

Chemistry, Functionality, and Coating Performance of Biobased Copolycarbonates from 1,4:3,6-Dianhydrohexitols

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ABSTRACT: Biobased polycarbonates were synthesized from 1,4:3,6-dianhydro-D-glucitol, 1,4:3,6-dianhydro-L-iditol, and 1,4:3,6-dianhydro-D-mannitol as the principal diols, using different types of carbonyl sources. The (co)polycarbonates resulting from polycondensation reactions in solution using triphosgene consisted of several types of polymer chains with respect to chain topology (e.g., linear or cyclic chains) and end-group structure (e.g., hydroxyl, chloroformate or alkyl chloride end-groups). The introduction of flexible comonomers seemed to increase the amount of cyclic structures in the product mixtures. The melt polymerization of diphenyl carbonate with 1,4:3,6-dianhydrohexitols required high reaction temperatures and led to almost exclusively hydroxy-functional poly(1,4:3,6-dianhydrohexitol carbonate)s. Copolymerizing the 1,4:3,6-dianhydrohexitols with 1,3-propanediol and diphenyl carbonate at high tem-

perature resulted in the partial loss of 1,3-propanediol. On the other hand, by melt polycondensation of 1,4:3,6-dianhydrohexitol-based bis(phenyl carbonate) monomers in combination with primary diols and/or triols, the insertion of the primary alcohols could be achieved in a more controlled way. OH-functional materials were prepared, having suitable molecular weights, T_g values, thermal stability, and melt viscosity profiles for (powder) coating applications. These functional biobased (co)polycarbonates were cured with polyisocyanate curing agents, resulting in colorless to pale yellow transparent, glossy coatings with good mechanical performance and solvent resistance. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1450–1463, 2011

Key words: polycarbonates; 1,4:3,6-dianhydrohexitols; renewable resources; functionality; coatings

INTRODUCTION

The preparation of high-performance polymers from renewable feedstock can be an attractive alternative to petrol-based polymers, and therefore receives significant attention in academia and industry alike. Apart from feedstock differentiation, there is also an opportunity to develop materials with unique properties, which cannot be obtained from traditional petrochemicals.^{1–3}

Thermosetting powder coatings are widely used for a broad range of products, such as metal and wooden furniture, tools, domestic appliances as well as automotive and engineering applications.^{4,5} The resins used in such systems are low molecular weight polymers with reactive end-groups. The glass transi-

tion temperatures (T_g) of these polymers must be well above room temperature to ensure sufficient physical stability of the powder during storage. Therefore, these resins are typically polyesters based on combinations of aromatic and aliphatic building blocks, mostly originating from fossil feedstock. The rigid aromatic building blocks provide the required chain stiffness.

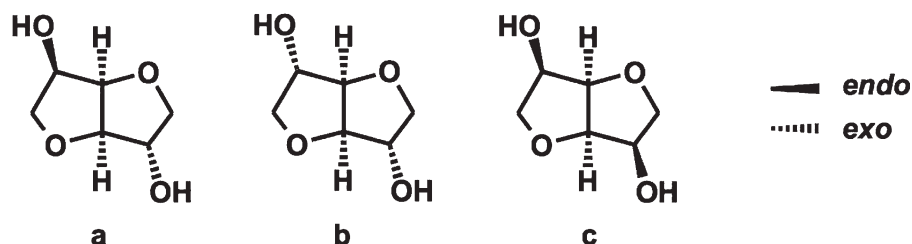
In previous publications, 1,4:3,6-dianhydrohexitols (DAH, Scheme 1) were identified to be useful alternative monomers to prepare functional polymer resins suitable for coating applications.^{6–8} The rigid, bicyclic DAHs are aliphatic monomers and are produced starting from sugars such as D-glucose. They provide rigidity to the polymer chains, leading to materials with relatively high glass transition temperatures, even if they are copolymerized with flexible dicarboxylic acids such as succinic acid.

The polyester systems based on the DAHs have several advantages, such as straightforward synthesis routes, flexibility in molecular design, and good final coating properties. In addition, these fully aliphatic polymers may provide enhanced UV stability compared to their aromatic counterparts. Still, we have also found that there is room for improvement

Additional Supporting Information may be found in the online version of this article.

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Scheme 1 The 1,4 : 3,6-dianhydrohexitols: (a) 1,4 : 3,6-dianhydro-D-glucitol (isosorbide, IS), (b) 1,4 : 3,6-dianhydro-L-iditol (isoidide, II), and (c) 1,4 : 3,6-dianhydro-D-mannitol (isomannide, IM).

in terms of, for example, hydrolytic stability, coating toughness, and appearance. We therefore investigated another class of step-growth polymers: polycarbonates. Conventional polycarbonates, such poly(bisphenol-A carbonate), are known for their high toughness, excellent transparency, and good solvent resistance. In addition, the carbonate links are more hydrolytically stable than esters.

Aromatic polycarbonates, however, are hardly applied in coating applications for several reasons. First of all, the T_g values of these polymers are quite high ($\sim 150^\circ\text{C}$), which means that flow of these materials at common curing temperatures of $\sim 180^\circ\text{C}$ – 200°C is insufficient to achieve good film formation. A second major disadvantage of such polycarbonates is their poor UV-stability because of their high aromatic content. Using poly(bisphenol-A carbonate) in exterior applications would lead to severe yellowing of the coating systems.

The ideal solution to these problems would be to design aliphatic polycarbonates of moderate molecular weight, having the right functionality and thermal properties for coating applications. Several types of aliphatic polycarbonates have already been investigated, such as oligo- and polycarbonates based on a range of linear glycols, materials synthesized by using cyclic carbonate monomers as carbonyl sources and systems based on oxiranes, using CO_2 as the carbonyl source.^{9–15} Other aliphatic polycarbonates were based on 1,4-bis(hydroxymethyl) cyclohexane. These materials were applied from solution as coatings, cured with polyisocyanates.¹⁶ Hyperbranched aliphatic polycarbonates having low T_g s have also been described for solvent borne coating applications.¹⁷ Radiation-curable powder coating resins were prepared by ring-opening polymerization of 2,2-dimethyl-1,3-trimethylene carbonate, followed by end-capping with methacrylate moieties.¹⁸ Different (co)polycarbonates based on the DAHs were also described in literature, but so far their functionalities and subsequent coating application were not elaborated upon.^{19–30}

In this article, the synthesis, characterization, and coating application of aliphatic polycarbonates, based on 1,4:3,6-dianhydrohexitols in combination with other diols or higher alcohols, are discussed.

Three different polymerization routes were investigated to synthesize linear and branched (co)polycarbonates with the required characteristics with respect to molecular weight, T_g , and functionality. First of all, polymers were prepared in solution using triphosgene, providing information concerning the effect of the different hydroxyl group orientations (i.e., *endo* or *exo*) on the polymerizations. Melt polycondensations were carried out using diphenyl carbonate as the carbonyl source. Finally, to enhance the control over 1,4:3,6-dianhydrohexitol and comonomer build-in, diaryl carbonate derivatives of the 1,4:3,6-dianhydrohexitols were synthesized, followed by melt polycondensation in the presence of several diols and triols. Special attention was paid to the polymer end-groups, as we are targeting functional polymers suitable for application in coating applications. The resulting polycarbonates were cured with conventional polyisocyanate crosslinking agents, and coating properties were assessed.

