (mg of KOH/g)
A	SA/IS [1:1.09]	SA/IS [1:1.09]	43.0	2000−2500	na	25	110
1a	SA/IS [1:1.10]	SA/IS[c] [1:1.06]	67.7	3100	1.6	8.8	40.0
1b	SA/IS [1:1.14]	SA/IS [1:1.11]	56.5	2400	1.8	1.5	65.0

[a] Composition data obtained from ^1H NMR spectra. [b] AV = acid value, and OHV = hydroxyl value [c] Data obtained after dissolution/precipitation from $CHCl_3$/MeOH.

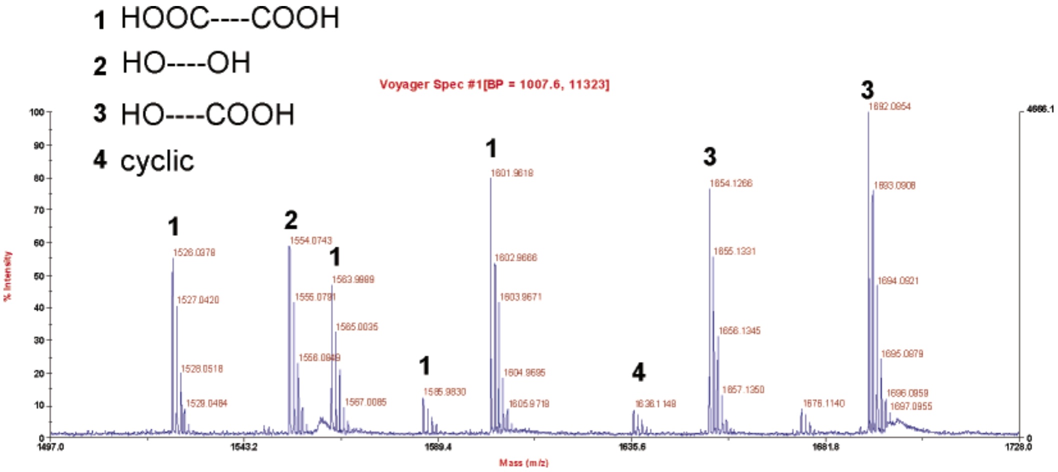


Figure 2. Section of the MALDI-TOF-MS spectrum of poly(isosorbide succinate), obtained after polymerization with an excess of succinic acid. Acid-functionalized species produce several peaks due to proton replacement by sodium and potassium, originating from the cationization agent.

and hydroxyl values than polyester **A**. We cannot exclude that the formation of cyclic structures contributes to this reduction of available functional groups (see Figure 6). As expected in this low molecular weight regime, the T_g of the polymer increases with molar mass (Table 1), which is advantageous for the envisioned application of these copolyesters.

Assuming that all the polyester end groups are IS moieties, it is possible to estimate the molecular weight of poly(isosorbide succinate) from ^1H NMR spectra. In the ^1H NMR spectrum of copolyester **1b** (Figure 3), the signals corresponding to IS and to IS end groups can be clearly discerned. The ratio SA:IS = 1:1.11 was determined by integration of IS signals c and k (or d, l, and n) relative to SA signal g,h. From this ratio, $\overline{M}_n$ was estimated to be 2200 g/mol (i.e., an average of 9.1 SA/IS repeating units and one IS moiety as the end group). From titration as well as MALDI-TOF-MS data, it is clear that there are also small amounts of acid functional chains (approximately 2−3% of all end groups are carboxylic acids) and cyclic chains. These are not taken into account in this calculation, which means that the actual $\overline{M}_n$ is probably somewhat lower than determined from NMR. From the total amount of titrated end groups per gram of sample (i.e., AV + OHV), a $\overline{M}_n$ value of 1700 g/mol is obtained. In this case, cyclic oligo- and polyester chains are not considered.

From Figure 3, the ratio of *endo* to *exo* hydroxyl end groups was determined. In DMSO-d_6, these two different OH groups give doublet signals at 4.90 ppm (r, *endo*) and at 5.15 ppm (q, *exo*). Their ratio is approximately 6:4. This was confirmed by comparing the n:c signal ration as well as the e:(j + m) signal

