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(54) Title: SYNTHESIS AND USE OF CARBOHYDRATE-BASED LINEAR POLYESTERS

(57) Abstract: The invention relates to the field of polymer chemistry, more in particular to the synthesis of novel biobased linear polymers and their applications, among others as rheology modifiers or thickeners in waterborne formulations. Provided is a method for providing a linear carbohydrate-based polyester, comprising (i) reacting a bicyclic acetalized galactaric acid derivative (Galx) with a diol in the presence of a suitable catalyst to obtain a Galx-based polyester; and (ii) subjecting said Galx-based polyester to a hydrolytic deacetalisation reaction to convert at least part of the diacetal moieties to chhydroxide moieties.



Title: Synthesis and use of carbohydrate-based linear polyesters.

5 The invention relates to the field of polymer chemistry, more in particular to the synthesis of novel biobased linear polymers and their applications, among others as rheology modifiers or thickeners in waterborne (coating) formulations.

 Additives have long been used in coating compositions for various
10 purposes. Thus, viscosity control agents, surfactants, sag-control agents, anti-foaming agents and other materials are added to coating compositions in minor amounts for their respective functions. Rheology modifiers are also added to such compositions not only for increasing the viscosity of the coating compositions but to maintain the viscosity at desired levels under
15 varying process conditions and end-use situations. Secondary effects obtained from the rheology modifiers include protective colloidal action, improvement in pigment suspension, leveling and flow. Some of these properties are also desired in similar type compositions, for instance textile treating compositions, cosmetics, paper compositions, well drilling,
20 firefighting foams, detergents, pharmaceuticals, agricultural formulations, and emulsions of all kinds. It can be seen rheology modifiers are used in a variety of compositions.

 While the discussion of the reaction products which follows is with reference to them as "rheology modifiers", it should be understood this term
25 is used broadly. That is, "rheology modifiers" as used herein is meant to encompass such terms as thickening agents, thixotropic agents, viscosity modifiers and gelling agents.

 The most common used rheology modifiers are bio-based or synthetic polymers. Natural products such as the alginates, casein, and gum
30 tragacanth and modified natural products such as functionalised cellulose,

gums (xanthan, guar), proteins (collagen) etc. are useful rheology modifiers. These mostly contribute due to their hydrodynamic volume and entanglements of the chains.

5 Many well-known rheology modifiers are used with varying degrees of success. Synthetic rheology modifiers have also been used. These materials include the carboxyvinyl ether copolymers, acrylic polymers and maleic anhydride/styrene copolymers. However, the known rheology
10 modifiers are susceptible to biological attack. Synthetic rheology modifiers are not subject to such attack yet most of them do suffer from having less than desirable thickening qualities over a wide range of end uses and/or film forming concentrations.

 Generally speaking, there are two main groups of thickeners:
15 -thickeners which rely on (macro)molecular structure factors (such as high molecular weight and presence of ionic groups), therefore on their chain entanglements and

 -thickeners which have as characteristic a dual hydrophilic-hydrophobic type of structure and where the hydrophobic groups tend to
20 cluster both at intra- and inter-molecular level, causing an increase in viscosity of the polymer solution.

 To the best of our knowledge, the most investigated classes of the latter group of polymers are hydrophobically modified polyurethanes and
25 polyethers. Despite their relative good performance these modified polyurethane rheology modifiers rely on the use of isocyanates for their synthesis.[1], [2] Thus, even though on one side the possibility of using a waterborne thickener seems already as the better option (as opposed to a mixture based on organic solvent), it still keeps the disadvantage of
30 exposure to relatively toxic and non-environmental friendly components

such as isocyanates.[4] This feature is even more relevant when the final application addresses cosmetics or detergents emulsion systems.

It would be desirable to obtain novel bio-based alternative to these, preferably bringing as added value an easy and adjustable synthesis to match the desired application i.e. by varying the feed ratio of one of the monomers in a copolymer structure obtaining a lower or higher thickening effect.

These goals are met by the provision of a two-step synthesis of linear chain novel galactaric acid based (Galx) polyesters by melt polycondensation, followed by a further hydrolytic (total/ partial) deprotection of acetal groups. The resulting novel (shear) thickener linear sugar based polyesters have the potential of addressing various water-based applications by way of controlled hydrophilicity of sugar based polyesters by varying the degree of deprotection and/or size/type/ configuration of one of the co-monomers.

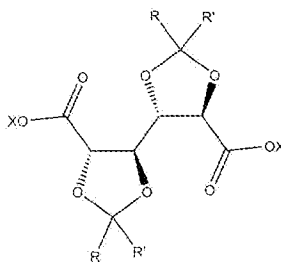
Herewith, the invention also provides a thickener for rheological systems where it is required in order to increase the viscosity and/or stabilise the suspension, emulsion media. This can be used for paints and coatings but also for cosmetic/detergent emulsion systems.

20

In one embodiment, the invention relates to a method for providing a linear carbohydrate-based polyester, comprising the steps of:

(i) reacting a bicyclic acetalized galactaric acid derivative (Galx) of the general formula I

25



Formula I

wherein X is H or a linear aliphatic moiety, preferably a linear C₁-C₅ alkyl;

R and R' are linear alkyl chains, more preferably C₁-C₃ alkyl;
 5 with a diol in the presence of a suitable catalyst to obtain a Galx-based polyester; and (ii) subjecting said Galx-based polyester to a hydrolytic deacetalisation reaction to convert at least part of the diacetal moieties to dihydroxide moieties.

10 In a preferred bicyclic acetalized galactaric acid derivative (Galx) of the general formula I, X is a linear C₁-C₅ alkyl; and/or R and R' are C₁-C₃ alkyl chains.

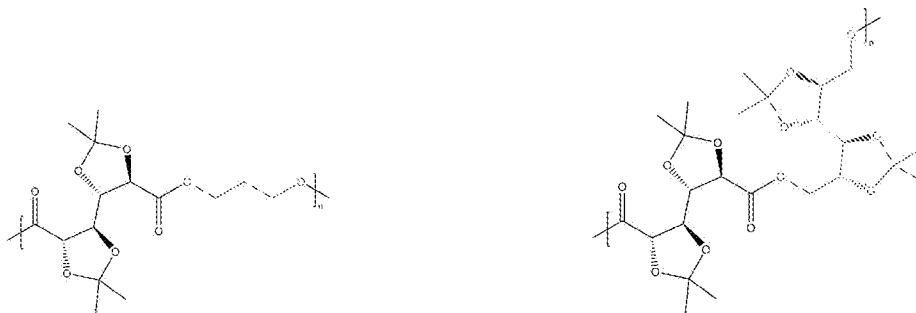
For example, said bicyclic acetalized galactaric acid derivative is dimethyl-
 15 2,3:4,5-di-O-isopropylidene-galactarate (Galx1)

In a method of the invention, the diol is preferably of the general formula



wherein  is a linear or cyclic aliphatic hydrophobic (e.g. cycloalkyl, aryl) unit. For example, the diol is selected from the group
 20 consisting of linear aliphatic α,ω-diols, such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 2,3:4,5-di-O-isopropylidene-galactitol or 2,3:4,5-di-O-methylene-galactitol.