EXPERIMENTAL

Materials

Isosorbide (polymer grade Polysorb[®] P, 98.5+ %) and isoidide (II) (99.8%) were obtained as gifts from Roquette Frères. Isomannide (IM) (97+ %) was a gift from the Agrotechnology and Food Sciences Group. 1,3-Propanediol (99.6+ %), glycerol (99.5+ %), phenyl chloroformate, pyridine (anhydrous, 99.8%), triethylamine (99.5%), zinc acetate, dibutyltin dilaurate (DBTDL), as well as normalized solutions of KOH in methanol were purchased from Aldrich. Diphenyl carbonate, trimethylolpropane (TMP), 4-dimethylaminopyridine, and acetic anhydride were bought from Acros Organics. Triphosgene (bis(trichloromethyl) carbonate, 99+ %) was obtained from Fluka, and 1,4-butanediol was purchased from Merck. All solvents were supplied by Biosolve. Chloroform-*d* was obtained from Cambridge Isotope Laboratories, DMSO-*d*₆ was bought from Campro Scientific. Irganox HP2921, a mixture of phenolic and phosphonic anti-oxidants, was a gift from Ciba Specialty Chemicals. Isophorone diisocyanate-based ϵ -caprolactam blocked

polyisocyanate (trade name: Vestagon B1530) was a gift from Degussa GmbH. Hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600) was a gift from Bayer AG. All chemicals were used as received.

Synthesis of (co)polycarbonates using triphosgene

(Co)polycarbonates were synthesized by polymerization of 1,4:3,6-dianhydrohexitols and comonomers (if any) by phosgenation using triphosgene. The procedure is described for isosorbide (IS) in combination with 1,3-propanediol (PD). Isosorbide (1.99 g, 13.6 mmol), triphosgene (3.23 g, 10.9 mmol), and 1,3-propanediol (1.03 g, 13.6 mmol) were weighed into a 250 mL round-bottom flask and subsequently dissolved in a mixture of 1,4-dioxane (20 mL) and dichloromethane (DCM, 100 mL). Pyridine (8.61 g, 108.9 mmol), diluted with DCM (20 mL), was added dropwise at 0°C, while stirring. After 20 h of stirring at room temperature, the reaction mixture was concentrated to a total volume of ~ 50–60 mL by applying vacuum and subsequently poured into cold methanol. The precipitated polycarbonate was isolated by filtration and washed a second time by dissolution/precipitation from dichloromethane/methanol. Upon isolation, the polycarbonate was dried overnight at 40°C *in vacuo*. Yield: 1.09 g (29%). Yields for this type of reactions were low because of nonoptimized conditions and solubility of part of the product in methanol during work-up.

Synthesis of (co)polycarbonates using diphenyl carbonate

OH-functional (co)polycarbonates were synthesized by polycondensation of the different 1,4:3,6-dianhydrohexitols, with or without other diol moieties, by transcarbonation with diphenyl carbonate. A typical melt polymerization was carried out according to the following procedure, described for II. II (15.31 g, 105 mmol), diphenyl carbonate (20.40 g, 95 mmol), zinc acetate (0.05 mol % relative to DPC), and Irganox HP2921 (0.20 g) 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 (in this case: phenol). During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate removal of phenol from the reaction mixture. While stirring, the mixture was heated to 160°C using a heating mantle, and a clear melt was obtained. Subsequently, the reaction temperature was increased stepwise up to 245°C to maintain distillation of phenol. After 4 h, vacuum processing was started at 245°C, with typical pressures ranging from 1–3 mbar. Vacuum proc-

essing was performed during 2 h and resulted in a rapid increase in melt viscosity. The polymer was discharged from the reactor and left to cool and solidify. The product is soluble in chloroform, DCM, and hexafluoroisopropanol (HFIP), but not in tetrahydrofuran (THF). Yield: 17.1 g (95%).

Synthesis of the bis(phenyl carbonate)s of IS, II, and IM

DAH bis(phenyl carbonate)s were synthesized based on the three different 1,4:3,6-dianhydrohexitols: IS, II, and IM. The procedure is described here for II. II (15.05 g, 103 mmol) and pyridine (17.96 g, 227 mmol) were dissolved in 200 mL of THF. Phenyl chloroformate (35.47 g, 227 mmol) was added dropwise during ~ 2 h at 5°C–10°C, while stirring. The reaction was continued for 4 h at room temperature. Subsequently, the reaction mixture was poured into demineralized water, affording a white precipitate. This solid was collected on a glass filter and washed with a 5 wt % aqueous solution of NaHCO₃ and several times with water. The crude product was recrystallized from ethyl acetate and dried *in vacuo* at 40°C.^{24,26} Yield: 26.15 g (65.7%), purity: 98+ %, mp: 107°C–109°C. Isosorbide bis(phenyl carbonate) (ISBPC) and IM bis(phenyl carbonate) (IMBPC) were prepared following the same procedure. ISBPC: yield: 64.7%, purity: 98+ %, mp: 151°C–153°C; IMBPC: yield: 79.4%, purity: 97+ %, mp: 131°C–132°C.

Synthesis of (co)polycarbonates from DAH bis(phenyl carbonate)s

A typical melt polymerization was carried out according to the following procedure, described for ISBPC. ISBPC (15.19 g, 39.3 mmol), IS (2.41 g, 16.5 mmol), 1,3-propanediol (2.09 g, 27.5 mmol), TMP (0.42 g, 3.1 mmol), zinc acetate (0.05 mol % relative to the amount of ISBPC), and Irganox HP 2921 (0.5 wt % relative to the amount of diols) were weighed into a 250 mL round-bottom glass flange reactor. The reactor was fitted with 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 removal of phenol. While stirring, the mixture was heated up to 185°C. Subsequently, the reaction temperature was increased stepwise to maintain distillation of the formed phenol. The maximum reaction temperature was 210°C. After 3 h, vacuum processing was started at 205°C–210°C, with typical pressures ranging from 1–5 mbar. Vacuum was applied until no more phenol was distilled off, after which the viscous polymer melt was discharged from the reactor and left to cool and solidify. The resulting transparent glassy polycarbonate is soluble in, for example,

chloroform, DCM, HFIP, and *N*-methyl-2-pyrrolidone (NMP), but not in THF. Yield: 9.31 g (72.8%).

Solvent casting and curing of biobased (co)polycarbonates

Hydroxy-functional (co)polycarbonates were cured using: (i) a trimer of hexamethylene diisocyanate (NCO equivalent weight = 183 g/mol, trade name: Desmodur N3600) and (ii) an ϵ -caprolactam blocked trimer of isophorone diisocyanate (NCO equivalent weight = 275 g/mol, trade name: Vestagon B1530). Ad i: A solution of 0.3–0.5 g of polycarbonate in 0.8 mL of NMP was prepared, as well as a separate solution of Desmodur N3600 (1.05M equivalent of NCO relative to the amount of OH-groups present in the polycarbonate sample, calculated from OH titration data) in 0.2 mL of NMP. The two solutions were mixed and applied to the aluminum substrate as a wet film with a thickness of 250 μm using a doctor blade. After drying at room temperature, the film was cured at 180°C under N_2 during 20 min. Ad ii: A solution of 0.3–0.5 g of polycarbonate, 1.05M equivalent of the crosslinker (relative to the amount of OH-groups present in the polymer sample) and 0.5 wt % (relative to the amount of polycarbonate used) of DBTDL in 1 mL of NMP was prepared. Subsequently, a wet film of $\sim 250 \mu\text{m}$ thickness was applied onto an aluminum panel. The film was left to dry at room temperature, followed by curing at 200°C during 30 min under nitrogen.