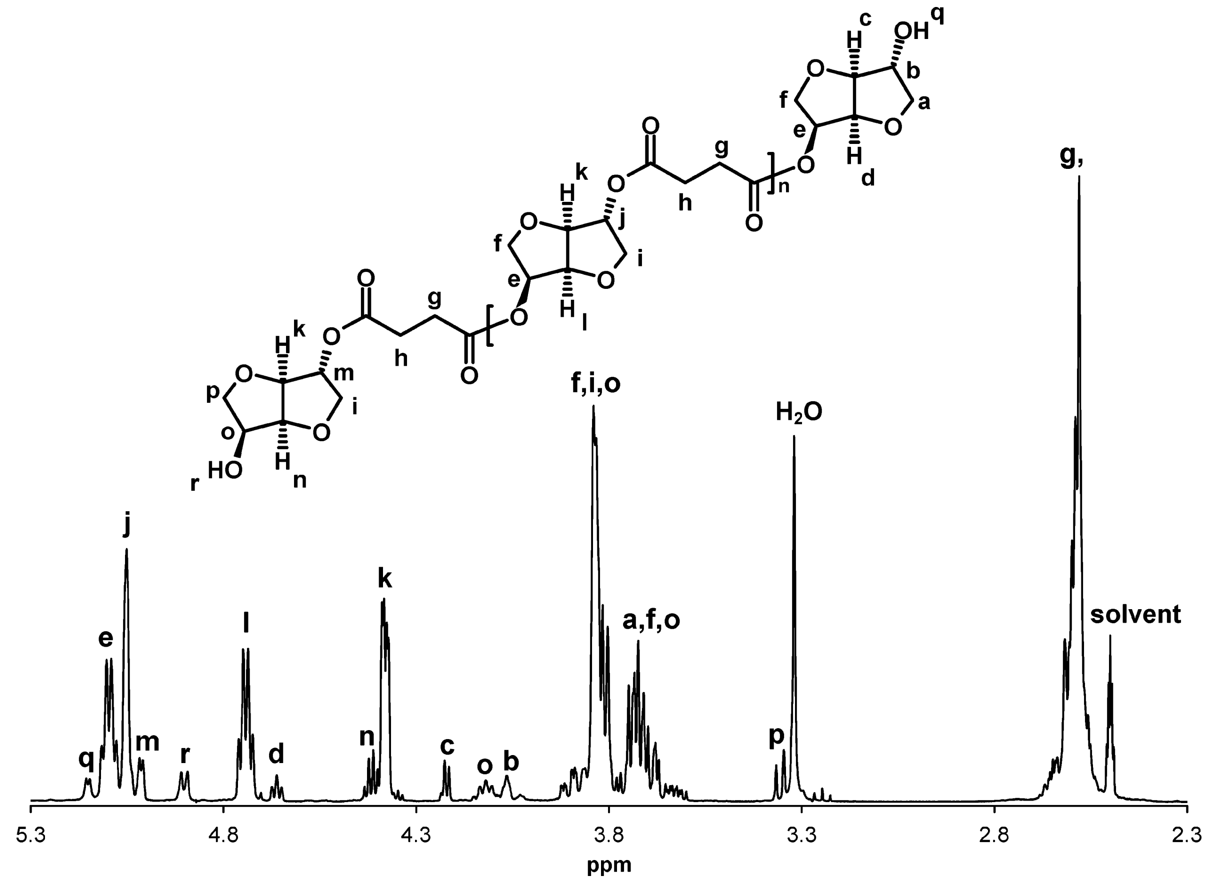


Figure 3. ^{1}H NMR spectrum of copolyester **1b**, recorded in DMSO-d_6.

ratio. From this ratio, we conclude that the majority of the hydroxyl end groups have the *endo* orientation. This observation confirms the difference in reactivity between the two IS hydroxyl functionalities: the *endo* OH is significantly less reactive than its *exo* counterpart.

Isosorbide-Based Terpolyesters. An important incentive for the use of isosorbide as a rigid monomer in polyesters is its T_g increasing effect with respect to that of linear aliphatic monomers, which opens possibilities to replace aromatic monomers. We therefore synthesized several series of linear and branched polyesters, containing isosorbide in combination with various comonomers. The glass transition temperatures of low molecular weight polymers, as those synthesized in this study, strongly depend on their $\overline{M}_n$ values and the presence of low molecular weight species. For example, copolymer **1a** based on succinic acid and isosorbide with a molecular weight of $\overline{M}_n$ = 3100 g/mol (relative to PS standards) has a glass transition temperature of 67.7 °C. For virtually the same copolymer, T_g is only 56.5 °C if $\overline{M}_n$ = 2400 g/mol (copolyester **1b**). The Fox−Flory equation describes this phenomenon, stating that polymer T_g increases with molecular weight, leveling off at a certain plateau value ($T_{g\infty}$).[30] Figure 4 shows the effect on T_g and $\overline{M}_n$ by systematic replacement of NPG by isosorbide in a succinic acid based polyester synthesized at constant reaction times and temperature.

The plot shows a decrease of $\overline{M}_n$ with increasing isosorbide content. This is probably due to the decreased reactivity of the secondary hydroxyl groups of this monomer, compared to the primary OH groups of NPG. Nevertheless, a significant increase in T_g with increasing isosorbide content can be observed. Taking into account the T_g decreasing effect of lower molecular weight polymers, one can expect that the increase in T_g should be even more pronounced when materials of equal molecular weights are compared. Figure 4 does therefore not provide maximum values for the glass transition temperatures of these polyesters. The results of these experiments demonstrate that it is possible to synthesize aliphatic polyesters containing isosorbide with sufficiently high T_g values, which are potential candidates for application in powder coatings. Within the molecular weight range of 3000−6000 g/mol (Figure 4), a minimum isosorbide content of approximately 60−70% of the total diol amount is required to obtain materials with T_g values above the boundary (>45 °C) for coating applications.

