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Synthesis and Characterization of Novel Biopolyesters from Suberin and Model Comonomers

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The synthesis of novel polyesters from model long-chain aliphatic monomers and from suberin reactive aliphatic fragments was conducted using mild polycondensation or polytransesterification conditions. The ensuing polyesters were characterized by means of various techniques. When mixtures of simple suberin-like monomers were used, the ensuing polyesters had very regular structures, with melting temperatures around 80 °C and glass transitions below room temperature. This first systematic study of the exploitation of suberin as a precursor to novel aliphatic polyesters confirmed the huge potential of using this abundant renewable resource to prepare macromolecular materials for promising applications.

Introduction

Suberin is an almost ubiquitous component of the outer bark cell walls of higher plants, representing typically 20–50 % of extractive-free bark weight.[1,2] This biopolymer is particularly abundant in the bark of oak cork (up to 50 %),[1,3–5] a species native to the Mediterranean region. The aliphatic suberin extract, obtained by hydrolysis (or methanolysis) of its cross-linked natural precursor, is mainly composed of C_{16}–C_{24} ω-hydroxyalkanoic acids and α,ω-alkanedioic acids, or the corresponding methyl esters.[1,2] Hence, the unique chemical composition of suberin, together with its abundant natural occurrence, makes this renewable resource an excellent precursor for the preparation of novel aliphatic polyesters. To the best of our knowledge, apart from a report[6] dealing with the synthesis of a homopolymer from the suberin monomer 9,10-epoxy-18-hydroxyoctadecanoic acid, the use of the above-mentioned suberin monomer mixtures to prepare novel polyesters has not been reported to date.

However, the synthesis of polyesters using commercial monomers bearing long aliphatic chains has been the subject of several investigations.[7–11] Olson and Sheares[9] prepared unsaturated linear aliphatic polyesters in bulk under reduced pressure and at relatively high temperatures ($\approx$130 °C) using tin(II) 2-ethylhexanoate as catalyst. Other researchers used milder conditions, for example, Takasu et al.[12] studied the polycondensation of 1,9-nonanediol with dodecanedioic acid, as well as of other homologous monomers, in water at 80 °C using an acidic surfactant as catalyst. The average molecular weights of these aliphatic polyesters ranged from 1.4 to 10.1 kDa, and their polydispersity indexes were close to 2. These investigations followed the pioneering work in emulsion polycondensation by Saam,[10] who adopted a reverse-micelle system in toluene. Ebata et al.[11] synthesized a copolyester of two hydroxyalkanoic acids using a lipase (*Candida antarctica*) as catalyst and studied the properties of the ensuing materials as a function of the monomer feed ratio. Surprisingly high molecular weights of around 100 kDa were reported with polydispersity indexes of about 3.

With the present study, we attempt to combine the growing demand for both greener synthetic pathways[11] and for polymers from renewable resources[13,14] within the much broader and emerging biorefinery concept,[14] through the polymerization of cork-based suberin monomer mixtures and some of their models. Importantly, note that the exploitation of cork in this context does not call upon its more "noble" morphologies, which find several high-tech applications as natural materials,[1,2] but rather the fine granular residue arising from the manufacture of stop-corks which is commonly known as "industrial cork powder". It seems clear to us that this residue, which amounts to as much as 20 % of the processed material and which is burned in the factory for energy production,[15] would be much more rationally exploited as a source of novel biodegradable polymeric materials.