Measurements

SEC analysis was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35°C). Injections were done by a MIDAS auto-injector, the injection volume being 50 μL . PSS (2 \times PFG-lin-XL, 7 μm , 8 mm \times 300 mm, 40°C) columns were used. HFIP was used as eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using PMMA standards. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, chloroform-*d* was used as the solvent (unless stated otherwise). The thermal stabilities of polymer samples were determined using a Perkin-Elmer Pyris 6 thermogravimetric analysis (TGA) apparatus. Approximately 10 mg of polymer was heated from 40°C to 700°C at a heating rate of 10°C/min under a N_2 flow of 20 mL/min. 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

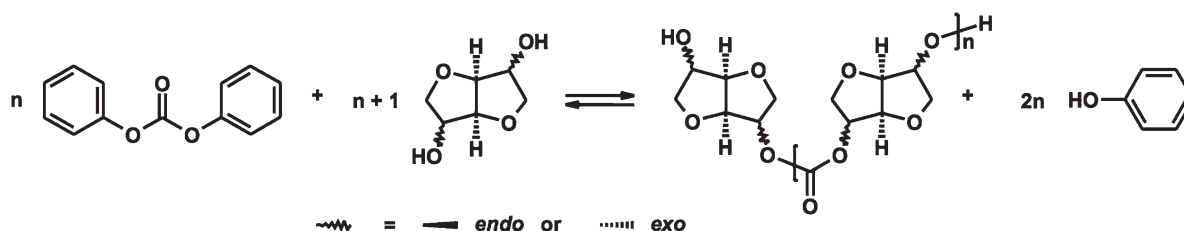
higher mass range. The mass accuracy was better than 0.2 Da, the mass resolution was $\sim m/z$ 12,000. DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99%) was used as cationization agent. Solutions of the matrix (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 in NMP solution using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. All titrations were carried out in duplo. Complex viscosities of polycarbonates were determined as a function of temperature using a TA Instruments AR1000-N Rheolyst rheometer with parallel plate geometry. Temperature sweeps were performed, during which the temperature was decreased, starting at a maximum temperature of 180°C. When the storage modulus G' exceeded 10^6 Pa, the measurements were stopped automatically. The following parameter settings were used: cooling rate = 3°C/min, strain = 1%, frequency = 1 Hz (= 6.283 rad/s). Data points were collected after every cooling step of 3°C and an equilibration time of 1 min. Data acquisition was done with Rheology Advantage Instrument Control software and data analysis with Rheology Advantage Data Analysis software. Crosslinking and coating performance at room temperature were evaluated using the following 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) and 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). The thicknesses of the obtained coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH).

RESULTS AND DISCUSSION

Synthesis and functionality of poly(isohexide carbonate)s

The three DAH isomers IS, II, and IM were polymerized using triphosgene (TPh)^{20,21,31,32} as well as diphenyl carbonate (DPC) to obtain the corresponding poly(1,4:3,6-dianhydrohexitol carbonate)s.

As an example, Scheme 2 depicts the reaction between diphenyl carbonate (DPC) and a 1,4:3,6-dianhydrohexitol. These homopolymers (Table I) serve as reference polymers for the copolymers which will be described in the next sections.



Scheme 2 Synthesis of a poly(DAH carbonate) from DPC and a DAH through a transesterification mechanism.³³

Polycarbonates prepared in solution using TPh (entries 1,3 and 5) were obtained as white powders, whereas those made through melt polycondensation (entries 2, 4 and 6) are pale yellow resins. The molecular weight distribution of poly(IM carbonate) (Table I, entry 5) is broader than those of polycarbonates 1 and 3. The broad PDI as well as the limited solubility of polymer 5 in CHCl_3 suggest that branching and/or crosslinking has occurred, possibly through acid catalyzed ring-opening of the anhydro ether ring of IM.^{34,35} This ether ring is known to be less stable than its counterparts present in IS and II.^{36–38} Polycarbonates 1 and 3 have PDI values below 2 and are fully soluble in CHCl_3 as well as in HFIP.

While entries 2 and 4 were viscous, transparent melts until the end of the polymerization, entry 6 became an opaque solid during the atmospheric step of the procedure. We did not succeed in obtaining a clear melt again, even when the temperature was increased to 260°C. However, this product does appear to be fully soluble in HFIP. Entry 4, synthesized from II, has the highest molecular weight of the three materials prepared in the melt, which is in agreement with the observation that II is the most reactive 1,4:3,6-dianhydrohexitol in melt polycondensations.⁸

The T_g values of poly(IS carbonate) and poly(II carbonate) are found to be between 131°C and 148°C

at \overline{M}_n values of $\sim 3,000$ – $4,500$ g/mol, approaching the T_g of poly(bisphenol-A carbonate) of 150°C.³⁰

End-group structures of poly(isohexide carbonate)s prepared using TPh

Linear polycarbonates should essentially be telechelic chains to be useful in cured coating systems. Therefore, we have applied MALDI-ToF-MS, NMR, as well as end-group titration to determine the type of end-groups present and the hydroxyl values (OHV).

The IS end-groups of polymer 1 (signals d and e) can be clearly distinguished in its $^1\text{H-NMR}$ spectrum (Fig. 1), indicating the presence of hydroxyl end-groups. Also, two singlets are visible at 3.7 ppm (signal h) and at 3.85 ppm (signal g, partly overlapping with the group of resonances f), which can respectively be attributed to methyl ether and methyl carbonate groups, resulting from the precipitation of the reaction mixture in methanol. Presumably, the methyl ether linkages are formed by the reaction of a pyridinium complex, present at the polymer chain end, with methanol. A mechanism for this reaction is proposed in the Supporting Information Scheme S1. The formation of ether linkages through decarboxylation of a carbonate group or through dehydration of two alcohol end-groups³⁹ seems unlikely at these relatively low reaction temperatures (0°C–25°C).

TABLE I
Properties of Poly(DAH Carbonate)s

Entry	Feed composition ^{a,b}	T_g (°C)	\overline{M}_n (g/mol)	\overline{M}_w (g/mol)	PDI	OHV ^c (mg KOH/g)
1	IS/TPh (1 : 0.33)	134.8	3,500	6,100	1.8	n.d.
2	IS/DPC (1.1 : 1)	138.0	3,200	7,200	2.2	55.0
3	II/TPh (1 : 0.33)	130.9	3,200	6,200	1.9	n.d.
4	II/DPC (1.1 : 1)	148.2	4,600	10,300	2.2	34.0
5	IM/TPh (1 : 0.33)	120.9	3,400	10,700	3.1	n.d.
6	IM/DPC (1.1 : 1)	91 ^d	3,700	7,500	2.0	n.d.

^a Reaction conditions (see Experimental section): entries 1,3 and 5: addition of pyridine solution to diol/TPh solution at 0°C, followed by stirring at room temperature for 20 h; entries 2,4 and 6: prepared in the melt, $T_{\text{max}} = 245^\circ\text{C}$, phenol removed *in vacuo*.

^b TPh, triphosgene; DPC, diphenyl carbonate; IS, isosorbide; II, isoidide; IM, isomannide.

^c Potentiometric titrations to determine OH-values (OHV) were only performed on materials available in sufficient quantities and at full solubility of the resins in NMP.

^d This T_g is an approximate value, since the transition in the DSC thermogram (observed in the first heating curve) was too faint to determine the T_g accurately. No melt transitions were observed.