25 Exemplary homopolyesters that may be provided in step (i) of a method of the invention include the following Galx1-1,3 propanediol and Galx1-2,3:4,5-di-O-isopropylidene-galactitol homopolyesters:



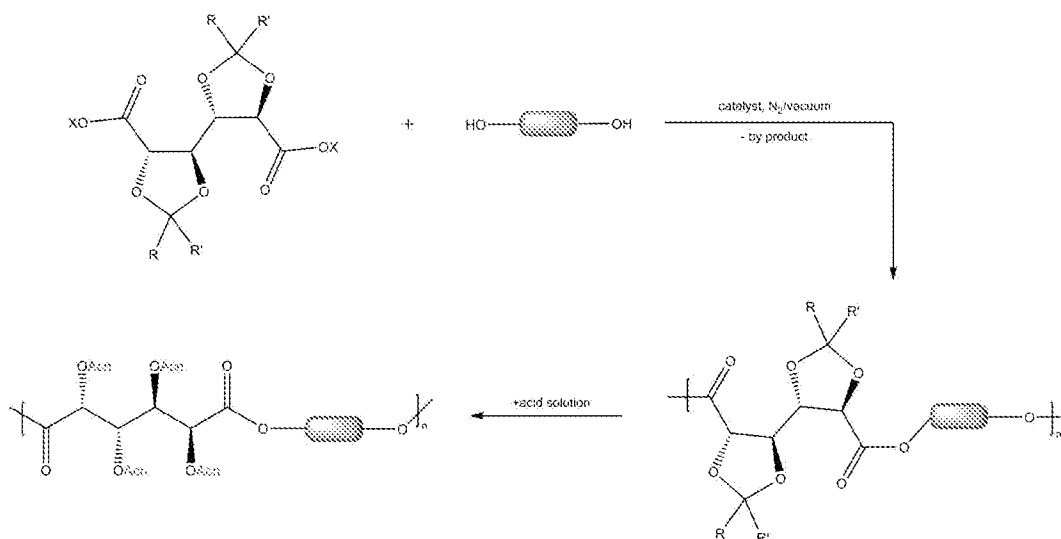
Step (i) of a method according to the invention may comprise reacting the bicyclic acetalized galactaric acid derivative and the alcohol in the presence
 5 of one or more further co-monomer(s). In one embodiment, the further monomer comprises a cross-linking moiety, such as an α,β -unsaturated functionality. For example, the further co-monomer is itaconic acid or ester thereof, such as dimethylitaconate or dibutylitaconate. The itaconic acid is preferably obtained from a renewable source. For example, it can be
 10 produced on an industrial scale via fermentation with *Aspergillus terreus* with a production intensity of 80 g L⁻¹. (T. Willke and K. D. Vorlop, Appl. Microbiol. Biotechnol., 2001, 56, 289–295). Notably, the presence of a cross-linking functionality *per se* does not result in a cross-linked polyester, but it allows for subsequent cross-linking of the resulting linear co-polyester if so
 15 desired e.g. by performing free radical polymerization-crosslinking.

Suitable catalysts for use in a method of the invention include dibutyltin oxide (DBTO) and other organometallic catalyst which act as Lewis acids, such as Ti alkoxides; Sb, Ge, Sn oxides; Zn, Mn, Ca, Co, Cd acetate.
 20 Nevertheless their activity may depend on the reaction conditions, on the solubility in the medium or even on the possibility of catalyzing also secondary reactions.

In step (ii) of a method of the invention, the Galx-based polyester is
 25 subjected to a deprotection reaction wherein at least part of the diacetal

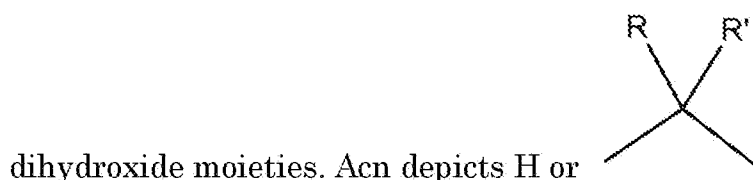
moieties are hydrolyzed to dihydroxide moieties. Preferably, this is performed by dissolving the Galx-based polyester in an (aqueous) acid solution and incubating at room temperature to obtain the desired degree of deacetalisation. See Scheme 1 below. Suitably, the Galx-based polyester is

5 purified, e.g. to remove catalyst, and dried prior to dissolving it in an acid solution.



Scheme 1: Exemplary polymerisation reaction using a Galx-derivative and an alcohol to form an acetalised poly(galactaric ester), followed by hydrolytic deacetalisation to convert at least part of the diacetal moieties to

10



In a preferred embodiment, the solution of acid is a aqueous solution of

15 sulfuric acid, hydrochloric acid, Amberlyst 15, p-toluene sulfonic acid, acetic acid, trifluoroacetic acid, more preferably formic acid. Very good results are obtained with formic acid or trifluoroacetic acid. In a specific aspect, a formic acid solution in chloroform, preferably 88% volumetric, is used.

The deprotection (deacetalisation) reaction can be performed up to the desired degree of hydrolysis is achieved. In one embodiment, it comprises incubating up to 4 hours, preferably up to 3 hours, more preferably up to 2 hours. Good results are obtained wherein step (ii) comprises incubating
5 during a time period of 15 to 180 minutes, preferably 20 to 150 minutes, more preferably 30 to 120 minutes.

In a preferred aspect, the deprotection reaction is not performed to completion such that the resulting polyester still comprises diacetal
10 moieties.

In one embodiment, at least 20%, preferably at least 30%, more preferably at least 50% of the diacetal moieties are converted to dihydroxide moieties. In one embodiment, up to 95%, 90% or 85% of the initial protecting groups is
15 hydrolyzed.

For example, 40-60%, 50-80%, 60-90% or of the diacetal moieties are hydrolyzed into dihydroxide moieties, thus leaving a significant amount of the Galx-residues in the polymer still in the acetalized form. In one
20 embodiment, at least 3%, preferably at least 5%, like 7, 8, 9, or 10% of the Galx-residues in the final linear polymer is still in the acetalized form. See also Example 3 showing that the degree of hydrolytic deacetalisation can be controlled, which is advantageously used to steer the (surface active) properties of the polymer. See Figure 7.

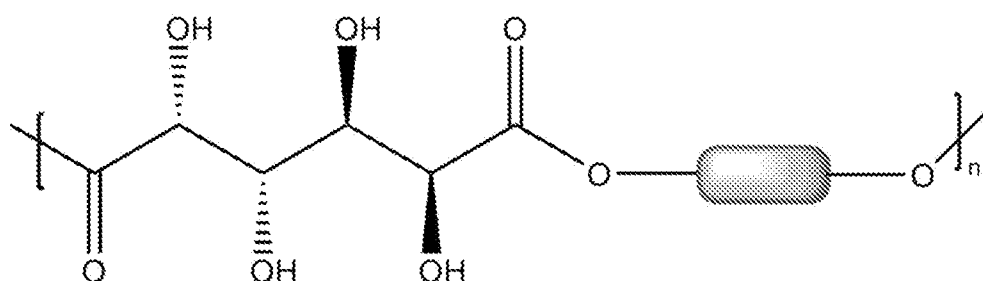
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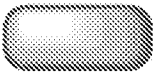
Following the deprotection step (ii), the Galx-based polyester comprising dihydroxide moieties obtained may be precipitated, washed and dried.

The invention also provides a linear Galx-based polyester obtainable by a
30 method according to the invention. The carbohydrate-based polyester can

have the numerical average molecular weight between 6000 and 30000 g/mol.

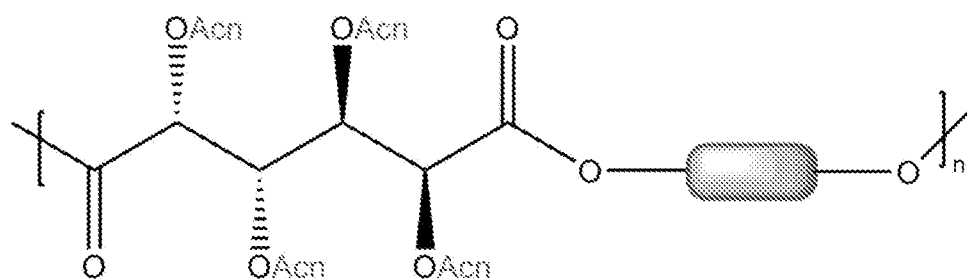
In one embodiment, the invention provides a fully deprotected linear
5 carbohydrate-based polyester of the general formula



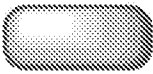
wherein  is a linear or cyclic aliphatic hydrophobic unit.