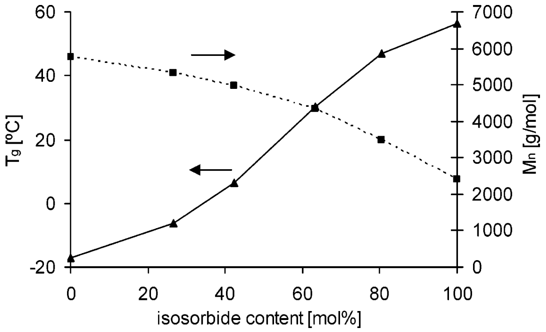


Figure 4. T_g (▲) and $\overline{M}_n$(■) as a function of isosorbide content for a polyester based on succinic acid, neopentyl glycol, and isosorbide (isosorbide mole percent relative to the total diol content). The lines in this figure are meant only as guides to the eye.

On the basis of the above conclusion, several terpolyesters were synthesized from SA, IS, and PD, BD, or NPG (Table 2). The isosorbide content was kept between 60 and 100 mol %, relative to the total amount of diols present.

The polyester composition as determined by ^{1}H NMR spectra (Figure 5) is in good agreement with the monomer feed ratio.

Table 2. Linear Terpolyesters Based on SA, IS, BD, PD, and NPG

polyester	feed composition	composition[a]	T_g (°C)	M_n (g/mol)	M_w/M_n	AV (mg of KOH/g)	OHV (mg of KOH/g)
2a	SA/IS/BD [1:0.92:0.23]	SA/IS/BD [1:0.87:0.19]	50.6	2700	1.9	0.2	48.6
2b	SA/IS/BD [1:0.69:0.46]	SA/IS/BD [1:0.65:0.36]	46.8	4600	1.6	2.0	32.0
3a	SA/IS/PD [1:0.85:0.20]	SA/IS/PD [1:0.83:0.25]	45.2	2700	2.0	4.7	43.9
3b	SA/IS/PD [1:0.69:0.46]	SA/IS/PD [1:0.63:0.45]	20.6	3500	1.5	1.5	37.7
4a	SA/IS/NPG [1:0.80:0.20]	SA/IS/NPG [1:0.87:0.21]	47.1	3500	1.5	13.6	33.5
4b	SA/IS/NPG [1:0.60:0.40]	SA/IS/NPG [1:0.69:0.40]	30.5	4300	1.5	7.5	34.0

[a] Composition data obtained from ^{1}H NMR spectra. For example, for polyester **3b** (see Figure 5), the composition is determined by integration of peaks h (4H, SA), c + c′ (1H, IS), and i (2H, PD).

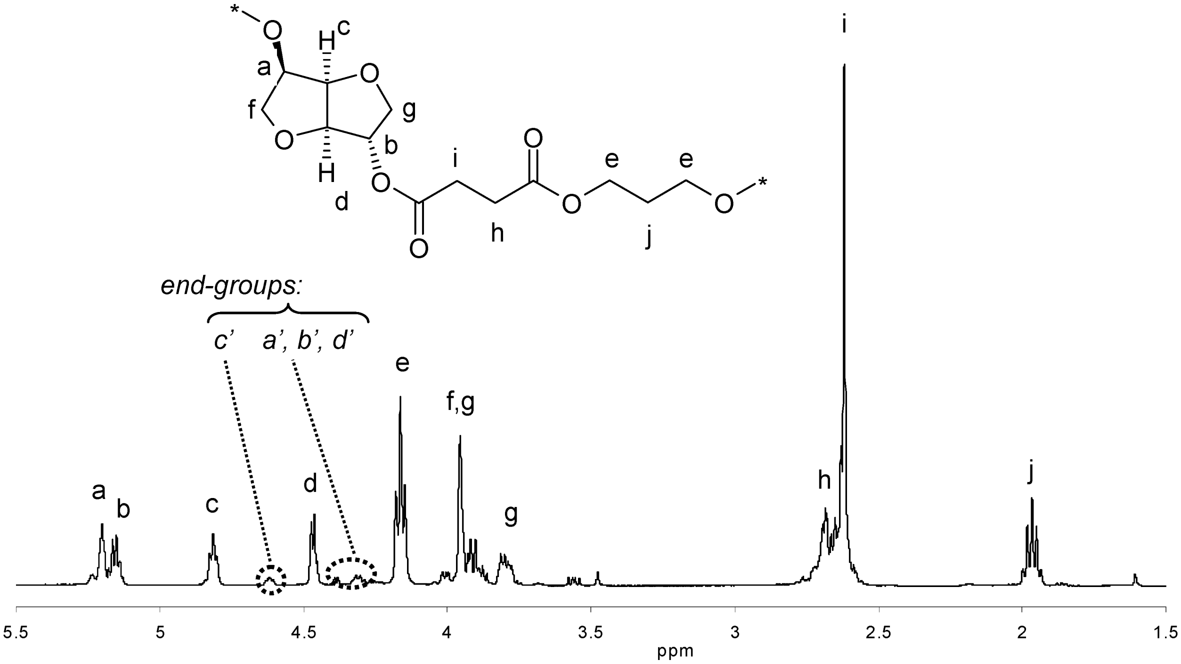


Figure 5. ^{1}H NMR spectrum of terpolyester **3b** in Table 2: poly(propylene-*co*-isosorbide succinate).