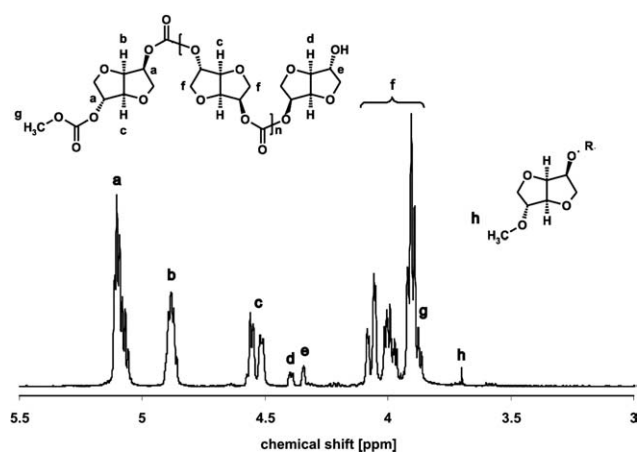


Figure 1 $^1\text{H-NMR}$ spectrum of poly(isosorbide carbonate), polymer **1**, prepared using TPh as a carbonyl donor.

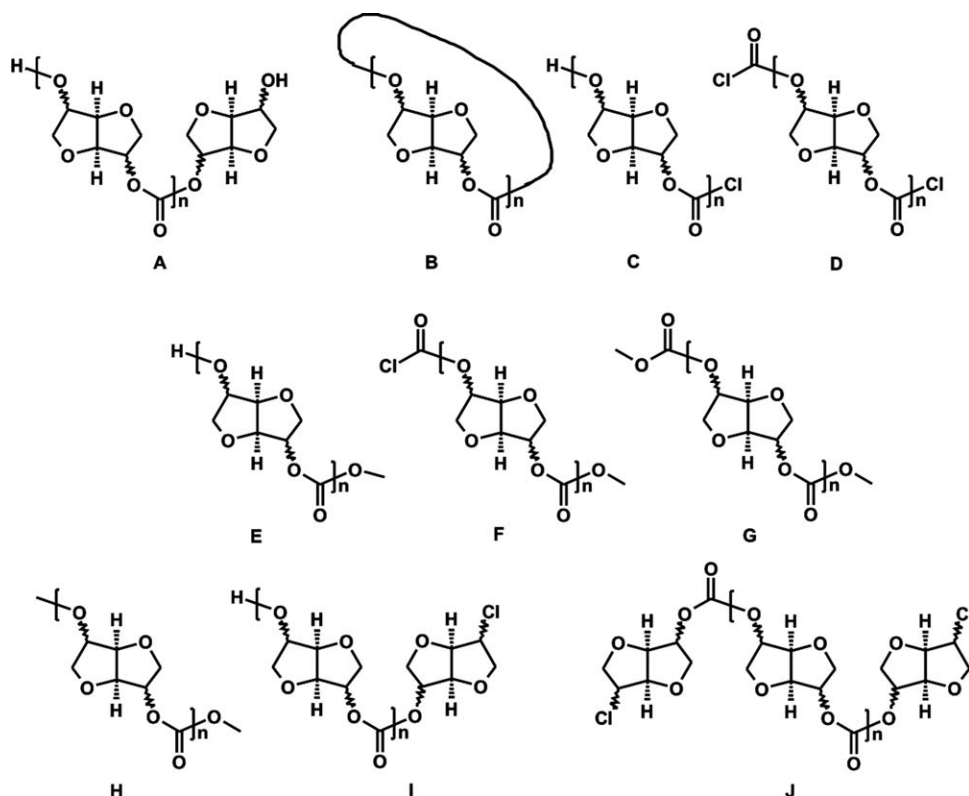
Contrary to what was observed previously for IS-based polyesters prepared by melt polycondensation,^{6,7,40,41} it appears that the *endo*-oriented OH-groups of IS have reacted to a higher extent (conversion = 97%) than the *exo*-oriented hydroxyls (conversion = 88%), as determined by integration of the signals **b** and **c** (Fig. 1). This confirms observations described in literature concerning this unexpected reactivity of these different types of OH-groups in the presence of, for example, pyridine hydrochloride.^{36,42–45} The $^1\text{H-NMR}$ spectrum

of polycarbonate **3** (Supporting Information Fig. S2) clearly shows hydroxyl end-groups, also indicating at least partial hydroxyl-functionality of the resin.

In fact, several types of polymer end-groups can result from the reaction between diols or polyols and TPh using pyridine as a catalyst and HCl scavenger.^{32,46} In Scheme 3, the various possible species are depicted for 1,4:3,6-dianhydrohexitol-based polycarbonates. Besides the desired structure **A**, having two hydroxyl end-groups, also cyclic structures **B** are formed. In addition, several types of linear species can be formed, such as polymer chains having one or two chloroformate-type end-groups (structures **C** and **D**). If the work-up procedure, applied to such chloroformate-terminated species, involves precipitation in methanol, structures such as **F**, **G**, and **H** are formed.

Precipitation of chloroformate-functional polycarbonates **C**, **D**, and **F** in water yields a carbonic acid ester. This end-group is not stable and will lose one molecule of CO_2 to form a hydroxyl group.^{47,48} Structures **I** and **J** can be formed by decarboxylation of the aliphatic chloroformate end-groups of **C**, **D**, and **F**, catalyzed by pyridine.

For example, the MALDI-ToF-MS spectra of the poly(isohexide carbonate)s **1**, **3**, and **5** (Supporting Information Fig. S3) show signals at the same molecular masses, but the relative intensities of these peaks differ for the different materials. The ratios of



Scheme 3 Potential products of the reaction between a 1,4 : 3,6-dianhydrohexitol and TPh (products **E**, **F**, **G**, and **H** are formed during work-up of the polymers, more specifically during precipitation in methanol).

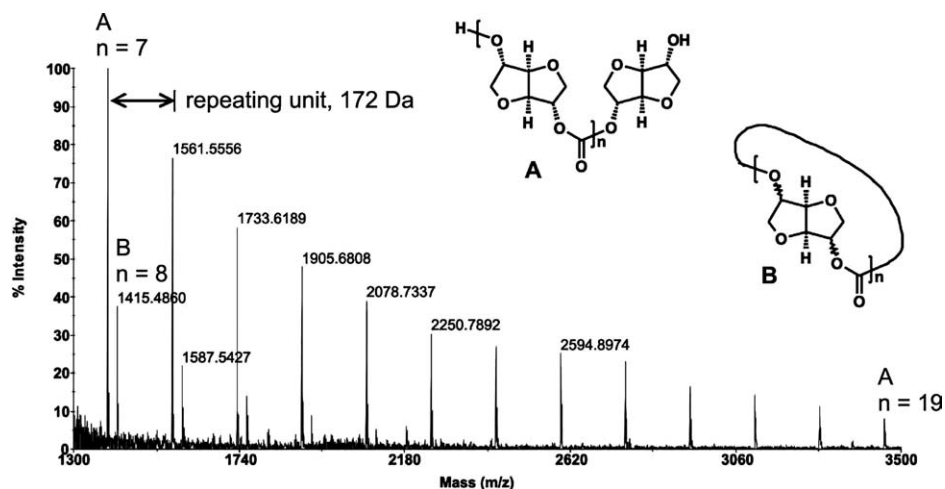


Figure 2 MALDI-ToF-MS spectrum of polycarbonate 4, poly(isoside carbonate), where species **A** represent linear chains, and species **B** represent cyclic chains.

linear versus cyclic chains are different for all three samples. First of all, peaks corresponding to linear chains having two hydroxyl end-groups (signals **A**) are abundant in the spectra of **1** and **2**, while they only have low intensities in spectrum **3**. On the other hand, the $^1\text{H-NMR}$ spectrum of polymer **3** has high intensity peaks attributed to cyclic polycarbonate chains (signals **B**). The II-based polycarbonate **2** shows very low levels of cyclic species according to MALDI-ToF-MS.