Results and Discussion

Suberin is a highly complex material, especially with regard to its chemical composition.[1,2] Here, prior to the polymerization reactions, mixtures of hydrolysis-depolymerization and methanolysis-depolymerization suberin, both from cork as a whole (hereafter termed "cork") and from industrial cork powder, were analyzed by GC-MS as described previously.[5] It was found, as expected, that the major groups of compounds are alkanedioic and ω-hydroxyalkanoic acids (or the homologous methyl esters) and the corresponding epoxy derivatives, together with smaller amounts of long-chain alkanols and alkanoic acids. The structures of the most abundant compounds identified by GC-MS in hydrolysis-depolymerization suberin are depicted in Figure 1.[5] The 18-hydroxyoctadec-9-enoic and 22-

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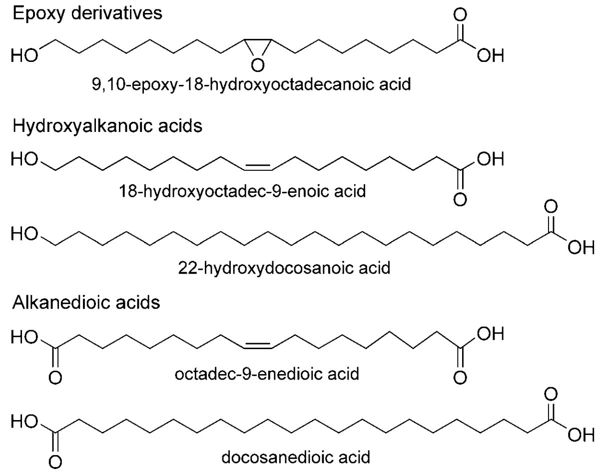

Figure 1. Structures of the most abundant components of hydrolysis-depolymerization suberin, as identified by GC-MS.[5]

hydroxydocosanoic acids were found to be the most abundant components (each representing 21 % of the identified components), followed by smaller amounts of the epoxy derivative 9,10-epoxy-18-hydroxyoctadecanoic acid (13 % of the identified components) and other long-chain lipophilic compounds. Octadec-9-enedioic acid (8 %) and docosanedioic acid (3 %) or the corresponding methyl esters were the most abundant alkanedioic acids found in both hydrolysis-depolymerization suberin and methanolysis-depolymerization suberin. The major difference between depolymerized suberin mixtures from cork and industrial cork powder sources was the lower yield of this fraction isolated from the powder.[5]

To gain insight into the reactivity of these complex mixtures in polycondensation reactions, we first studied the behavior of several suberin model systems of growing complexity.

Suberin Model Polyesters

Several emulsion polycondensation conditions were tested using *p*-dodecylbenzenesulfonic acid and mixtures of variable complexity of different model monomers (Table 1). The yields of isolated polymers varied between 23 and 58 %, the number-average molecular weights ranged from 800 to 5000 (with good agreement between values from size-exclusion chromatography (SEC) and vapor-pressure osmometry (VPO)), while the polydispersity index was always close to 2 (SEC determinations) as expected for linear polycondensation polymers. These results show that it is possible to synthesize aliphatic polyesters from complex mixtures of monomers through a very simple experimental procedure based on an emulsifying acidic catalyst, with no need to remove the ensuing water from the reaction media. This result was encouraging with respect to extension of this process to suberin-based systems.

Next, the lipase-catalyzed polymerization of decanedioic acid and 1,12-dodecanediol was carried out. The yield of the polyester increased significantly from 25 to 44 %, but its molecular weight followed the opposite trend decreasing to 1000, as compared to 3000 for the counterpart obtained using *p*-dodecylbenzenesulfonic acid.

The FTIR and the ^{1}H NMR spectra of these polyesters confirmed their expected structures. The major FTIR features included the ester peaks at 1725 and 1249 cm^{-1}, and those arising from the CH elongation of the CH$_2$ moieties at 2916 and 2850 cm^{-1}. A comparison of the ^{1}H NMR spectra of the monomers and the corresponding polyesters revealed that the OCH_2 resonance was shifted downfield from $\delta = 3.60$ ppm for the diol to $\delta = 4.05$ ppm for the polymer, owing to the presence of the neighboring carbonyl group (see Table 2). This observation confirmed the formation of the polyesters.