Isosorbide end groups can be readily distinguished (for example, peaks a′, b′, c′, and d′) in these low molecular weight polyesters. The differences in shifts between peaks a and b as well as between peaks c and d are direct results of the *endo* and *exo* positioning of the two OH groups of isosorbide. The broadening of the CH_2 signal of succinic acid at 2.6−2.8 ppm (peaks h and i) is caused by the presence of two different diol moieties (isosorbide and 1,3-propanediol), as well as by the *endo* and *exo* character of the isosorbide OH groups, leading to different chemical shifts.[28]

The difference in reactivity between the secondary hydroxyl groups of isosorbide and the primary hydroxyl groups of 1,3-propanediol could potentially lead to blocky terpolyesters if randomization by transesterification does not occur to a sufficient extent. However, the catalyst used for these terpolyester syntheses, $Ti(OBu)_4$, is known to be an efficient transesterification catalyst.[31−33] Moreover, ^{13}C NMR spectra do not give any indication that blocky structures are present in the final products. This was determined by comparing the integrals of signals corresponding to the carbonyls of the different repeating units present in the terpolyesters.

Figure 6 shows an example of a part of a MALDI-TOF-MS spectrum of terpolyester **2a** (SA:IS:BD = 1:0.87:0.19, composition determined from ^{1}H NMR analysis). The main species observed in the spectrum are hydroxyl functional chains. However, chains having one OH and one COOH end group are also visible, as well as chains with two acid end groups. As expected, cyclic oligoesters are also observed. These rings do not participate in the network formation during cross-linking and can act as plasticizers for the cured coating, lowering its T_g. Carboxylic acid functionalities are undesirable as well, since they do not participate in the curing reaction.

Terpolymer series **2**−**4** (Table 2) have lower glass transition temperatures than the copolyester of isosorbide with succinic acid, due to the increase in chain flexibility. Moreover, it can be seen that 1,3-propanediol and NPG (series **3** and **4**, respectively) affect T_g more strongly than 2,3-butanediol (series **2**). This can be explained by the more flexible nature of 1,3-propanediol and NPG as compared to 2,3-butanediol. Hence, by selecting different diols and diol ratios, the T_g values of the polyesters can be effectively adjusted. Figure 7 shows the T_g development of these terpolyester series as a function of isosorbide content (relative to the total diol content). Again, $\overline{M}_n$ has an effect on polyester T_g. However, the number average molecular weights of the polyesters in Figure 7 are within the same range to make a fair comparison.

An important parameter for polyesters used in powder coatings is their thermal stability. Curing of powder coating formulations occurs at temperatures between 160 and 200 °C. The thermal stability of the polyesters was investigated by thermogravimetric analysis (TGA). No significant weight loss was observed up to 250 °C (see the Supporting Information).

Isosorbide-Based Polyesters with Enhanced Functionality. Polyester functionality (*f*) is a crucial parameter in thermosetting coatings. Depending on the applied curing agent, the polyester

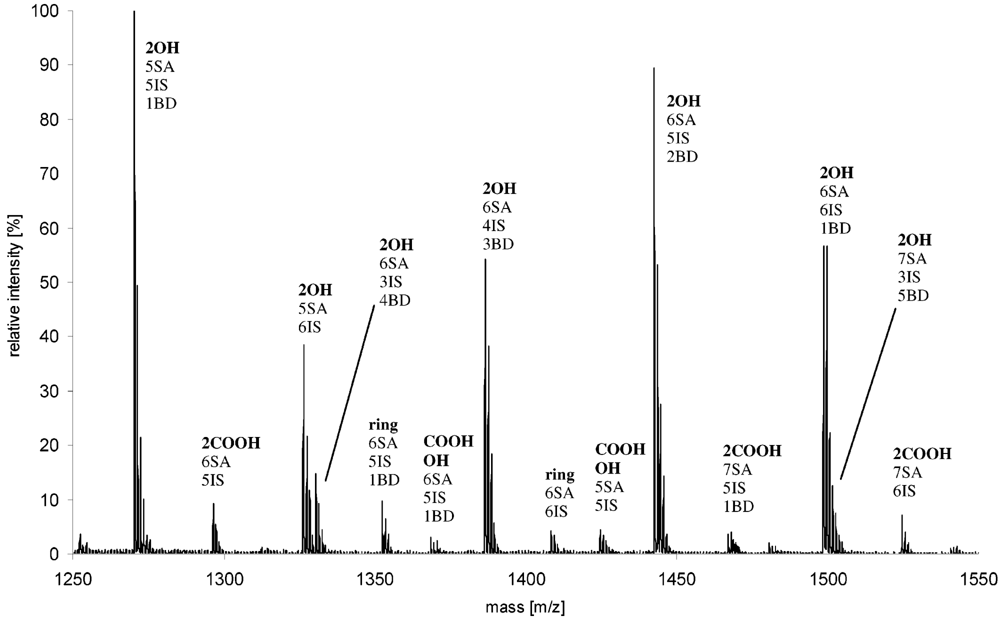


Figure 6. Section of the MALDI-TOF-MS spectrum of terpolyester **2a**. Peak labeling (example): 2OH = number and type of end groups, 5SA = number of SA moieties, 5IS = number of IS moieties, 1BD = number of BD moieties.