Although a quantitative interpretation of the MALDI spectra in terms of relative concentrations of linear and cyclic species is not possible, the trend observed here is as may be expected when considering the orientations of the OH-groups of the different 1,4:3,6-dianhydrohexitols. Possibly, the conformation of poly(IM carbonate) **3** is such that cycle formation is favored. The observation that polymerization of II, having two *exo*-oriented hydroxyl groups, apparently yields even less cyclic polymer chains than are observed in poly(IS carbonate), may indicate that the *exo*-orientation of the hydroxyl groups of the 1,4:3,6-dianhydrohexitols favors the formation of more extended, linear polycarbonate chains. Similar results were published for polycarbonates prepared from IS and IM using diphosgene. MALDI-ToF-MS spectra of homopolycarbonates of IS hardly show signals corresponding to cyclic species, while the MALDI-ToF-MS spectra of copolycarbonates containing both IS and IM feature high intensity signals of cyclic chains.²¹

Thus, the types of end-groups encountered in polymer sample prepared using TPh depend on several factors such as DAH OH-group orientation, stoichiometry, reactant concentrations, as well as on the work-up procedure.

End-group structures of poly(isohexide carbonate)s prepared using DPC

$^1\text{H-NMR}$ spectroscopy reveals the terminal 1,4:3,6-dianhydrohexitol moieties (and, thus, their hydroxyl end-groups) of the poly(isohexide carbonate)s prepared by polycondensation in the melt, as shown for entry **4** in the Supporting Information Figure S4. If polymers, synthesized using DPC, contain phenyl carbonate end-groups, this should lead to resonances at chemical shifts between 7 and 8 ppm. However, no such resonances were observed in the $^1\text{H-NMR}$ spectra of polycarbonates **2** and **4**. The hydroxyl-values, determined by titration (Table I), also indicate significant OH-functionality of these polymers. Assuming that the chains are telechelic OH-functional materials, their number-average molecular weights can be estimated from the OH-values. For entry **2**, this yields a value of 2040 g/mol and for entry **4** the molecular weight calculated is 3300 g/mol. These results suggest that SEC over-estimates the molecular weights of these polycarbonates, as was previously demonstrated for polyesters from 1,4:3,6-dianhydrohexitols.⁶

Figure 2 depicts the MALDI-ToF-MS spectrum of poly(II carbonate) (entry **4**). The main signals correspond to linear species **A**, having two hydroxyl end-groups, while some peaks of lower intensity corresponding to cyclic species (signals **B**) are observed as well. The MALDI spectrum of poly(IS carbonate), entry **2** (Supporting Information Fig. S5), is quite similar to that of polymer **4**. On the other hand, the MALDI spectrum of poly(IM carbonate), entry **6**, is strikingly different. The latter spectrum displays strong signals corresponding to linear chains having one or two phenyl carbonate end-groups, indicating that conversion was insufficient because of

TABLE II
DAH-Based Copolycarbonates Prepared Using TPh and DPC

Entry ^a	Feed composition ^b	Composition (NMR)	T_g (°C)	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PDI
TPh route						
7	IS/1,3-PD/TPh (0.5 : 0.5 : 0.33)	IS/1,3-PD (0.49 : 0.51)	42.9	1,300	1,900	1.4
8	IS/1,3-PD/TPh (0.5 : 0.5 : 0.38)	IS/1,3-PD (0.53 : 0.47)	57.2	1,800	2,500	1.4
9	IS/1,3-PD/TPh (0.5 : 0.5 : 0.40)	IS/1,3-PD (0.50 : 0.50)	83.0	2,600	4,200	1.6
10	II/1,3-PD/TPh (0.5 : 0.5 : 0.35)	II/1,3-PD (0.47 : 0.53)	48.1	1,800	2,300	1.3
11	IM/1,3-PD/TPh (0.5 : 0.5 : 0.38)	IM/1,3-PD (0.54 : 0.46)	46.7	1,900	3,200	1.7
12	IS/GLY/TPh (0.91 : 0.09 : 0.37)	IS/GLY (0.9 : 0.1)	109.8	3,900	12,900	3.3
DPC route						
13 ^c	DPC/IS/1,3-PD (1 : 0.56 : 0.56)	IS/1,3-PD (0.57 : 0.43)	48.1	3,200	5,300	1.7

^a Reaction conditions (see Experimental Section): addition of pyridine solution to diol/TPh solution at 0 °C, followed by stirring at room temperature for 20 h.

^b IS, isosorbide; II, isoidide; IM, isomannide; 1,3-PD, 1,3-propanediol; TPh, triphosgene; GLY, glycerol; DPC, diphenyl carbonate.

^c Prepared in the melt, $T_{max} = 245^\circ\text{C}$.

the solidification of the reaction mixture, as described earlier.

Synthesis and functionality of DAH-based copolycarbonates using TPh and DPC

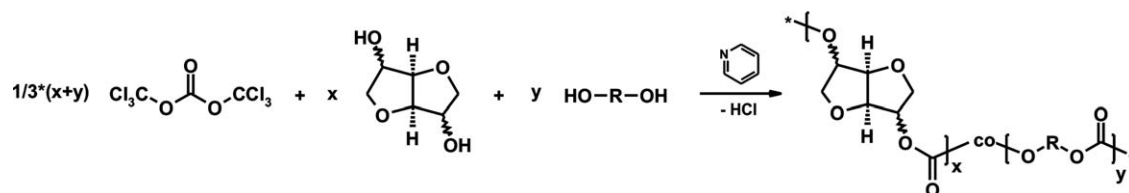
DAH-based copolycarbonates were synthesized to reduce the T_g toward enhanced processability of these polymers in coating applications. Again, the TPh and DPC routes were investigated. The effect of the ratio TPh/diols on molecular weight, T_g , and functionality of poly(IS -*co*-propylene carbonate)s was studied. The maximum functionality of these linear polycarbonates is $\bar{F}_n = 2$, in the ideal case that telechelic chains are obtained. The functionality can be increased by introducing monomers with more than two OH-groups, such as glycerol (Table II, entry 12). Overall, the TPh reaction between diols and/or polyhydric alcohols yielding (co)polycarbonates can be summarized as depicted in Scheme 4.

The molecular weights of most of the copolymers in Table II are significantly lower than those obtained when preparing DAH-based homopolycarbonates using TPh (i.e., entries 1, 3, and 5 in Table I). The reaction conditions were optimized by increasing the amount of TPh relative to the amount of diols. The ratio diols/triphosgene has a strong influence on the molecular weight of the polymer obtained, and it is clear that the \bar{M}_n as well as the T_g increase when

increasing the amount of triphosgene in the reaction mixture (compare entries 7–9). When using a stoichiometric amount of TPh, the molecular weight will be relatively low since phosgene moieties are lost during the reaction, and it is therefore necessary to use an excess of triphosgene.^{47,49} The pyridine solution was added to a solution of the diols and triphosgene to prevent an excess of pyridine to exist in the reaction vessel, minimizing decomposition of triphosgene and/or chloroformate groups.