In some instances, ^{1}H NMR spectroscopy gave additional information related to the reactivities of the different monomers,

Table 1. Experimental data for the emulsion polycondensation reactions of model compounds using *p*-dodecylbenzenesulfonic acid.[a]

Run		*t* [h]	OH/COOH	Yield [%]	M_n (SEC)[b]	M_w/M_n[c]	M_n (VPO)[d]
1	decanedioic acid	48	1.01	25	3000	1.2	3200
2[e]	+1,12-dodecanediol	48	0.99	44	1000	1.1	–
3		48	0.96	–	–	–	2100
4	dodecanedioic acid	48	1.05	23	700	2.3	–
5	+1,12-dodecanediol	120	0.99	36	800	1.9	–
6		144	1.06	45	1800	1.7	–
7	12-hydroxydodecanoic acid	48	1.00	57	1600	1.4	2900
8	12-hydroxyoctadecanoic acid	48	1.00	32	–	–	–
9	12-hydroxydodecanedioic acid +12-hydroxyoctadecanoic acid	48	1.00	24	3500	1.8	3500
10	12-hydroxydodecanoic acid +dodecanedioic acid +1,12-dodecanediol	48	0.99	37	5000	1.7	–
11	12-hydroxyoctadecanoic acid +dodecanedioic acid +1,12-dodecanediol	48	1.00	58	800	1.1	–
12	12-hydroxydodecanoic acid +12-hydroxyoctadecanoic acid +dodecanedioic acid +1,12-dodecanediol	48	0.99	43	1700	1.6	–

[a] Reactions carried out at 80 °C; *p*-dodecylbenzenesulfonic acid (0.49 mmol mmol^{-1}). [b] Number-average molecular weight, determined by SEC in CHCl$_3$. [c] Weight-average molecular weight. [d] Determined by VPO in CH$_2$Cl$_2$. [e] Reaction carried out at 70 °C, *Candida antarctica* lipase (5 % w/w), 48 h.

Table 2. Main peaks from ^{1}H NMR spectra of decanedioic acid, 1,12-dodecanediol, and their corresponding polyester (Table 1, run 1).

δ [ppm]	Mult.[a]	Relative integration area [H]			Assignment
		diacid	diol	polymer	
1.30	s	8.0	16.0	6.0	(CH_2)
1.61	q	4.0	4.0	2.0	$(CH_2)CH_2COO$; $(CH_2)CH_2O$
2.28	t	4.0		1.0	$(CH_2)COO$
3.60	t	–	4.0	0.1	$(CH_2)OH$
4.05	t	–	–	0.9	$(CH_2)O$
4.91	s	–	2.0	–	OH

[a] s = singlet, t = triplet, q = quartet.

through the extent of their relative incorporation into the polymer backbone. This issue is quite relevant to the polymerization of suberin monomers, characterized by the presence of a mixture of different types of monomers. Thus, for example, the ^{1}H NMR spectrum of the copolymer prepared from 12-hydroxydodecanoic acid and 12-hydroxyoctadecanoic acid (Table 1, run 9) displayed both the typical resonances of the corresponding homopolymers at $\delta = 4.86$ ppm (-C*H*(O)- of 12-hydroxyoctadecanoic acid units) and $\delta = 4.05$ ppm (-CH_2O- of 12-hydroxydodecanoic acid units). The ratio between 12-hydroxyoctadecanoic acid and 12-hydroxydodecanoic acid monomeric units in the copolymer was then estimated by the integration ratio (*r*) of the peaks for the corresponding protons, and it was seen that the dodecanoic acid had been slightly more reactive than the octadecanoic acid, with $r = 0.9$, despite their initial stoichiometric feed ratio. In another experiment involving monomers with a primary and a secondary OH group (Table 1, run 11), the latter showed a slightly lower extent of incorporation, with $r = 0.9$, suggesting, however, that such a type of monomers in the depolymerized suberins should participate without any major hindrance in the corresponding polycondensation reactions.