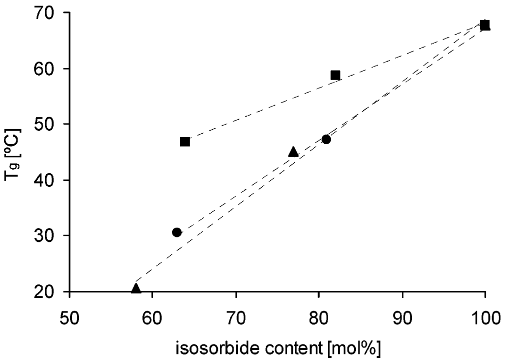


Figure 7. T_g as a function of the isosorbide content for the copolyester SA/IS/diol 2, with diol 2 being (▲) 1,3-propanediol, (●) neopentyl glycol, or (■) 2,3-butanediol.

should be either fully acid or fully hydroxyl functional ($f \geq 2$). Besides the chain functionality, the concentration of the functional end groups (OHV or AV) has a strong influence on the cross-link density, and thus on coating properties such as toughness, hardness, and solvent resistance. The linear copolyesters reported in Table 2 mainly have hydroxyl end groups due to the excess of diol monomers added during their synthesis. However, as was discussed already, not all chains have two OH end groups. To increase the functionality of the hydroxyl functional polymers, branched polyesters were synthesized by addition of trimethylolpropane (approximately 10 mol % relative to the total amount of diols present) in the polymer synthesis. This led to polyesters with increased OH functionality, as can be seen in Table 3. The broadening of the molecular weight distribution indicates that branching has occurred. A disadvantage of using TMP is the pronounced lowering of the polyester T_g (compare polymers **5a** and **5b** with **1b** and **2a**, respectively).

While the addition of TMP works well for hydroxyl-functionalized polyesters, the synthesis of branched-acid-functionalized polymers cannot be achieved in a similar way, as was discussed previously. To obtain acid functional polymers with $f > 2$, we followed a different approach: OH functional linear polyesters were reacted with CA after the polycondensation without further addition of a catalyst. If a hydroxyl chain end reacts with a citric acid molecule, this results in a chain end having two carboxylic end groups and one tertiary hydroxyl end group (Scheme 2). In theory, one would therefore expect the OHV to remain constant and the AV to increase from its initial value to a value twice as high as the OHV, as long as the molecular weight is constant.

However, different side reactions can occur. First of all, citric acid has three carboxylic acid groups available for reaction with hydroxyl functional chains, which might lead to chain extension, branching, and/or cross-linking of the polyester during the modification. Another possible side reaction is acidolysis of the ester bonds by citric acid. If this occurs, polyester chains can be broken up in two fragments, as shown in Scheme 3. This interchange reaction leads to two acid-functionalized chain ends. Finally, alcoholysis of ester bonds can occur by the tertiary hydroxyl group of citric acid. Preliminary results of model reactions carried out using ^{13}C-labeled citric acid and OH functional polyesters indicate that 75−80% of the citric acid moieties react once, as proposed in Scheme 2. The remaining citric acid molecules react either twice (10−15%) or three times, leading to chain extension and a certain degree of branching. So far, no evidence was found for the occurrence of acidolysis of the polyester by CA. An extensive study of these and other model reactions is beyond the scope of this paper and will therefore be described in a separate publication.

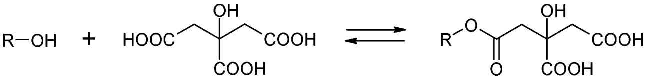
Upon citric acid modification, the solubility of the polyesters in THF for SEC purposes decreases. Therefore, the starting polyesters as well as the CA-modified polymers were characterized using SEC in hexafluoro-2-propanol (HFIP), calibrated using poly(methyl methacrylate) (PMMA) standards. Entries **6a** and **6b** (Table 3) are the products of reactions between citric acid and resins **1b** and **3a**, respectively. For both CA-modified polyesters, a broadening of the polydispersity index is observed. This indicates that side reactions such as those discussed above take place during the modification. Polymer **6a** has a higher $\overline{M}_n$ and T_g than **1b**, suggesting that some branching has indeed occurred. The OHV of **6a** remains constant, while the AV

Table 3. Copolyesters with Increased Functionality, Obtained by Adding TMP during the Polyester Synthesis or by Citric Acid Modification of an OH Functional Polyester

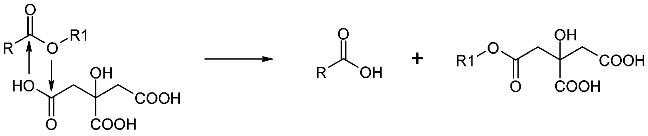
polyester	feed composition	composition (NMR)	T_g (°C)	M_n (g/mol)	M_w/M_n	AV (mg of KOH/g)	OHV (mg of KOH/g)
5a	SA/IS/TMP [1:1.1:0.1]	SA/IS/TMP [1:1.03:0.09]	43.5	2100	2.3	1.3	91.7
5b	SA/IS/BD/TMP [1:0.86:0.24:0.1]	SA/IS/BD/TMP [1:0.83:0.18:0.1]	44.3	3100	3.8	0.5	74.1
1b	SA/IS [1:1.14]	SA/IS [1:1.09]	56.5	3000[b]	2.0[b]	1.5	65.0
6a	OH/CA[a] [1:1.1]	SA/IS/CA [1:1.11:0.2]	68.7	3500[b]	2.3[b]	108.3	65.2
3a	SA/IS/PD [1:0.85:0.20]	SA/IS/PD [1:0.83:0.25]	45.2	3600[b]	2.2[b]	4.7	43.9
6b	OH/CA[a] [1:1.1]	SA/IS/PD/CA [1:0.81:0.21:0.15]	45.2	3400[b]	2.3[b]	81.2	50.5

[a] The amount of citric acid added to the OH functional polyesters was based on the OHV data of these polymers. [b] Determined by SEC in HFIP, calibrated with PMMA standards.