The T_g values of the polymers increase with increasing 1,4:3,6-dianhydrohexitol content (compare polymers 1 and 9, for example), as was already demonstrated for 1,4:3,6-dianhydrohexitol-based polyesters.⁶ This increase is a result of the increased rigidity of the polymer chains by the rigid bicyclic 1,4:3,6-dianhydrohexitol. Obviously, the considerably higher molecular weight of polycarbonates 1, 3, and 5 compared with those of polymers 7–11 also partly causes the higher T_g of the homopolycarbonates.⁵⁰ Copolycarbonate 13, prepared from DPC, IS and 1,3-PD, and having an OH-value of 57.2 mgKOH/g, has a significantly lower T_g than the homopolycarbonate 2 (Table I) at similar molecular weight, as a result of the incorporation of the flexible 1,3-PD.

The ¹H-NMR spectra of the poly(IS -*co*-propylene carbonate)s 7–9 reveal that the *endo*-oriented hydroxyl group of IS reacts to a higher conversion than its *exo*-oriented counterpart under these



Scheme 4 Polycondensation of 1,4 : 3,6-dianhydrohexitols and, optionally, comonomers (with $0 < x \leq 1$ and $x + y = 1$) using triphosgene (TPh) as the carbonyl source.

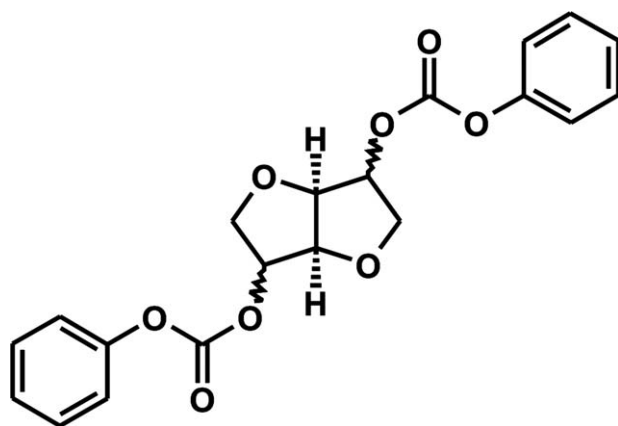
reaction conditions, confirming the previously described results for poly(IS carbonate) **1**.

End-group structures of copolycarbonates prepared using TPh and DPC

All the polycarbonate samples prepared using triphosgene have several types of end-groups, including methyl carbonate groups and alkyl chloride groups. A constant factor for these copolycarbonates is that cyclic chains are always present in significant amounts, as was previously observed for DAH-based copolycarbonates prepared using diphosgene.²⁰ Apparently, appreciable levels of hydroxyl-functionality in 1,4:3,6-dianhydrohexitol-based copolycarbonates can only be obtained when using relatively low amounts of TPh relative to the amount of diols (e.g., polycarbonate **7**), but this leads to polymers with rather low molecular weights. A better synthetic method toward hydroxyl-functional materials might be to work with higher amounts of triphosgene during the polymerization, affording chloroformate end-groups. Subsequent precipitation of the reaction mixture in a large excess of diols or triols will probably lead to enhanced OH-functionality. However, a disadvantage of such a procedure might be the formation of alkyl chloride end-groups.

The MALDI-ToF-MS spectrum of the copolycarbonate **13** (Supporting Information Fig. S6), prepared via the DPC route, shows only low intensity peaks for linear polycarbonate chains with two hydroxyl end-groups, while high intensity peaks are present for several species of linear chains with one or two phenyl end-groups. The composition (Table II) of this polycarbonate suggests that 1,3-propanediol was partly lost from the reactor, possibly through evaporation as such or in the form of trimethylene carbonate.⁵¹ This explains that, at the end, an excess of phenol was left, leading to the presence of phenyl end-groups. Another interesting observation is that ether linkages are present in polycarbonate **13**, which probably means that these chains have lost one (or more) molecules of CO₂ through decarboxylation. The presence of ether linkages in the main chain of coating resins is disadvantageous since they are labile toward UV radiation. In addition, resin **13** does not have enough hydroxyl groups at the chain ends to afford well cured networks upon curing with a polyisocyanate.

To sum up, the two synthetic procedures described so far, using TPh or DPC as carbonyl donors, yield DAH-based (co)polycarbonates with suitable molecular weights and *T_g* values for powder coating applications. However, various types of end-groups are observed in the MALDI-ToF-MS spectra of polymers prepared via the TPh route. This shows that it is difficult to obtain appropriate polymer properties while maintaining the desired type of



Scheme 5 General structure of the three DAH bis(phenyl carbonate) isomers.

end-group. The DPC route, because of the high processing temperature, leads to a loss of the more volatile comonomers and to ether formation. Therefore, we decided to investigate a different, less common route to prepare aliphatic polycarbonate resins.

Synthesis and functionality of copolycarbonates using DAH bis(phenyl carbonate)s

The high reaction temperatures (up to 250°C) used in the DPC route are needed to convert the secondary DAH OH-groups of moderate reactivity to carbonate links and to maintain a polymer melt of acceptable viscosity. To control the build-in of the 1,4:3,6-dianhydrohexitols and its comonomers into the polycarbonates, highly reactive phenyl chloroformate was used to convert the three 1,4:3,6-dianhydrohexitols into their respective bis(phenyl carbonate)s. These monomers can subsequently be reacted with species containing primary OH-groups, such as flexible alkylene diols, glycerol, or TMP in the presence of a transesterification catalyst. As a result of the higher reactivity of such primary alcohols, the reaction temperature can be reduced (as compared to DPC-based polymerizations).²⁶ A similar approach was followed by Sablong et al., to achieve incorporation of IS into poly(butylene terephthalate).⁵²

A procedure to synthesize the bis(phenyl carbonate)s of IS and IM is described in literature.^{24,26} We applied the procedure to all three 1,4:3,6-dianhydrohexitol isomers, resulting in three different isohexide bis(phenyl carbonate) monomers having the general structure shown in Scheme 5. The ¹H-NMR spectrum of II bis(phenyl carbonate) (IIBPC) is displayed in the Supporting Information Figure S7.

The DAH bis(phenyl carbonate) monomers (Scheme 5) were used to synthesize linear and branched (co)polycarbonates that will be compared with polymers synthesized using TPh or DPC. Table III

TABLE III
Linear Copolycarbonates Synthesized Using the DAH bis(Phenyl Carbonate)s

Entry ^a	Feed composition ^b	Composition (NMR)	T_g (°C)	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PDI	OHV (mg KOH/g)
14	ISBPC/IS/1,3-PD (0.42 : 0.16 : 0.42)	IS/1,3-PD (0.57 : 0.43)	89.7	4,200	8,100	1.9	47.3
15	IIBPC/1,3-PD (0.45 : 0.55)	II/1,3-PD (0.44 : 0.56)	35.6	3,100	6,400	2.1	76.4
16	IMBPC/1,3-PD (0.45 : 0.55)	IM/1,3-PD (–) ^c	30.9	3,700	8,000	2.2	n.d. ^c
17	ISBPC/EG (0.48 : 0.52)	IS/EG (0.92 : 0.08)	123.8	3,600	5,500	1.5	28.8
18	ISBPC/1,4-BD (0.45 : 0.55)	IS:1,4-BD (0.45 : 0.55)	37.8	5,000	9,800	2.0	32.1
19	IIBPC/1,4-BD (0.45 : 0.55)	II:1,4-BD (0.44 : 0.56)	36.3	6,300	14,400	2.3	39.0

^a Prepared in the melt, $T_{max} = 210^\circ\text{C}$.