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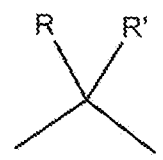
In another embodiment, only a part of the acetal moieties is hydrolyzed to provide a partially deprotected linear carbohydrate-based polyester of the general formula



15

wherein  is a linear or cyclic aliphatic hydrophobic unit and

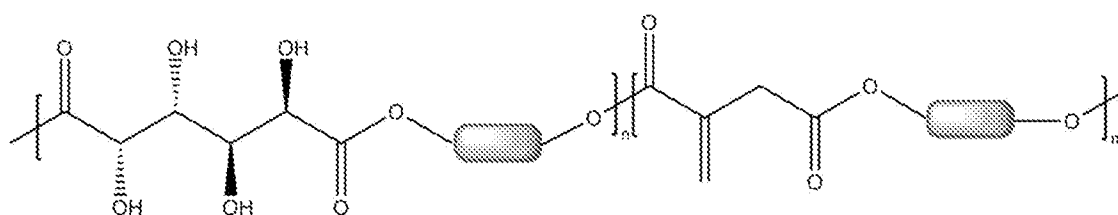
wherein at least two but not all of the Acn groups together form



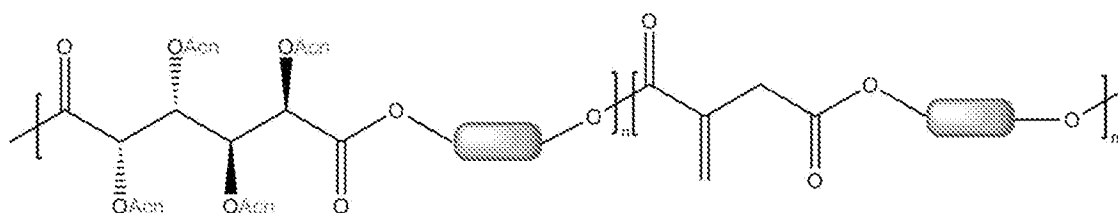
wherein R and R' are C₁-C₃ alkyl, and wherein the remaining Acn groups are H.

In one embodiment, 40-60% , 50-80% or 60-90%, of the Acn- groups are H.

- 5 In case a further co-monomer comprising an α,β -unsaturated functionality is used in the polymerization reaction of the present invention, the polyester may be of the formula



10 or



wherein at least 20%, preferably at least 40%, more preferably at least 60% of the Acn moieties are H.

- 15 A linear Galx-based polyester provided in the present invention is not taught or suggested in the prior art. US 3,083,187 describes polyesters with a polymeric backbone constructed by reacting aliphatic or aromatic dibasic acids (A) with aliphatic diols (B). The polymeric backbone is substituted with polyalkyleneglycols, i.e. the polyalkyleneglycols are not part of the
- 20 polymeric backbone. The polymeric backbone is substituted with monoalkylethers of polyalkyleneglycols using two methods. In the first method, the substitution is established by reacting such polyalkylene glycols with reactive centers in the polymeric backbone: the hydroxyl groups of dibasic acids of e.g. mucic acid. In the second method, reactive hydroxyl

groups in e.g. mucic acid are used as a starting point for ethylene oxide polymerization. In both methods of US 3,083,187, the resulting products are substituted with polyalkyleneglycols. In contrast, according to the present invention, acetalized galactaric acid is reacted with linear or cyclic aliphatic diols to yield an acetalized polyester which is further de-acetalized. Hence, the products of US 3,083,187 are structurally distinct.

Lavilla *et al.* (Biomacromolecules, Vol. 12, no. 7, 2011, pp. 2642-2652; ref. [9]) discloses carbohydrate-based polyesters made from bicyclic acetalized galactaric acid. Unlike the present invention, the polyesters are fully protected by acetal groups. Lavilla *et al.* is completely silent about converting at least part of the acetal groups to hydroxides.

It was surprisingly found that a linear (partially) deacetalised Galx-based polyester as provided herein has unique properties, and is advantageously used as rheology modifier or thickener.

They also find their use as surfactant. Hence, also provided is an emulsion composition comprising a linear (partially) deacetalised Galx-based polyester according to the invention. For example, said composition is a cosmetic or detergent composition, an adhesive, coating or paint composition

A still further embodiment relates to a hydrogel comprising a linear (partially) deacetalised Galx-based polyester according to the invention.

LEGEND TO THE FIGURES

Figure 1. FTIR analysis comparison before and after deacetalisation of A-G1G2-ol-62 polyester showing the formation of a broad peak in the 3500-3300 cm^{-1} area corresponding to the O-H stretch in alcohol groups as the acetal groups are being removed

Figure 2. Overlay ^1H NMR spectra of A-G1G2ol-62 polyester sample before deacetalisation and after 0.5 hours, 1 hour, 2 hours, 4 hours respectively 5 hours of incubation at room temperature

Figure 3. (A) Conversion deacetalisation A-G1G2ol-62 polyester in HCOOH 88% as function of the reaction time. (B) the degree of acetal removal can be controlled by adjusting the concentration of the used aqueous acid. hydrolytic removal of the acetal group by using a solution of trifluoroacetic acid (TFA). Two samples of 200 mg of dry and catalyst-free A-G1G1ol-64 polyester were dissolved in a volume of 1ml TFA 65% solution in water, respectively in 1ml TFA 90% solution in water.

Figure 4. Viscosity as a function of temperature measured for G1PD-58 10wt% in water measured at fixed shear rate= 9.6 s^{-1}

Figure 5. Viscosity as function of shear rate measured for G1PD-58 in water at 2.5wt%, 5wt.% and 10wt. %

Figure 6. Viscosity as function of shear rate measured for: G1PD-58, G1G2ol-62 at a concentration of 2wt.% in water a) and for G1PD-58 and G1G1ol-64 4wt.% in water b)

Figure 7. Viscosity as a function of shear rate measured for G1G1ol-64 samples partially and fully acetal deprotected at 4wt% concentration in water.

Figure 8. Viscosity as function of shear rate measured for G1G2ol-62 2wt.% in water at pH=4, or at pH=7, respectively.

Figure 9. Overview surface tension as function of concentration of fully and partially deprotected G1PD-58 and G1G1ol-64 samples in water.

5

EXPERIMENTAL SECTION

Methods and equipment

Characterisation of the solid-state thermoplastics

For confirming the structure of the obtained polyesters, NMR (Nuclear
10 Magnetic Resonance) and FTIR (Fourier Transform Infrared Spectroscopy) analysis methods were used.

The NMR spectra were recorded using a Varian Mercury Plus equipment operating at 400MHz. Approximately 10 respectively, 50mg of sample were dissolved in 1 mL of deuterated solvent for ^1H NMR and ^{13}C NMR. A total
15 of 64 scans were acquired for the ^1H and 5000 for the ^{13}C spectra, with a relaxation delay of 1s.

The FTIR spectra were recorded with a Shimadzu IR Tracer 100 equipped with an ATR accessory (diamond crystal, Graseby Specac), using a Happ-Genzel apodisation. For an absorbance spectrum, 64 scans were recorded
20 with a 4cm^{-1} resolution in the range $4000\text{-}600\text{ cm}^{-1}$.

The average molecular weight and polydispersity of the polymer samples prior to the deprotection reaction were determined using a Viscotek Gel Permeation Chromatography system. Chloroform was used as mobile phase and the molecular weight values of the samples were determined based on a
25 universal calibration method. For calibration, polystyrene standards were used.

Rheological characterization of the poly(galactaric ester) samples in water

Dry and catalyst free poly(galactaric esters) powder samples were suspended in water at different concentrations starting from 0.2% up to 4%. The polymer powder was swelled in water at room temperature for several
5 hours until complete dissolution by visual inspection. Samples which did not dissolve completely were kept in the ultrasonic bath for few minutes until a stable dispersion was formed.

For the samples prepared in basic environment the same procedure as described above was first applied and subsequently 20-40 μl NaOH 0.1M
10 were added to the volume of 2 ml polymer-water dispersion.

The rheological measurements were performed with a Thermo Fisher Scientific Haake Mars III rheometer. A volume of 2 ml of poly(galactaric esters) in water was placed in the cone-plate unit and the viscosity response was measured as function of a shear rate increasing from 0.1 to 1750 s^{-1} .
15 The surface tension of the polymer solutions was determined with a DataPhysics OCA equipment at room temperature with the pendant drop method. The values were calculated as average of 7 recorded measurements.

**EXAMPLE 1 : Polymerisation in melt of linear poly(galactaric
20 esters)**

This example describes an exemplary general protocol for synthesising the acetalized poly(galactaric esters).