Scheme 2. Reaction of a Hydroxyl End Group with Citric Acid



Scheme 3. Acidolysis of a Polyester by Citric Acid



increases dramatically. Acid functional polyesters were thus obtained from the reactions between OH functional polyesters and CA.

The OHV of polyester **6b** is significantly higher than that of the starting polymer **3a**. This could mean that the reaction between polyester **3a** and citric acid was not carried out to sufficient extent. The molecular weight and PDI only show a slight change, while T_g is constant. This implies that side effects such as branching did not occur as extensively as with polyester **6a**.

Curing of Renewable Polyesters. Coatings were formulated with the described biobased polyesters and conventional curing agents. To be able to work on a small scale, polymer films were applied from solution, rather than by powder application. Formulation of the various coating compositions was based on data from end group titrations. A slight excess (1.05 mol equiv) of curing agent with respect to polyester end groups was used. Hydroxyl functional polyesters were cured using three different commercially available curing agents (Figure 8): a polyisocyanate based on isophorone diisocyanate, blocked with ε-caprolactam, and a hexamethylene diisocyanate-based polyisocyanate and its ε-caprolactam-blocked version. Carboxylic acid functional polymers were cross-linked with TGIC and *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)adipamide.

Curing reactions carried out with **I** and **III** (Figure 8) were catalyzed with dibutyltin dilaurate (0.5 wt % with respect to the amount of polyester). These curing reactions were performed at relatively high temperature for 30 min, to facilitate deblocking of the isocyanate moieties and removal of ε-caprolactam. The curing process was monitored by ATR-FTIR spectroscopy. For OH functional polyesters cured with **II**, disappearance in time of the isocyanate absorption peak at 2271 cm^{-1} could be observed (Figure 9). After 4.5 min of curing at 180 °C, most of the −NCO moieties had reacted, as is evident from the disappearance of the isocyanate signal in the IR spectrum. It should be mentioned that, at $t = 0$, the sample was already heated to the reaction temperature, which took approximately 30 s. This means that reaction had already started shortly before the first measurement was carried out. All obtained films were glossy and transparent, ranging from almost colorless to slightly yellow. The coating color strongly depends on the purity of the isosorbide grade used for the polyester synthesis.

Complete curing of the acid functional polyesters with TGIC (**IV**) seems to occur slightly faster, i.e., within 3−4 min. Curing was also followed by taking samples for SEC analysis. The results are in line with the IR data, since they show rapid gelation of the coating formulations. The weight average molecular masses of the coating formulations increase exponentially toward infinity, leading to insolubility of the networks in THF. For OH functional branched polyesters, cured with the free isocyanate groups of **II**, this occurs within 5−6 min. When the same polymers are cured with the corresponding ε-caprolactam-blocked curing agent **III** in the presence of 0.5 wt % dibutyltin dilaurate, gelation occurs within 4 min. Acid functional polyesters cured with **IV** again show faster network formation: after 1 min at 180 °C (without catalyst), the material is no longer soluble and SEC analysis has become impossible.

Coating Properties. To determine the effect of enhanced polyester functionality on coating properties such as chemical resistance and mechanical performance (i.e., impact resistance and hardness), both linear and branched OH functional polyesters were cured with the same cross-linkers. Characteristics of the resulting coatings based on OH functional polyesters are given in Table 4.

Film **F1** shows the best characteristics of all the coatings based on the linear OH functional copolyesters. With respect to chemical and mechanical properties, it was the only coating that passed all the different tests. This is thought to be a result of the relatively low molecular weight of polyester **1b** and, as a result, its high hydroxyl number (OHV = 65.0 mg of KOH/g) compared to those of polyester series **2** and **3**. The degree of cross-linking increases with decreasing molecular weight, which improves performance. Apart from entry **F1**, all films from linear polyesters have poor to moderate acetone resistance. The main reason for this is probably insufficient polymer functionality. **F1**, **F3**, and **F6** show intermediate to good impact resistance, which is mainly due to the flexible nature of cross-linker **II**. Surprisingly, curing with the ε-caprolactam-blocked version (**III**) of this HMDI trimer leads to poor results. Optimization of curing conditions and/or catalysis is necessary to further investigate this observation. Values for the König hardness of these coatings are rather high (the König hardness of glass, measured on the same pendulum tester, is approximately 235 s). **F6** is much softer at room temperature, which can be explained by the low T_g of polyester **3b** (T_g = 20.6 °C). Film thicknesses of the dry coating vary considerably. This is a result of the method of application and the solvent used. The liquid film has time to flow out over the substrate, since NMP evaporates slowly. When the substrate is not perfectly horizontal, the film will be thicker