^b ISBPC/IIBPC/IMBPC, isosorbide/isoidide/isomannide bis(phenyl carbonate); 1,3-PD, 1,3-propanediol; EG, ethylene glycol; 1,4-BD, 1,4-butanediol; ISBEC/IIBEC, isosorbide/isoidide bis(ethyl carbonate); Ph, phenol.

^c Not determined due to insolubility of the resin.

lists the properties of linear copolycarbonates prepared from the DAH bis(phenyl carbonate)s.

These copolycarbonates are pale yellow, transparent polymers. The molecular weights of entries 14–19 are in the desired range, and the corresponding T_g values depend on the molecular weights as well as on the compositions of the polycarbonates. According to the copolymer compositions determined by $^1\text{H-NMR}$, the monomers are generally built-in into the polymer chains in the same ratio as the monomer feed. A notable exception is polycarbonate 17, showing a dramatic loss of ethylene glycol residues during the polycondensation, which was mainly because of the formation of the cyclic monomer ethylene carbonate through an unzipping degradation mechanism.^{15,53,54}

Ethylene carbonate is a stable molecule with a boiling point of 246.7°C and was easily distilled off during the second stage of this polymerization at $\sim 210^\circ\text{C}$ *in vacuo*. The resulting polymer has significant amounts of phenyl carbonate end-groups, as determined by MALDI-ToF-MS. This is because of the fact that, along with ethylene glycol, the initial excess of OH-groups is lost. The reduction in OH-content is also reflected in the relatively low OH-value of the final product (Table III). Similar losses of the flexible diol monomers were not observed in other reactions with DAH bis(phenyl carbonate)s, indicating that the reaction temperatures were low enough to prevent sig-

nificant loss of 1,3-propanediol or 1,4-butanediol or the cyclic carbonates derived from these diols.

End-group structures of polycarbonates prepared using DAH bis(phenyl carbonate)s

In the MALDI-ToF-MS spectra of copolycarbonates 15, 18, and 19, the main signals can be attributed to linear species having two hydroxyl end-groups. As an example, a section of the MALDI spectrum of poly(II-*co*-butylene carbonate) (entry 19) is shown in the Supporting Information Figure S8. According to the MALDI-ToF-MS spectra of the polycarbonates 14, 16, and 17, these materials have significant amounts of phenyl carbonate end-groups. By increasing the processing time, especially of the vacuum stage, this problem may be overcome. Otherwise, a slightly larger amount of excess diols could be added to the reaction mixture.

To improve polycarbonate functionality, branched polycarbonates were also prepared (Table IV). Polymers 20 and 21 are especially promising resins for powder coating applications because their T_g values are in the proper range, as are their molecular weights and OH-values. Their polydispersities are larger than 2, indicating that the introduction of TMP has indeed led to branching of the polymer chains. Entry 22 has a very high PDI, higher than can be expected based on the TMP content. This

TABLE IV
Branched Copolycarbonates Synthesized Using Several DAH bis(Phenyl Carbonate)s

Entry ^a	Feed composition ^b	Composition (NMR)	T_g (°C)	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PDI	OHV (mg KOH/g)
20	ISBPC/IS/1,3-PD/TMP (1 : 0.42 : 0.70 : 0.08)	IS/1,3-PD/TMP (1 : 0.28 : 0.06)	78.8	3,600	11,600	3.2	50.4
21	IIBPC/II/1,3-PD/TMP (1 : 0.42 : 0.70 : 0.08)	II/1,3-PD/TMP (1 : 0.24 : 0.05)	83.4	2,900	6,600	2.3	56.8
22	IMBPC/1,3-PD/TMP (1 : 1.16 : 0.04)	IM/1,3-PD/TMP (1 : 1.09 : 0.04)	40.7	5,300	33,300	6.3	39.0
23	IIBPC/1,3-PD/GLY (1 : 1.1 : 0.07)	II/1,3-PD/GLY (1 : 0.89 : 0.07)	51.8	1,600	2,800	1.7	139.0

^a Prepared in the melt, $T_{max} = 210^\circ\text{C}$.

^b TMP, trimethylolpropane; GLY, glycerol.

may indicate that apart from branching because of TMP, some degradation of IM has occurred because of its inferior thermal stability compared with IS and II. Glycerol appears to be less effective as a branching agent under these reaction conditions since the PDI of entry **23** is below 2. This is probably caused by the reduced reactivity of the secondary OH-group present in glycerol. Also, the molecular weight of this resin is rather low and, as a consequence, the OHV (139 mgKOH/g) is too high for practical applications.

Thermal stability and viscosity profiles of DAH-based (co)polycarbonates

The thermal stability of several of the (co)polycarbonates prepared in this study was evaluated using TGA (Fig. 3).

The homopolycarbonates **2**, **4**, and **6** are clearly more thermally stable than the copolycarbonates **18** and **20**. It is possible that the copolycarbonates are more prone to degradation by alcoholysis, since primary hydroxyl end-groups are present in these polymers. For all samples, significant weight loss is not observed below $\sim 250^\circ\text{C}$, and the homopolycarbonates **4** and **6** are even stable up to 300°C .

Before evaluating the coating performance of the various prepared polycarbonates, the melt viscosities of these materials were investigated. In powder coating systems, film formation occurs through flow and subsequent coalescence of the powder paint. Directly upon flowing and coalescence of the powder particles, the formed film is irregular and the resin needs to flow out over the substrate to obtain a smooth film. If the melt viscosity of the polymeric resin is too high, this process does not occur properly and gelation of the formulation will occur before a smooth film is obtained. The melt viscosity of a polymer depends on the T_g , the molecular weight, the degree of branching, and on intermolecular interactions such as hydrogen bonding. Obvi-

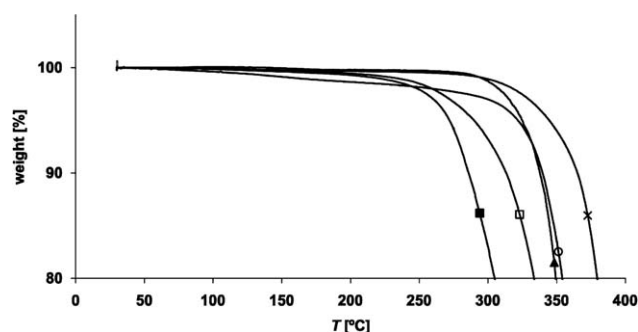


Figure 3 Results of thermogravimetric analysis (TGA) of poly(isosorbide carbonate) **2** (○), poly(isoidide carbonate) **4** (▲), poly(isomannide carbonate) **6** (×), poly(isosorbide-*co*-butylene carbonate) **18** (□) and poly(isosorbide-*co*-propylene-*co*-TMP carbonate) **20** (■).

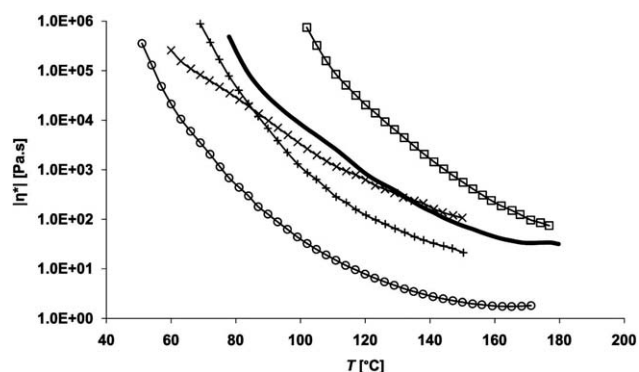


Figure 4 Complex viscosity as a function of temperature for polycarbonates **13** (+), **15** (○), **19** (×) and **20** (□) and a commercially available polyester resin (—), used in powder coatings.

ously, the addition of additives such as pigments and flow agents will also strongly affect the behavior of the powder paint during film formation.⁴ In Figure 4, the complex viscosities of several of the prepared biobased polycarbonates are plotted as a function of temperature. In the same plot, the complex viscosity of a typical commercially available polyester resin, used in powder coatings, is shown.