An equimolar mixture of dimethyl-2,3:4,5-di-O-isopropylidene-galactarate
25 (Galx1) with a linear aliphatic or cyclic diol are brought into a 3-neck cylindrical flask equipped with a magnetic coupling stirrer. A Lewis acid catalyst, i.e. dibutyltin oxide (DBTO), is added to the mixture and the flask

is connected to a distillation setup. Prior to the reaction, nitrogen is flushed through the reaction setup and subsequently a constant flow is maintained during the first stage of the reaction in order to remove the formed by-product. During the second stage, the distillation setup is replaced with a vacuum adapter and high vacuum is applied until the end of the reaction.

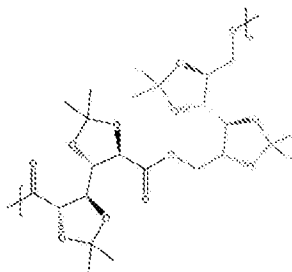
The average molecular weight of the obtained polyesters can be adjusted by increasing the reaction time. Since no solvent is used during the polymerisation, there are some practical limitations related to the higher viscosity of the melt with longer reaction times (i.e. difficulty in the removal of the formed by-product). Even so, in most cases, the numerical average molecular weight varies between 6000 and 30000g/mol.

Besides DBTO [9], [10], other organometallic catalysts which act as Lewis acids have been reported for similar reaction systems. Notable examples are Ti alkoxides; Sb, Ge, Sn oxides; Zn, Mn, Ca, Co, Cd acetate [3], [5], [6]. Nevertheless, their activity may depend on the reaction conditions, on the solubility in the medium or even on the possibility of catalysing also secondary reactions.

Example 1A

An equimolar mixture of dimethyl-2,3:4,5-di-O-isopropylidene-galactarate (Galx1) and 2,3: 4,5-di-O-isopropylidene-galactitol (Galx1ol) together with an amount corresponding to 0.4%mol (to the monomers) of DBTO, were brought into a 3-neck cylindrical flask equipped with a magnetic coupling stirrer, a nitrogen gas inlet and a temperature controlled distillation setup. The temperature of the reaction was set to 142°C (temperature of the oil bath) and a 250 ml/min nitrogen flow was set during the first stage of the reaction (3.5 hours). During the second stage, high vacuum was applied (0.01 mbar) for 5 hours.

The resulting product is dissolved in chloroform and precipitated in diethyl ether. The polymer powder is recovered by vacuum filtration and it is dried of solvent until constant weight in the vacuum oven.

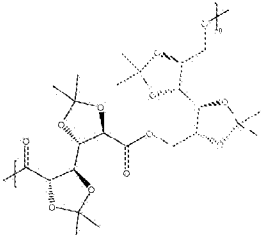


5 Scheme 2. Chemical structure of an A-G1G1ol homopolymer

Table 1.1 herein below provides an overview of exemplary acetalized poly(galactaric esters).

Table 1.1

Polyesters			
Code entry	Chemical structure	Mn* (g/mol)	D*
A-G1PD-58		8000	1.6
A-G1EG-172		6500	2.4
A-G1G2ol-62		8500	2.4

A-G1G1ol-64		9000	1.6
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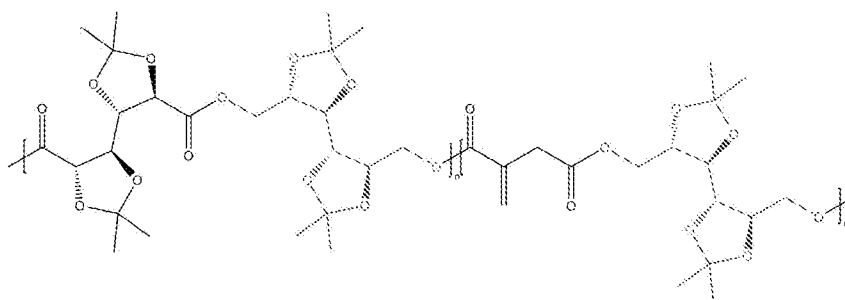
*Mn and D as determined from GPC (universal calibration, PS standards) of the acetalized starting polymer;

Example 1B

- 5 This example describes a method wherein a bicyclic acetalized galactaric acid derivative and alcohol are reacted in the presence of a co-monomer comprising a cross-linking moiety.

A mixture of 3 mmol Galx1, 3.7 mmol Galx1ol and 0.5 mmol dimethyl itaconate (DMI) together with an amount corresponding to
 10 0.4%mol (to the monomers) of DBTO, were brought into a 3-neck cylindrical flask equipped with a magnetic coupling stirrer, a nitrogen gas inlet and a temperature controlled distillation setup. Before the start of the reaction 0.5wt.% radical inhibitor, 4-methoxy-phenol, was added and the reaction was started under a 100 ml/min nitrogen flow at 142°C (temperature of the
 15 oil bath). After 4 hours, high vacuum was applied (0.01 mbar) for 2 more hours.

The resulting acetalized co-poly(galactaric ester) product is dissolved in chloroform and precipitated in diethyl ether. The polymer powder is recovered by vacuum filtration and it is dried of solvent until constant
 20 weight in the vacuum oven.



Scheme 3. Chemical structure of an A-IG1G1ol random co-polyester

5 Table 1.2 Overview exemplary acetalized co-poly(galactaric esters).

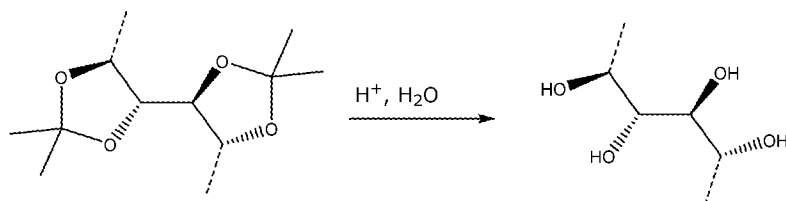
Code entry	Chemical structure	Composition DMI (%) **	Mn* (g/mol)	D*
A-IG1G1ol-MP2		3	13000	1.5
A-IG1G1ol-MP2.3		5	5700	1.9
A-IG1G1ol-MP3		7	6800	1.9

*Mn and D as determined from GPC (universal calibration, PS standards) of the acetalized starting polymer;

10 ** composition of the itaconate unit in the random co-polyesters, as determined from the ¹H NMR spectra.

EXAMPLE 2: Deprotection of the acetal group

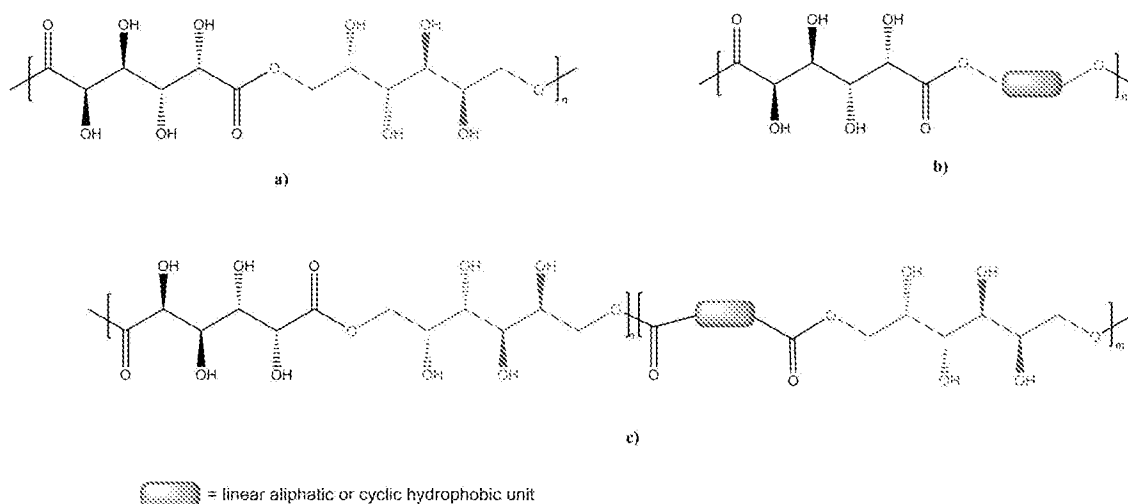
This example describes the general deacetalisation procedure of a method according to the invention. The hydrolytic deprotection of the acetal group
5 can be performed by using an aqueous acid solution.