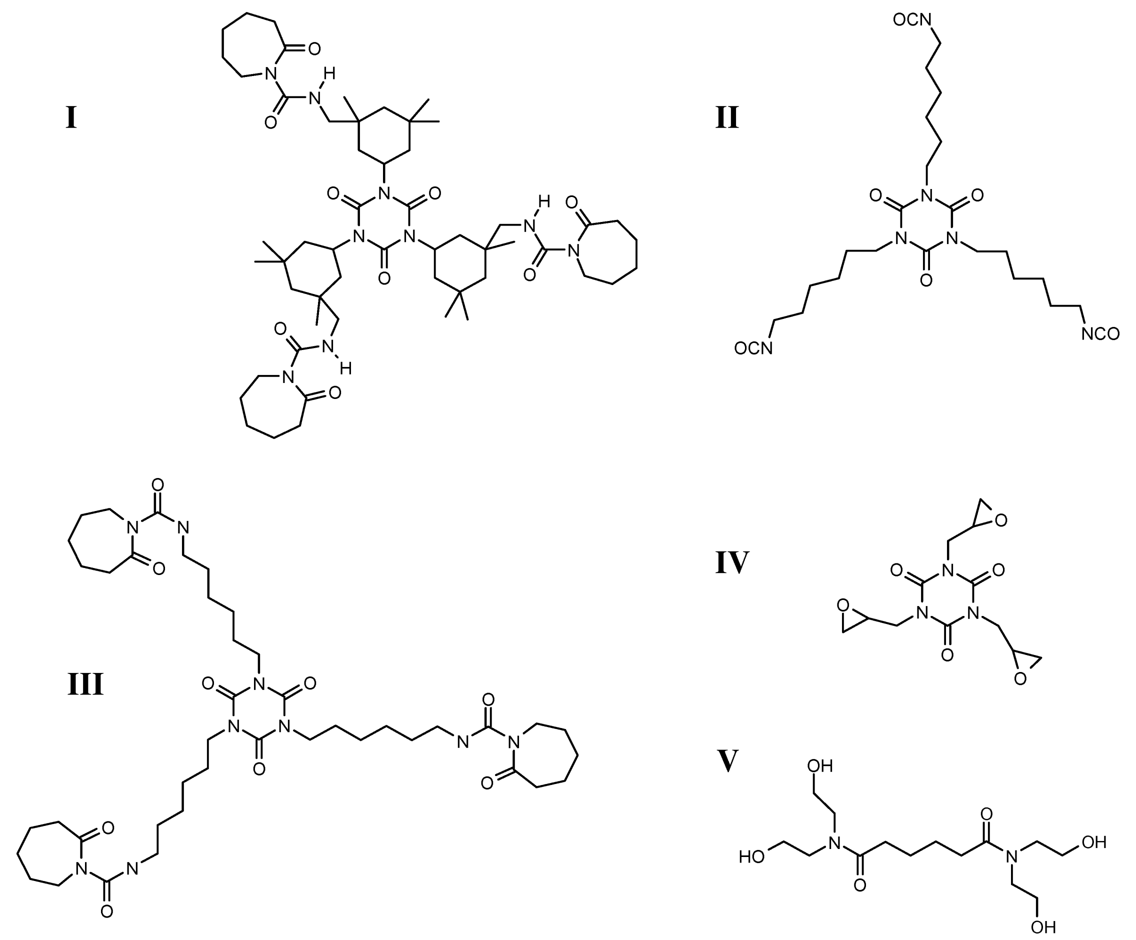


Figure 8. Conventional curing agents: (**I**) ϵ-caprolactam-blocked isophorone diisocyanate-based polyisocyanate (trade name Vestagon B1530, approximate structure), (**II**) hexamethylene diisocyanate-based polyisocyanate (trade name Desmodur N3600, approximate structure), (**III**) ϵ-caprolactam-blocked hexamethylene diisocyanate-based polyisocyanate (trade name Desmodur BL3272, approximate structure), (**IV**) TGIC, and (**V**) *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)adipamide (trade name Primid XL-552).

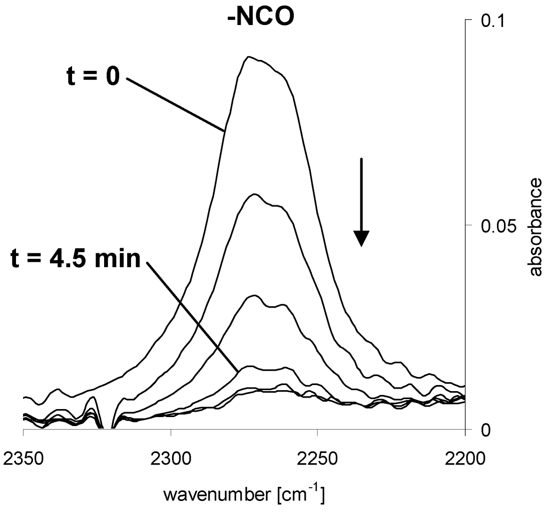


Figure 9. ATR-FTIR absorption peak for isocyanate (2271 cm^{-1}) functionalities during the curing reaction between OH functional polyester **5a** and curing agent **II** (Figure 8). Spectra were measured at $t = 0$, 1, 2, 4.5, 7.5, and 10 min at 180 °C.

on one side of the aluminum panel. Application of these materials by powder coating will lead to homogeneous film thicknesses.