The thermal transitions of the model polyesters are summarized in Table 3. These polymers, especially those prepared from linear model compounds (excluding 12-hydroxyoctadecanoic acid units), display very regular structures, as confirmed by their ^{1}H NMR spectra and as reflected by differential scanning calorimetry (DSC) measurements. The thermograms displayed well-defined melting peaks typically at temperatures around 80 °C, in agreement with those reported for other long-chain aliphatic polyesters.[11] Their amorphous phases gave T_g values below room temperature, as expected for such flexible macromolecular chains, with the exception of the polyester from dodecanedioic acid and 1,12-dodecanediol (Table 1, run 3) which gave a T_g value of 25 °C. The copolyesters incorporating 12-hydroxyoctadecanoic acid units displayed multiple melting peaks over the region 19–110 °C, consistent with a much less regular structure induced by the presence of the pendant alkyl branches and hence with the formation of different crystalline assemblies.

Table 3. Glass transition (T_g) and melting temperatures (T_m) of the polyesters prepared from model compounds.

Monomers	Run[a]	T_g [°C]	T_m [°C]
decanedioic acid + 1,12-dodecanediol	1	−8	80
dodecanedioic acid + 1,12-dodecanediol	3	25	81
	5	–	77
12-hydroxydodecanoic acid	7	−1	83
12-hydroxydodecanedioic acid + 12-hydroxyoctadecanoic acid	9	–	19, 31, 44
12-hydroxydodecanoic acid + dodecanedioic acid + 1,12-dodecanediol	10	–	78
12-hydroxyoctadecanoic acid + dodecanedioic acid + 1,12-dodecanediol	11	−19	26, 50, 110

[a] See Table 1.

Polyesters from Depolymerized Suberin Mixtures

Hydrolysis-depolymerization suberin (free carboxylic acid groups) samples both from cork and industrial cork powder were polymerized either by direct polycondensation with *p*-dodecylbenzenesulfonic acid or using lipase as a catalyst (Table 4), whereas methanolysis-depolymerization suberin (methyl ester moieties) clearly called upon polytransesterification systems (Table 6).

Table 4. Experimental conditions related to the polycondensation of hydrolysis-depolymerization suberin.

Run	Experimental conditions	Yield [%]
cork suberin		
1	80 °C, *p*-dodecylbenzenesulfonic acid (1.4 mmol g^{-1}), 48 h	27
2	80 °C, *p*-dodecylbenzenesulfonic acid (5.8 mmol g^{-1}), 48 h	8
3	80 °C, *p*-dodecylbenzenesulfonic acid (1.5 mmol g^{-1}), 6.5 h	6
4	70 °C, lipase (5 % w/w), 48 h	24
industrial cork powder suberin		
5	80 °C, *p*-dodecylbenzenesulfonic acid (0.50 mmol g^{-1}), 48 h	14
6	80 °C, *p*-dodecylbenzenesulfonic acid (1.5 mmol g^{-1}), 48 h	49

The ensuing polymers were obtained in rather moderate yields and contained variable proportions of an insoluble fraction, which suggested the formation of cross-linked structures arising from the intervention of monomers with a functionality higher than 2. Their FTIR and ^{1}H NMR spectra confirmed the formation of polyesters, which represent the first reported polymers of this type. As already observed with the model polymers, the FTIR spectra of these novel materials based on renewable resources showed a new band around 1733 cm^{-1} (as in the typical spectrum shown in Figure 2) attributed to the C═O elongation

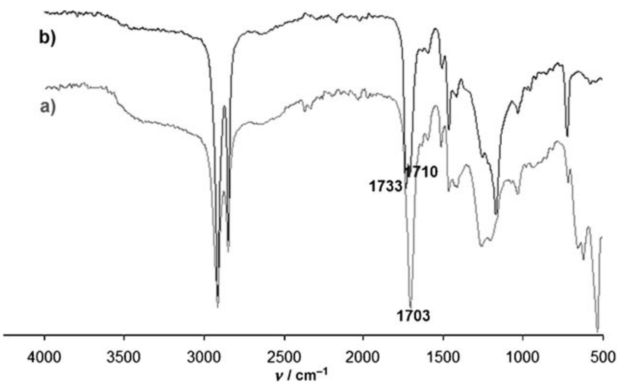

Figure 2. ATR-FTIR spectra of a) hydrolysis-depolymerization suberin and b) the corresponding polyester formed by polycondensation using *p*-dodecylbenzenesulfonic acid (Table 4, run 3).