Scheme 4. Hydrolytic deacetalisation reaction of Galx1 derived groups under
10 acidic conditions

A sample of purified and vacuum dried acetalised poly(galactaric ester) is dissolved in the aqueous acid solution and kept at room temperature. The concentration and the reaction time are chosen depending on the desired degree of deacetalisation (see examples below). Subsequently, the polymer
15 solution is precipitated and washed several times with a cold non-solvent, mostly diethyl ether. The recovered product is dried in the vacuum oven until constant weight.

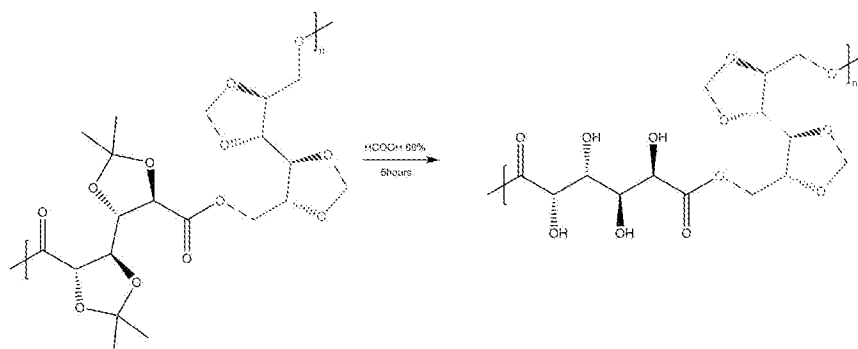
Examples of suitable acids for the acetal removal reaction are: sulfuric acid, hydrochloric acid, para-toluene sulfonic acid, acetic acid, formic acid,
20 trifluoroacetic acid etc. Examples include strongly acidic resins of the styrene-divinylbenzene type, e.g. sold, inter alia, under the trade name Amberlyst 15. Formic acid and trifluoroacetic acid are preferred.



Scheme 5. General chemical structures of poly(galactaric esters), a) and b), respectively of random galactaric co-polyester, c) (upon deacetalisation)

5 Example 2A

The hydrolytic removal of the acetal group was performed using a solution of formic acid (HCOOH). 20 mg of dry and catalyst-free A-G1G2ol-62 polyester sample was dissolved in a volume of 1 ml HCOOH 88% solution in chloroform and with 2% water. The resulted polymer solution was kept at room temperature and samples were taken after 0.5, 1, 2, 4 respectively 5 hours. The sampled polymer was precipitated and washed several times with cold diethyl ether. The recovered products were dried in the vacuum oven until constant weight.



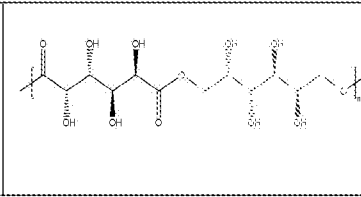
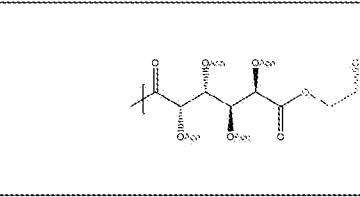
Scheme 6. Complete hydrolytic deacetalisation reaction of A-G1G2ol-62 polyester using HCOOH 88% solution

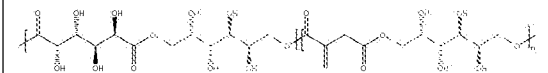
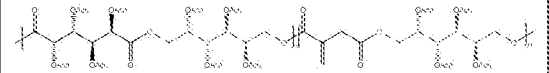
Figure 1 shows the FTIR analysis comparison before and after
5 deacetalisation of A-G1G2-ol-62 polyester. The formation of a broad peak in the 3500-3300 cm⁻¹ area is observed, which corresponds to the O-H stretch in alcohol groups resulting from the acetal groups are being removed

Example 2B

- 10 A sample of 200 mg dry and catalyst free A-IG1G1ol-MP3 polyester was dissolved in 1 ml TFA solution 90% vol. and kept at room temperature reacting for 30 minutes. Subsequently, the polymer solution was precipitated and washed several times with ice cold diethyl ether. The recovered product was dried in the vacuum oven until constant weight.
- 15 Table 2. Overview examples poly(galactaric esters) respectively co-poly(galactaric esters).

Polyesters		
Code deacetalised structure	Structure fully deacetalised sample	Structure partially deacetalised sample
G1PD-58		
G1EG-172		
G1G2ol-62		

G1G1ol-64		
-----------	---	--

Co-Polyesters		
Code deacetalised structure	Structure fully deacetalised sample	Structure partially deacetalised sample
IG1G1ol-MP2 (3% DMI)		
IG1G1ol-MP2.3 (5% DMI)		
IG1G1ol-MP3 (7% DMI)		

*Mn and D as determined from GPC (universal calibration, PS standards) of the acetalized starting polymer;

5 ** composition of the itaconate unit in the random co-polyesters, as determined from the 1H NMR spectra

EXAMPLE 3: Controlling the degree of hydrolytic deacetalisation.

10 This example demonstrates that the degree of deprotection in step (ii) of a method of the invention can be controlled in order to accommodate for specific properties of the resulting polymer.

i) *By adjusting the deacetalisation reaction time*

Figure 2 shows an overlay ¹H NMR spectra of A-G1G2ol-62 polyester sample before deacetalisation and after 0.5 hours, 1 hour, 2 hours, 4 hours
5 and 5 hours of incubation at room temperature, respectively.

The gradual hydrolytic deacetalisation reaction was confirmed by the decrease in intensity until complete disappearance of the chemical shift corresponding to the protons from the acetalic methyl groups in the 1.3-1.4 ppm region.

10 As another example, conversion from the fully isopropylidene protected G1G2ol-62 polymer to about 50% acetalisation is achieved in less than one hour in an aqueous HCOOH (88%) solution with a complete removal of all acetal groups within 5 hours (see figure 3A).

15 ii) *By adjusting the concentration of the aqueous acid solution*

The hydrolytic removal of the acetal group is suitably performed by using a solution of trifluoroacetic acid (TFA). Two samples of 200 mg of dry and catalyst-free A-G1G1ol-64 polyester were dissolved in a volume of 1ml TFA
20 65% solution in water, respectively in 1ml TFA 90% solution in water. The resulted polymer solutions were kept at room temperature for 0.5 hours. Subsequently the polymer was precipitated and washed several times with cold diethyl ether. The recovered products were dried in the vacuum oven until constant weight.

25 Similarly to varying the deacetalisation time, the degree of acetal removal can also be controlled by adjusting the concentration of the used aqueous acid. By treating the A-G1G1ol-64 sample with a TFA solution 65vol%, the conversion of the acetal groups to free OH groups is less than 40%, reaching

almost complete conversion when increasing the concentration to 90vol.% (see Fig. 3B).

EXAMPLE 4: Application of poly(galactaric esters) as rheology 5 modifiers

This example demonstrates the added value of these novel poly(galactaric esters) by showing their rheological and surface tension in water as response to the change of different parameters.

- 10 Depending on the concentration and/or pH, the poly(galactaric esters) can be dissolved or suspended in water. Since the molecular weight of the polymers is in the 10^3 - 10^4 g/mol region, no (or up to a low extent) associative behaviour due to chain entanglements is expected to happen. More likely, strong intermolecular interactions such as hydrogen bonding between the
15 free OH groups and the water molecules along with hydrophobic strong associations between the internal non-polar units are the ones assumed to give the thickener response of the polyester samples in an aqueous system.

The water-polyester system shows relatively good stability in the room temperature domain with a gradual decrease in viscosity when increasing
20 the temperature. Figure 4 shows the thickening effect of the exemplary poly(galactaric ester) G1PD-58 (10 wt% in water) as a function of temperature.

As expected in this case, the response to the steadily increasing shear rate is a high viscosity in the low shear rate range (0.01 - 1 s^{-1}) with a lower viscosity
25 in the intermediate and high shear rate region (1 - 1000 s^{-1}). This type of behaviour is characteristic to a pseudoplastic or shear-thinning fluid. Different shear thinning response can be observed when modulating different parameters of the water-polyester thickener system. Concrete examples are depicted in Figures 5 and 6.

Figure 5 illustrates the dependence on the concentration of polymer in the water solution/ dispersion. Shown is the viscosity as function of shear rate measured for G1PD-58 in water at 2.5wt%, 5wt.% and 10wt.%. Surprisingly, by increasing the concentration of the polymer, a higher viscosity response is obtained while maintaining the shear thinning behaviour.