The results in Table 4 clearly show that increasing the polyester functionality by branching leads to improved coating properties. Acetone resistance is significantly improved when using branched polyesters, due to increased cross-link density. Coatings based on polymer **5a** all pass the reverse impact test (i.e., impact applied to the back of the coated panel), which means that resistance against rapid deformation is also increased, compared to that of films based on linear polyesters. Impact resistance, however, greatly depends on the film thickness. Thick coatings are damaged more easily upon impact, which is probably the main reason why coating **F7** shows some slight cracking. As expected, T_g of the cured films is significantly higher than that of the corresponding polyesters. For example, T_g of **F8** is 76.1 °C, compared to 43.5 °C for its corresponding polyester **5a**.

Polyesters modified with CA (i.e., polyesters **6a** and **6b**) are probably slightly branched materials. Linear, 100% carboxylic acid-functionalized copolyesters from succinic acid and isosorbide were not obtained, as previously discussed. Therefore, we only discuss curing of COOH functional polyesters obtained by CA modification of OH functional polyesters.

As displayed in Table 5, curing of acid functional polyesters results in coatings with good to excellent solvent resistance. The impact resistance of **F10** is good, while some slight cracking is observed in **F11**. In general, it was observed that coatings cured with curing agent **IV** (Figure 8) perform better than those cured with curing agent **V**, with respect to mechanical performance and film appearance. Films based on polyester **6b** do not pass impact testing. This is thought to be mainly due to insufficient conversion of the reaction of OH functional polyesters with citric acid. Further optimization of reaction conditions will lead to better results. Another possible cause of

Table 4. Coatings Based on Hydroxyl Functional Polyesters

film	polyester	curing agent[a]	T_{cure} (°C)	t_{cure} (min)	acetone resistance[b]	impact test (1 kg, 100 cm)[b]	König hardness (s)	av film thickness (mm)
Linear OH Functional Polyesters								
F1	**1b**	**II**	180	20	+	+	204	43
F2	**2a**	**I**	200	30	−	−	222	40
F3	**2a**	**II**	180	20	−	±	nd	38
F4	**2a**	**III**	200	30	−	−	216	69
F5	**3a**	**II**	180	20	−	−	211	27
F6	**3b**	**II**	180	20	−	+	61	34
Branched OH Functional Polyesters								
F7	**5a**	**I**	200	30	+	±	211	103
F8	**5a**	**II**	180	15	+	+	n.d.	44
F9	**5a**	**III**	200	30	+	+	200	72

[a] See Figure 8. [b] Key: + = good, ± = moderate, − = poor.

Table 5. Coatings Based on Carboxylic Acid Functional Polyesters

film	polyester	curing agent[a]	T_{cure} (°C)	t_{cure} (min)	acetone resistance[b]	impact test (1 kg, 100 cm)[b]	König hardness (s)	av film thickness (mm)
F10	**6a**	**IV**	180	10	+	+	226	38
F11	**6a**	**V**	200	10	+	±	nd	35
F12	**6b**	**IV**	200	10	+	±	215	42
F13	**6b**	**V**	200	10	+	−	nd	44

[a] See Figure 8. [b] Key: + = good, ± = moderate, − = poor.

reduced impact resistance of these coatings is their rather high T_g (approximately 80 °C). This might be improved by increasing the chain flexibility through incorporation of a more flexible diol comonomer or replacement of part of the succinic acid by adipic acid. Coating hardnesses for films based on acid functional polyesters are comparable to hardness values observed for films **F1**−**F9**.

These observations demonstrate that it is possible to synthesize and apply thermosetting coatings based on renewable aliphatic polyesters. The films combine good solvent resistance with a good ability to withstand rapid deformation. In addition, the pendulum damping test (i.e., König hardness test) shows that the coatings are also resistant against slow deformation/indentation.

Conclusion

Linear and branched polyesters based on renewable resources were synthesized via bulk polycondensation from isosorbide and succinic acid to yield hydroxyl and carboxylic acid functional polymers. Terpolyesters from succinic acid, isosorbide, and either 2,3-butanediol or 1,3-propanediol, containing at least 60−70% isosorbide, have glass transition temperatures suitable for powder coating applications. Reaction of linear OH functional polyesters with citric acid leads to acid functional materials with significantly increased acid functionality. Coatings formulated from linear polymers in combination with nonrenewable conventional curing agents show moderate solvent resistance and mechanical performance. On the other hand, films from branched polyesters have good solvent resistance, excellent impact resistance, and high hardness. Provided that isosorbide of high purity is used, these coatings are transparent and colorless. This, in combination with their excellent mechanical properties, makes them very promising materials for coating applications. Due to the high attainable T_g values, these renewable polyesters can even be used in powder coating formulations.

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Supporting Information Available. SEC traces of the SA/IS polycondensation reaction in time and TGA data for the different co- and terpolyesters. This material is available free of charge via the Internet at http://pubs.acs.org.

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