of an ester moiety. Additionally, the C=O vibration of carboxylic acids at 1710 cm^{-1} was still present, suggesting that in this hydrolysis-depolymerization suberin there were more carboxylic groups than hydroxy groups. This was confirmed by both GC-MS analysis and ^{1}H NMR group analysis with trichoroacetylisocyanate.[16,17] This lack of stoichiometry explains the low polymer yields, which could be increased, however, through the use of a compensating diol or polyol. These systems are presently under investigation.

Table 5 compares the characteristic features of the ^{1}H NMR spectra of hydrolysis-depolymerization suberin and its corresponding soluble polymer (Table 4, run 3). Both spectra exhibited typical peaks of esterified structures, that is, peaks at δ = 4.06 and 2.30 ppm, despite the severe alkaline hydrolysis conditions used to isolate the suberin. However, after the polymerization, the (C*H*$_2$)CO/(C*H*$_2$)COOH peak area ratio increased from 0.2 to 3.5, which confirmed that a polycondensation reaction had indeed taken place. An estimate of the degree of polymerization based on the relative area of (C*H*$_2$)/(C*H*$_2$)CO peaks gave a value of approximately 20.

Table 5. Main peaks from ^{1}H NMR spectra of hydrolysis-depolymerization suberin and one of its polyesters prepared using *p*-dodecylbenzenesulfonic acid (Table 4, run 3).

δ [ppm]	Mult.[a]	Relative integration area [H] suberin	polymer	Assignment
0.95	m	19	32	(CH$_3$)
1.24, 1.30	d	54	497	(CH$_2$)
1.61	m	13	76	(C*H*$_2$)CH$_2$COO; (C*H*$_2$)CH$_2$O
2.30	t	1	21	(CH$_2$)CO
2.35	t	6	16	(CH$_2$)COOH
3.65	t	1	5	(CH$_2$)OH
4.06	t	1	19	(CH$_2$)O
5.34	q	2	2	CH=CH

[a] d = doublet, t = triplet, q = quartet, m = multiplet.

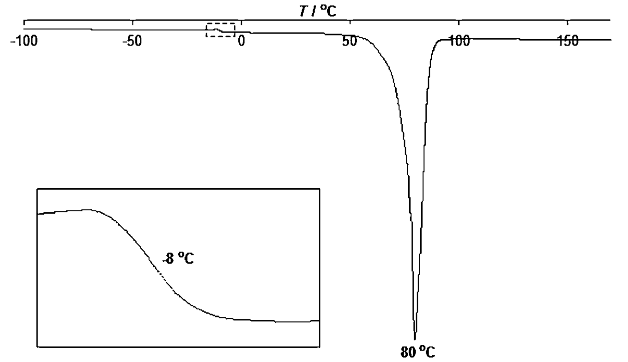

Figure 3. DSC trace of the polyester prepared by the polycondensation of hydrolysis-depolymerization suberin (Table 4, run 3). The inset shows a close-up of the glass transition.

The DSC thermogram (Figure 3) of the hydrolysis-depolymerization suberin polyester (Table 4, run 3) displayed a melting peak around 72 °C and a glass transition temperature of around −8 °C. This thermal behavior is very similar to that observed for the corresponding linear model polyesters discussed above, with T_m values around 80 °C and most T_g values below room temperature (Table 3).

The conditions associated with the polytransesterification of methanolysis-depolymerization suberin are summarized in Table 6. Both potassium carbonate and antimony(II) oxide (Table 6, runs 1–3) led to the formation of polyesters in relatively good yields under the appropriate conditions. The titanium catalyst produced a black insoluble product (Table 6, run 4) which was not characterized.