Figure 6 illustrates the dependence on the type of co-monomer (type of hydrophobic unit). Shown is the viscosity as function of shear rate measured for (panel A) G1PD-58, G1G2ol-62 at a concentration of 2wt.% in water; and (panel B) for G1PD-58 and G1G1ol-64 4wt.% in water.

The strength of the formed hydrophobic clusters and therefore the thickening effect is dependent on parameters such as distance or size of the hydrophilic spacer but also on the molar volume of the associative hydrophobic units. Therefore, due to its flexibility an alkyl unit can contribute to stronger associative interactions than a cyclic structure. (figure 6A). Furthermore, the number of hydrophobic groups along with their internal distribution inside the chain will influence the rheological behaviour. As depicted in figure 6B, a hydrophobic unit of 3 carbon atoms contributes to stronger interactions than a -CH₂- group.

Figure 7 illustrates the dependence of the shear thinning behaviour on the degree of deacetalisation. Shown is the viscosity as a function of shear rate measured for G1G1ol-64 samples partially (30%) and fully acetal deprotected at 4wt% concentration in water.

This demonstrates that, related to the type of monomer influence on the rheological properties, a partial removal of the acetal groups (therefore influencing the hydrophilicity- hydrophobicity ratio but also the chain conformation possibilities) has an effect on the overall shear thinning response. On one side the initial viscosity at very low shear rates will be comparable. However, the sample which still contains some residual bulky

acetal groups favours fewer inter-molecular and more intra-molecular associations and thus a lower viscosity value at high sheer rates.

Figure 8 demonstrates the dependence on the change in pH. Shown is the viscosity as function of shear rate measured for G1G2ol-62 2wt.% in water
5 at pH=4, or at pH=7, respectively.

The poly(galactaric esters) show a better solubility in water at $\text{pH} \geq 7$ (concentration dependent). There is little influence on the rheological profile of the solution as shown in figure 8. However, with respect to practical
10 applications of the polymer and from the compounding point of view, an increased solubility will also reduce the possibility of the polymer precipitating from the water phase.

EXAMPLE 5: Surfactant activity

15 Figure 9 shows the surface tension as a function of the concentration of exemplary polyesters G1PD-58 and G1G1ol-64 samples in water. Even in the dilute concentration region (up to 4wt.%) the surface tension of the water can be decreased by adding the hydrophilic poly(galactaric esters). The figure also shows the surface tension of partly deprotected Galx
20 polyesters. Dispersions of 4wt.% G1PD-58 and G1G1ol-64 (30% deprotected) in demineralised water were prepared. The determined surface tension values are comparable with the ones obtained for the fully deacetalised homologues polyesters at 1.5wt% concentration in water.

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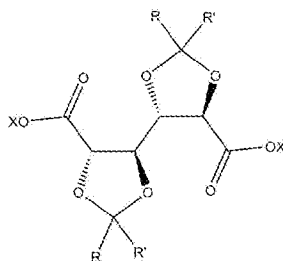
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- 5 [10] Munoz Guerra, S., & Lavilla Aguilar, C. (2013). Síntesis de homopoliésteres y copoliésteres aromáticos y alifáticos a partir de derivados de alditos y ácidos aldáricos diacetilizados, así como homopoliésteres y copoliésteres aromáticos y alifáticos obtenidos de dicho procedimiento. Spain: Universitat Politècnica de Catalunya.

Claims

1. A method for providing a linear carbohydrate-based polyester, comprising the steps of:

5

- (i) reacting a bicyclic acetalized galactaric acid derivative (Galx) of the general formula I



10

wherein X is H or a linear aliphatic moiety, preferably a linear C₁-C₅ alkyl;

R and R' are linear alkyl chains, more preferably C₁-C₃ alkyl;

15

with a diol in the presence of a suitable catalyst to obtain a Galx-based polyester; and

- (ii) subjecting said Galx-based polyester to a hydrolytic deacetalisation reaction to convert at least part of the diacetal moieties to dihydroxide moieties.

20

2. Method according to claim 1, wherein X is a linear C₁-C₅ alkyl.

25

3. Method according to any one of the preceding claims, wherein said bicyclic acetalized derivative is selected from the group consisting of dimethyl-2,3:4,5-di-O-isopropylidene-galactarate and dimethyl-2,3:4,5-di-O-methylene-galactitol.

4. Method according to any one of the preceding claims, wherein said diol is of the general formula



wherein  is a linear or cyclic aliphatic hydrophobic unit.

5

5. Method according to claim 4, wherein said diol is selected from the group consisting of linear aliphatic α,ω -diols, such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 2,3:4,5-di-O-isopropylidene-galactitol or dimethyl-2,3:4,5-di-O-methylene-galactitol.

10

6. Method according to any one of the preceding claims, wherein step (i) comprises reacting said bicyclic acetalized galactaric acid derivative and said alcohol in the presence of a further co-monomer comprising a cross-linking moiety.

15

7. Method according to claim 6, wherein said further co-monomer comprises an α,β -unsaturated functionality, preferably wherein the co-monomer is itaconic acid or ester thereof, such as dimethylitaconate or dibutylitaconate.

20

8. Method according to any one of the preceding claims, wherein the catalyst used in step (i) is selected from the group consisting of DBTO and other organometallic catalyst which act as Lewis acids, such as Ti alkoxides; Sb, Ge, Sn oxides; Zn, Mn, Ca, Co, Cd acetate.

25

9. Method according to any one of the preceding claims, wherein step (ii) comprises dissolving the Galx-based polyester in an acid solution and incubating at room temperature to obtain the desired degree of deacetalisation, preferably wherein said solution of acid is an aqueous

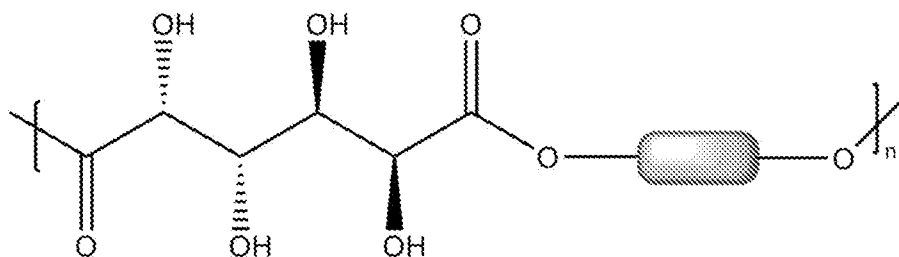
solution of sulfuric acid, hydrochloric acid, p-toluene sulfonic acid, acetic acid, trifluoroacetic acid, more preferably formic acid.

10. Method according to any one of the preceding claims, wherein at
5 least 20%, preferably at least 40%, more preferably at least 60% of the diacetal moieties are converted to dihydroxide moieties.

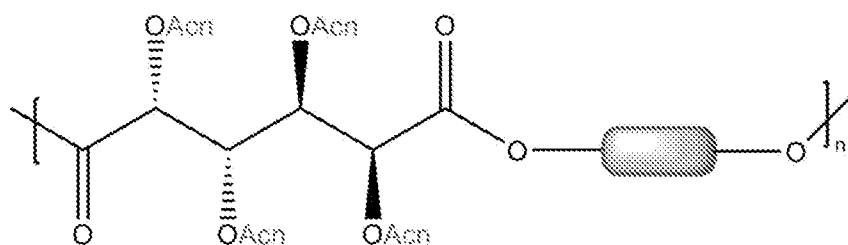
11. Method according to any one of the preceding claims, further
10 comprising step (iii) wherein the Galx-based polyester comprising dihydroxide moieties obtained in step (ii) is precipitated, washed and dried.