Poly(isosorbide-*co*-propylene carbonate) **13** has a similar viscosity profile as the commercial polyester, showing a rapid drop in viscosity between $\sim 70^\circ\text{C}$ and 170°C to viscosity values between 10^1 and 10^2 Pa s. The viscosity of poly(isoidide-*co*-butylene carbonate) **19** starts to decrease at slightly lower temperatures, viz. around 60°C , which is probably because of its relatively low T_g (36.3°C). On the other hand, its drop in viscosity is less steep than for the other resins, which might be a disadvantage in powder coating applications. Polymer **15** has a significantly lower melt viscosity over the whole temperature range, which is thought to be caused by its low T_g (35.6°C) in combination with its moderate molecular weight compared to polymer **19** ($\bar{M}_n = 3100$ g/mol versus $\bar{M}_n = 6300$ g/mol, respectively). The branched polycarbonate **20** has the highest melt viscosity, and its viscosity only starts to decrease at $\sim 100^\circ\text{C}$. Should this resin be used in a powder coating formulation, extrusion (to mix the resin with the curing agent, pigments and other additives) and powder paint application would have to be carried out at slightly higher temperatures than for the other polymers described. Polycarbonates **13**, **15**, and **20** seem to have suitable viscosity profiles for powder coating applications when compared to the commercial polyester resin.

Coating properties of cured DAH-based (co)polycarbonates

To perform powder coating application tests, relatively large amounts of polymer resin are required.

TABLE V
Solvent Cast Coating Formulations and the Resulting Coating Properties

Film	Polycarbonate	Curing agent ^a	T_{cure} (°C)	t_{cure} (min)	Acetone resistance ^b	Impact test (100 kg×cm) ^b	Av. film thickness (μm)
Linear OH-functional polycarbonates							
F1	2	I	180	20	+	–	23
F2	4	I	180	20	+	+	24
F3	13	II	200	30	–	–	30
F4	13	I	180	20	–	–	27
F5	14	I	180	20	±	±	n.d.
F6	15	II	200	30	+	–	35
F7	15	I	180	20	+	+	40
F8	18	I	180	20	+	+	38
F9	19	I	180	20	+	+	29
Branched OH-functional polycarbonates							
F10	20	II	200	30	+	–	40
F11	20	I	180	20	+	+	32

^a I, polyisocyanate based on hexamethylene diisocyanate; II, ϵ -caprolactam blocked polyisocyanate based on isophorone diisocyanate, see Supporting Information, Scheme S9.

^b +, good; ±, moderate; –, poor.

Sufficient quantities of the DAH-based polycarbonates were not available. Therefore, solvent-borne coating formulations were prepared based on various (co)polycarbonate resins. Table V lists the coating formulations and some of their properties. Several polycarbonates were cured to form poly(carbonate urethane) networks, using both a polyisocyanate based on hexamethylene diisocyanate as well as a ϵ -caprolactam blocked polyisocyanate based on isophorone diisocyanate (structures I and II, depicted in the Supporting Information Scheme S9). The amount of curing agent (0.05 excess) added to the formulations was calculated based on the OH-values of the different resins.

The coatings obtained upon curing of the polymer/crosslinker mixture onto aluminum Q-panel substrates are transparent, glossy, colorless or slightly yellow films. Coating F1, containing poly(IS carbonate) with a T_g of 138°C as the polymeric binder, shows good solvent resistance but poor resistance to rapid deformation. The high T_g of the resin probably contributes to the brittle behavior of the cured system. Surprisingly, F2 did pass the reverse impact test and also showed good solvent resistance. Even though coating F2 is rather thin, the fact that this coating passes the reverse impact test still indicates that this cured system is a rather tough material. The significant difference in impact resistance between F1 and F2 may be related to an enhanced level of curing because of higher reactivity of the *exo*-oriented hydroxyl end-groups of resin 4. Coatings F3 and F4 containing resin 13, showed poor chemical and mechanical resistances, which was expected since it was previously determined that at least part of the end-groups of this polycarbonate were phenyl carbonate groups. Therefore,

curing of this polymer certainly results in incomplete network formation and in poor coating properties. The moderate performance of F5 can be explained in a similar way as for F3 and F4. Coatings based on resins 15, 18, and 19 perform well, confirming that they have the proper functionality for curing purposes. Coating F6 does not pass the impact test, which is probably because of the generally observed brittle behavior of DAH-based polymers cured with this particular curing agent based on isophorone diisocyanate. The same can be said for coating F10, which also shows poor impact resistance. When the same resins (15 and 20) are cured with the more flexible curing agent I (i.e., a polyisocyanate based on hexamethylene diisocyanate), the rapid deformation during the impact test does not cause any damage to the coating. In general, the coatings based on this branched polycarbonate show excellent chemical and mechanical resistances in combination with a good appearance.

Future work will include a more detailed evaluation of these coating systems, in which also the curing agents will be biomass-based, affording fully bio-based poly(carbonate urethane)s.

CONCLUSIONS

Three different synthetic routes were screened towards OH-functional biobased polycarbonates for coating applications. When using triphosgene as a carbonyl source, polymers having suitable molecular weights and T_g values can be prepared by controlling the ratio of 1,4:3,6-dianhydrohexitols and other, more flexible diols that are incorporated into the polymer. However, an important disadvantage of this route is that it is difficult to control the type of

end-groups obtained. Precipitation of the reaction mixture in a large excess of diols or triols might be a suitable way to enhance the hydroxy-functionality of the obtained polymer. In addition, copolycarbonates made via this route tend to contain significant amounts of cyclic chains, which do not participate in curing reactions. Interestingly, the reactivity of the *endo*-oriented OH-groups of IM and IS appears to be higher than of the *exo*-oriented hydroxyls, which is contrary to the situation in melt polycondensations. This difference is thought to be caused by the enhanced nucleophilicity of the *endo*-oriented hydroxyl group because of internal hydrogen bonding and the presence of pyridine/pyridine hydrochloride. Homopolycarbonates of IS and II, prepared using the conventional carbonyl source diphenyl carbonate, have mainly hydroxyl end-groups and rather high T_g values. When attempting to synthesize copolycarbonates by adding 1,3-propanediol as a comonomer, part of this flexible diol was lost from the reactor because of the required high reaction temperatures. Copolycarbonates were also prepared using DAH bis(phenyl carbonate)s. In these melt polymerizations, the reaction temperatures were significantly lower than when using DPC in combination with the DAHs as such. This synthetic route resulted in several linear and branched copolycarbonates having suitable molecular weights, T_g values, and OH-functionalities. Curing of the various biobased linear and branched aliphatic (co)polycarbonates using conventional polyisocyanate crosslinkers yielded colorless to pale yellow, transparent, glossy coatings, having excellent chemical and mechanical resistances. It can be concluded that this last synthetic route is the most promising method to prepare DAH-based polycarbonates, suitable for powder coating applications.

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