Table 6. Experimental conditions for the polytransesterification of methanolysis-depolymerization suberin from cork.

Run	Experimental conditions	Yield [%]
1	K_2CO_3 (0.9 mmol g^{-1}), 73–120 °C, 220 min, ≈10^{-3} mbar	54
2	Sb_2O_3 (0.1 mmol g^{-1}), 150–185 °C, 80 min, ≈10^{-6} mbar	17
3	Sb_2O_3 (0.1 mmol g^{-1}), 100–190 °C, 525 min, ≈10^{-6} mbar	50
4	$Ti(OC_2H_5)_4$ (0.2 mmol g^{-1}), 100–120 °C, 155 min, ≈10^{-6} mbar	[a]

[a] Not characterized (see text for details).

The FTIR spectra of these polyesters were very similar to those of their counterparts prepared with hydrolysis-depolymerization suberin, except, of course, for the lack of the COOH carbonyl peak. Their ^{1}H NMR spectra displayed similar features to those of their precursor (Table 7), except for a substantial decrease in the relative intensity of the methyl ester protons.

Contact Angles

All the polyesters prepared in this study displayed contact angles with water ranging between 95 and 100°, independent of the specific structure examined. This is not surprising given the fact that all the materials bear long aliphatic chains, which orient themselves at the surface of the polymer film; that is, the water drop always comes into contact with the same non-polar moieties. It follows that these new suberin-based polyesters are indeed highly hydrophobic materials.

Table 7. Main peaks from ^1H NMR spectra of methanolysis-depolymerization suberin and one of its polyesters prepared using Sb_2O_3 (Table 6, run 2).

δ [ppm]	Mult.	Relative integration area [H] suberin	Relative integration area [H] polymer	Assignment
0.96	m	53	53	(CH_3)
1.24, 1.31	d	239	129	(CH_2)
1.61	m	73	119	$(CH_2)CH_2O$, $(CH_2)CH_2CO$
2.29	t	29	51	$(CH_2)CO$
3.66	s	30	18	$O(CH_3)$
4.04	t	6	9	$O(CH_2)$
5.34	q	2	2	CH=CH

Conclusions

The aliphatic fragments of suberin arising from cleavage of its ester group proved readily suited to polymerization by classical polycondensation processes to give polyesters whose properties mimicked those of model counterparts. The possibility of producing polyesters efficiently from hydrolysis-depolymerization suberin by polycondensation under emulsion polymerization conditions or by using *Candida antarctica* lipase are doubly beneficial approaches from a green perspective, as they avoid the use both of methanol during the depolymerization of suberin as well as of organic solvents as reaction media. This first systematic investigation has shown that the major component of cork is a valuable renewable resource for the preparation of novel hydrophobic materials whose properties resemble those of petroleum-based aliphatic polyesters. These polymeric materials may have potential applications, for example, in terms of latex arising from the emulsion polymerization and hence in coatings. Work is in progress to improve the properties of the studied materials and also to assess their biodegradability.

Experimental Section

Materials: 1,12-Dodecanediol (99%), decanedioic acid (99%), dodecanedioic acid (98%), 12-hydroxydodecanoic acid (97%), 12-hydroxyoctadecanoic acid (99%), *p*-dodecylbenzenesulfonic acid (90%), antimony(III) oxide ($\geq$99%), titanium(IV) ethoxide (97%), and lipase from *Candida antarctica* immobilized in an acrylic resin were purchased from Sigma–Aldrich Chemicals Co. (Madrid, Spain). Potassium carbonate was purchased from Merck (Lisbon, Portugal). *Quercus suber* L. cork planks, "Amadia" grade, were sampled in the southern part of Portugal (Herdade da Moinhola, Amorim Florestal mill, Portugal; March 2005). The industrial cork powder was sampled in the Corticeira Amorim mill, (Portugal; February 2005). The samples were ground, and only the 40–60 mesh fractions were used.