12. A linear carbohydrate-based polyester obtainable by a method according to any one of claims 1-11.

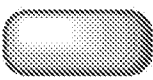
15 13. Linear carbohydrate-based polyester of the general formula

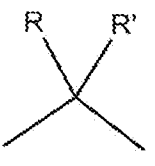


or



20

wherein  is a linear or cyclic aliphatic hydrophobic unit and

wherein at least two but not all of the Acn groups together form ,
 wherein R and R' are C₁-C₃ alkyl, and wherein the remaining Acn groups
 are H, for a partially deacetalised structure

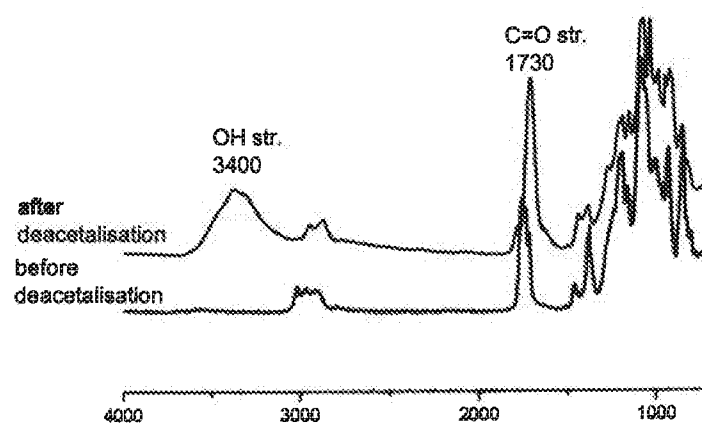
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14. Use of a linear carbohydrate-based polyester according to claim 12
 or 13 as rheology modifier.

15. Use of a linear carbohydrate-based polyester according to claim 12
 10 or 13 as surfactant.

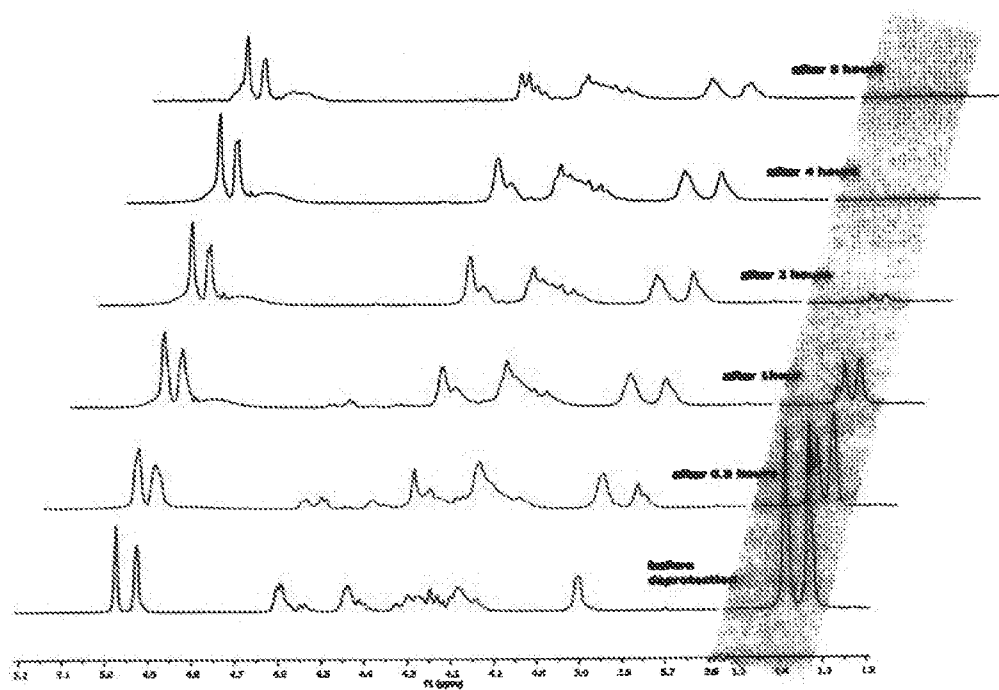
16. A water-borne emulsion comprising a linear carbohydrate-based
 polyester according to claim 12 or 13, preferably wherein said composition is
 a cosmetic or detergent composition, an adhesive, coating or paint
 15 composition.

Figure 1



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Figure 2



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Figure 3A

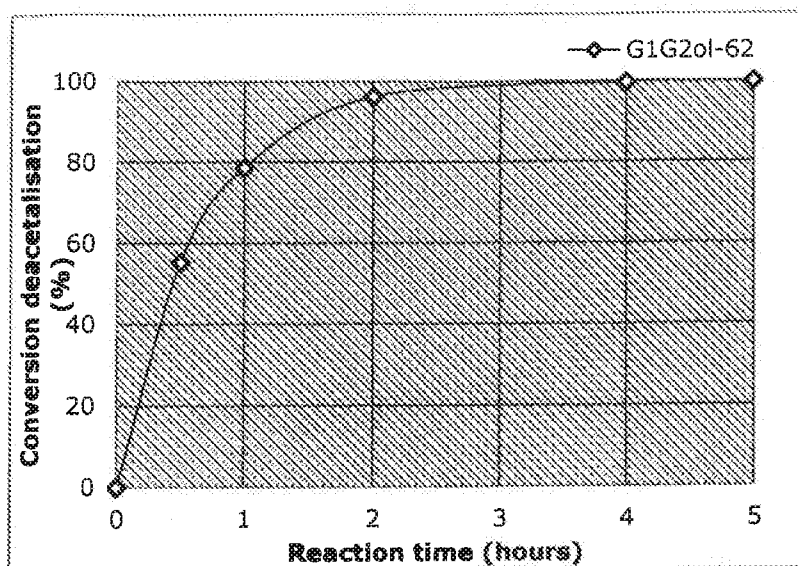
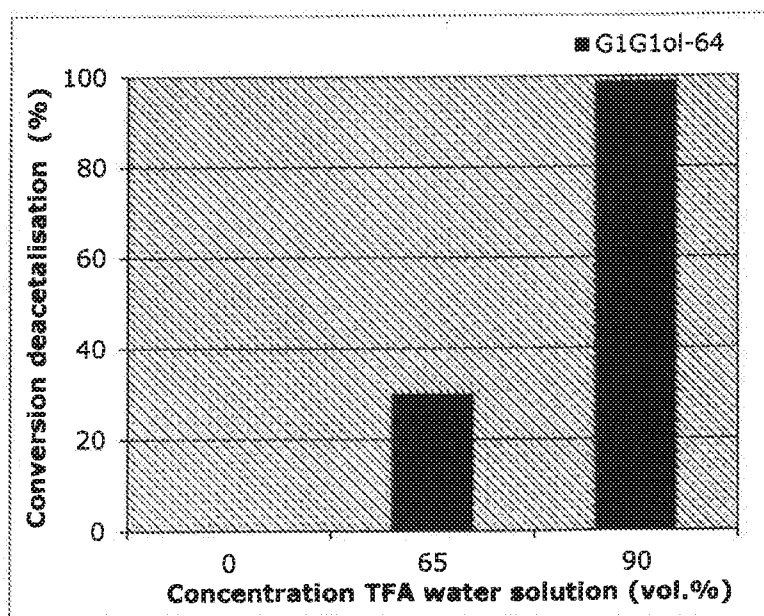