Suberin Isolation: The suberin depolymerization products were isolated from both cork and industrial cork powder samples, which were submitted to two different depolymerization procedures, namely alkaline hydrolysis or alkaline methanolysis. Alkaline hydrolysis was carried out with a 0.5 M KOH solution in ethanol/water (9:1 v/v) at 70 °C for 1.5 h.[18] The ensuing mixture of hydrolyzed suberin monomers was cooled to room temperature and acidified with dilute hydrochloric acid to pH 3–3.5 and extracted three times with dichloromethane. The solvent was then removed in a rotary evaporator, and the residue was weighed. This residue (29% yield),[5] was identified above as hydrolysis-depolymerized suberin. Alkaline methanolysis was conducted by refluxing the cork powder with a solution of 0.6 M $NaOCH_3$ in dry methanol for 4 h, followed by filtration of the solid residue and a further 1 h of refluxing with methanol.[3] The combined liquid fractions were acidified to pH 3–3.5 with diluted hydrochloric acid and then extracted three times with dichloromethane. The solvent was removed in a rotary evaporator, and the residue was weighed. This residue (33% yield),[5] was identified above as methanolysis-depolymerized suberin.

Emulsion Polycondensation: Reactions were typically carried out using 1 mmol of suberin-like monomers, or 1 g of hydrolysis-depolymerized suberin, suspended in water in the presence of *p*-dodecylbenzenesulfonic acid (1.5 mmol g^{-1} and 0.49 mmol mmol^{-1}, respectively). The mixture was stirred at 80 °C for variable times (see Tables 1 and 4). Then, the mixtures were dissolved in dichloromethane (15 mL) and the polymer was precipitated by pouring the solution into an excess of cold methanol to remove *p*-dodecylbenzenesulfonic acid and unreacted monomers, then filtered and dried under vacuum.

Bulk Polycondensation: Reactions were conducted in bulk by mixing 1 g of hydrolysis-depolymerized suberin or 1 g of suberin-like monomers and the lipase from *Candida antarctica* (5% w/w) at 70 °C for 48 h, with vigorous stirring. The polymerization mixture was then dissolved in dichloromethane (100 mL), and the insoluble enzyme was separated by filtration. The excess of dichloromethane was then removed in a rotary evaporator, and the polymer was precipitated by pouring the residue into an excess of cold methanol to remove unreacted monomers, then filtered and dried under vacuum.

Bulk Polytransesterification: reactions were carried out in bulk using 1 g of methanolysis-depolymerized suberin and one of the following catalysts: K_2CO_3 (10% w/w), Sb_2O_3 (4% w/w), or $Ti(OC_2H_5)_4$ (5% w/w). The mixture was heated progressively to 120–190 °C with constant stirring and then kept for several hours at that maximum temperature under high vacuum ($\sim 10^{-6}$ Pa) to ensure the thorough removal of the released methanol. The ensuing polymer was precipitated by pouring into an excess of cold methanol to remove unreacted monomers, filtered and dried under vacuum.

Analyses: GC-MS analyses of the hydrolysis- and methanolysis-depolymerized suberin samples were performed using a Trace GC 2000 gas chromatograph coupled with a mass-selective Finnigan Trace MS detector as described elsewhere.[5] ATR-FTIR spectra were recorded with a Brucker IFS FTIR spectrophotometer equipped with a single horizontal Golden Gate ATR cell. ^1H NMR spectra of the polymers dissolved in $CDCl_3$ were recorded using a Bruker AMX 300 spectrometer operating at 300.13 MHz. All chemical shifts are expressed as parts per million downfield from tetramethylsilane (TMS). Size-exclusion chromatography (SEC) analyses were performed with a Polymer Laboratories PL-GPC110 system equipped with a RI detector, using a set of two Tosoh G2000HHR columns (30.0 cm × 7.8 mm i.d.) and one Tosoh HHR-L guard column (4.0 cm × 6.0 mm i.d.), kept at 40 °C and previously calibrated with polystyrene standards (Polymer Laboratories) in the range 580–7000 Da. Chloroform was used as the mobile phase with a flow of 0.7 mL min^{-1}. All polymer samples were dissolved in chloroform (ca. 12.5 mg mL^{-1}). Vapor-pressure osmometry (VPO): M_n determinations were carried out with a Knauer K7000 instrument operating with dichloromethane at 35 °C (calibrated with *n*-tetracosane standard) using polymer solutions with concentrations ranging from 3.9 to 10.3 mg mL^{-1}. M_n results were calculated as the average of three concordant values. Differential scanning calorimetry (DSC) thermograms were obtained with a Setaram DSC92 calorimeter using aluminum pans. Scans were conducted under nitrogen with a heating rate of 10 °C min^{-1} in the temperature range of -140 to 176 °C. Contact angles with water were measured at room temperature with a "Surface Energy Evaluation System" commercialized by Brno University, Czech Republic. Each θ value reported here was the average of three measurements carried out on a flat film of the polyester substrate deposited onto a glass plate.

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Keywords: cork · polymers · polymerization · renewable resources · suberin

[1] A. J. D. Silvestre, C. Pascoal Neto, A. Gandini, *Monomers, Polymers and Composites from Renewable Resources* (Eds.: M. N. Belgacem, A. Gandini), Elsevier, Amsterdam, **2008**, Chapter 14.
[2] A. Gandini, C. Pascoal Neto, A. J. D. Silvestre, *Prog. Polym. Sci.* **2006**, *31*, 878–892.
[3] M. H. Lopes, A. M. Gil, A. J. D. Silvestre, C. Pascoal Neto, *J. Agric. Food Chem.* **2000**, *48*, 383–391.
[4] N. Cordeiro, M. N. Belgacem, A. J. D. Silvestre, C. Pascoal Neto, A. Gandini, *Int. J. Biol. Macromol.* **1998**, *22*, 71–80.
[5] P. C. R. O. Pinto, A. F. Sousa, A. J. D. Silvestre, C. Pascoal Neto, A. Gandini, C. Eckerman, B. Holmbom, *Ind. Crops Prod.*, DOI: 10.1016/j.indcrop.2008.04.015
[6] A. Olsson, M. Lindstrom, T. Iversen, *Biomacromolecules* **2007**, *8*, 757–760.
[7] C. J. Fu, Z. P. Liu, *Polymer* **2008**, *49*, 461–466.
[8] A. Takasu, Y. Shibata, Y. Narukawa, T. Hirabayashi, *Macromolecules* **2007**, *40*, 151–153.
[9] D. A. Olson, V. V. Sheares, *Macromolecules* **2006**, *39*, 2808–2814.
[10] J. C. Saam, *J. Polym. Sci. Part A-Polym. Chem.* **1998**, *36*, 341–356.
[11] H. Ebata, K. Toshima, S. Matsumura, *Macromol. Biosci.* **2008**, *8*, 38–45.
[12] A. Takasu, A. Takemoto, T. Hirabayashi, *Biomacromolecules* **2006**, *7*, 6–9.
[13] *Monomers, Polymers and Composites from Renewable Resources* (Eds.: M. N. Belgacem, A. Gandini), Elsevier, Amsterdam, **2008**.
[14] *Biorefineries—Industrial Processes and Products* (Eds.: B Kamm, P. R. Gruber, M. Kamm), Wiley VCH, Weinheim, **2006**.
[15] L. Gil, *Biomass Bioenergy* **1997**, *13*, 59–61.
[16] A. R. Donovan, G. Moad, *Polymer* **2005**, *46*, 5005–5011.
[17] A. F. Sousa, A. J. D. Silvestre, A. Gandini, C. Pascoal Neto, *unpublished results*.
[18] R. Ekman, C. Eckerman, *Pap. Puu* **1985**, *67*, 255–273.

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