Figure 3B



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Figure 4

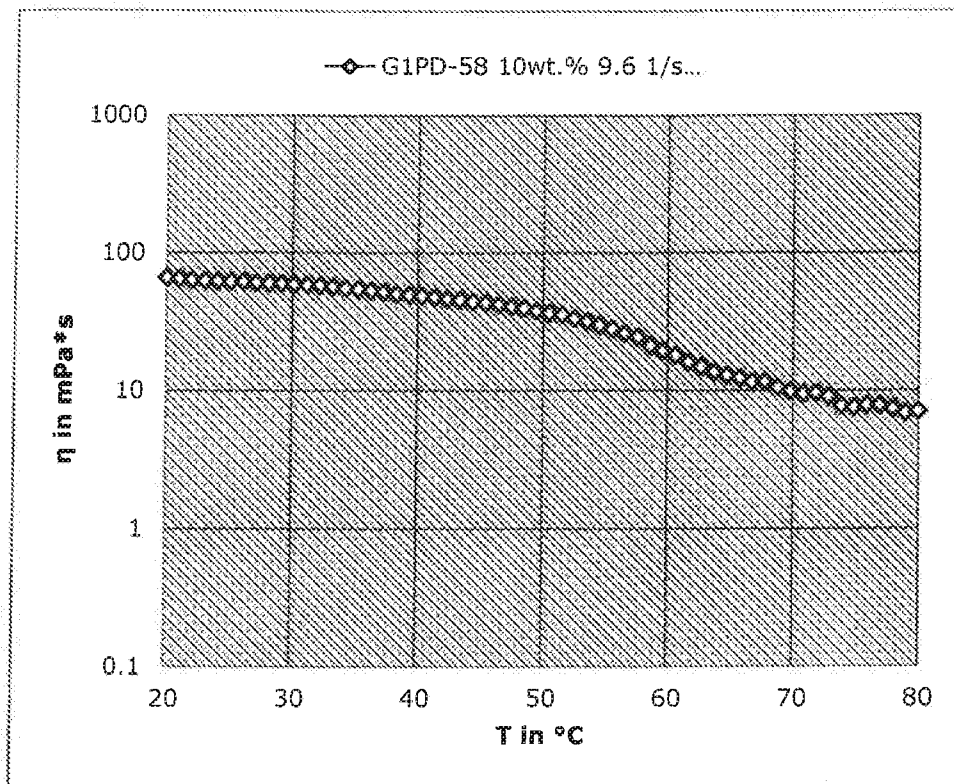


Figure 5

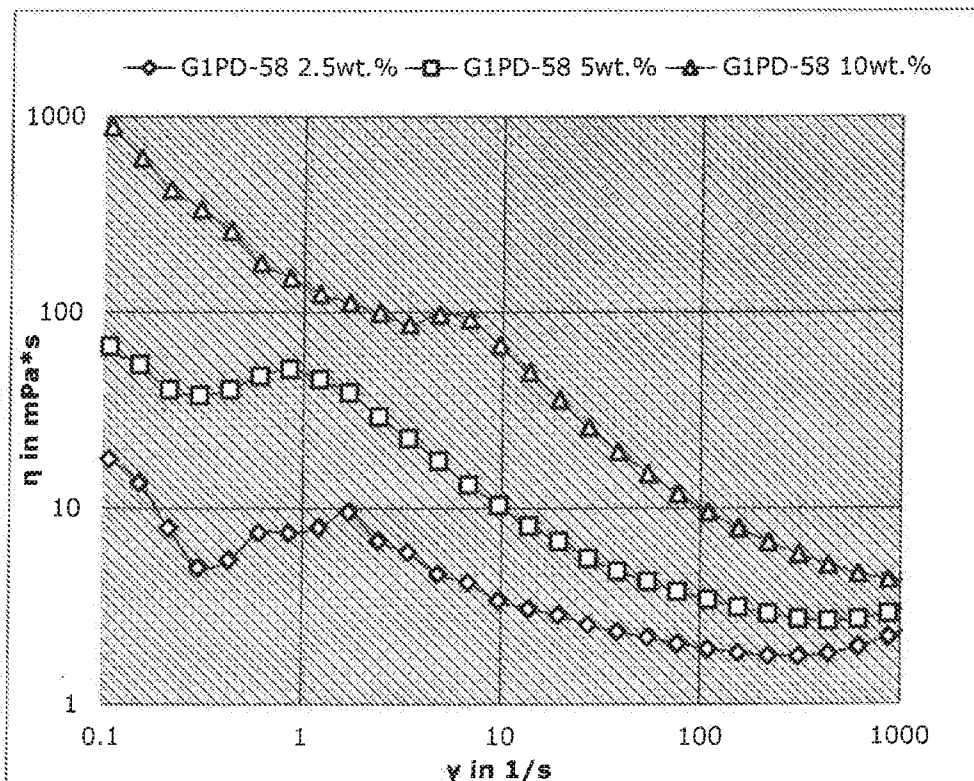


Figure 6A

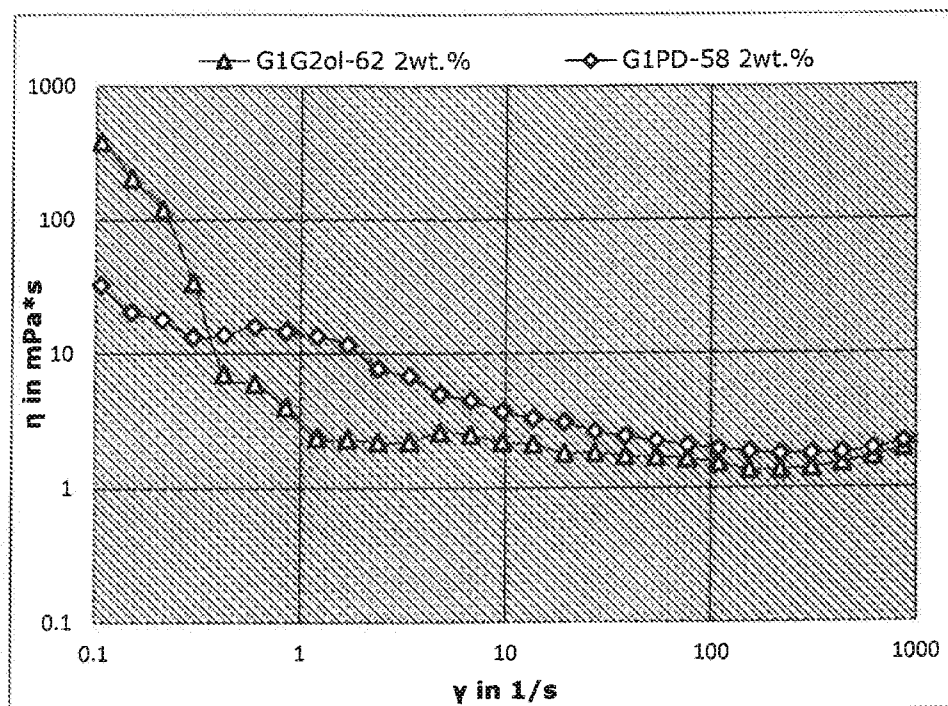


Figure 6B

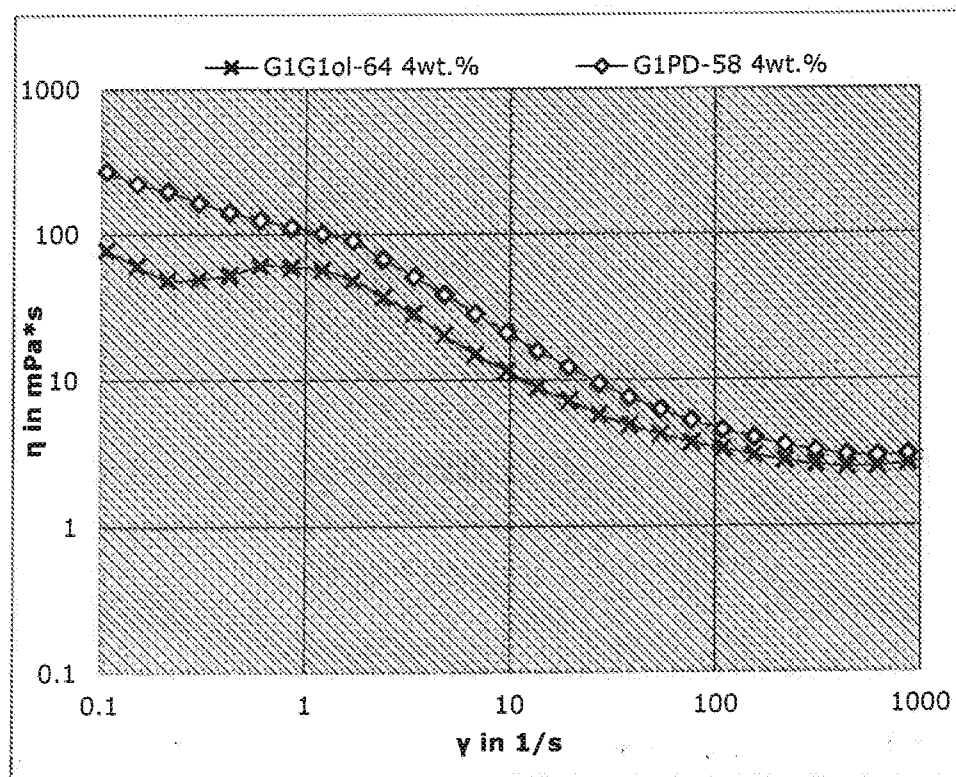


Figure 7

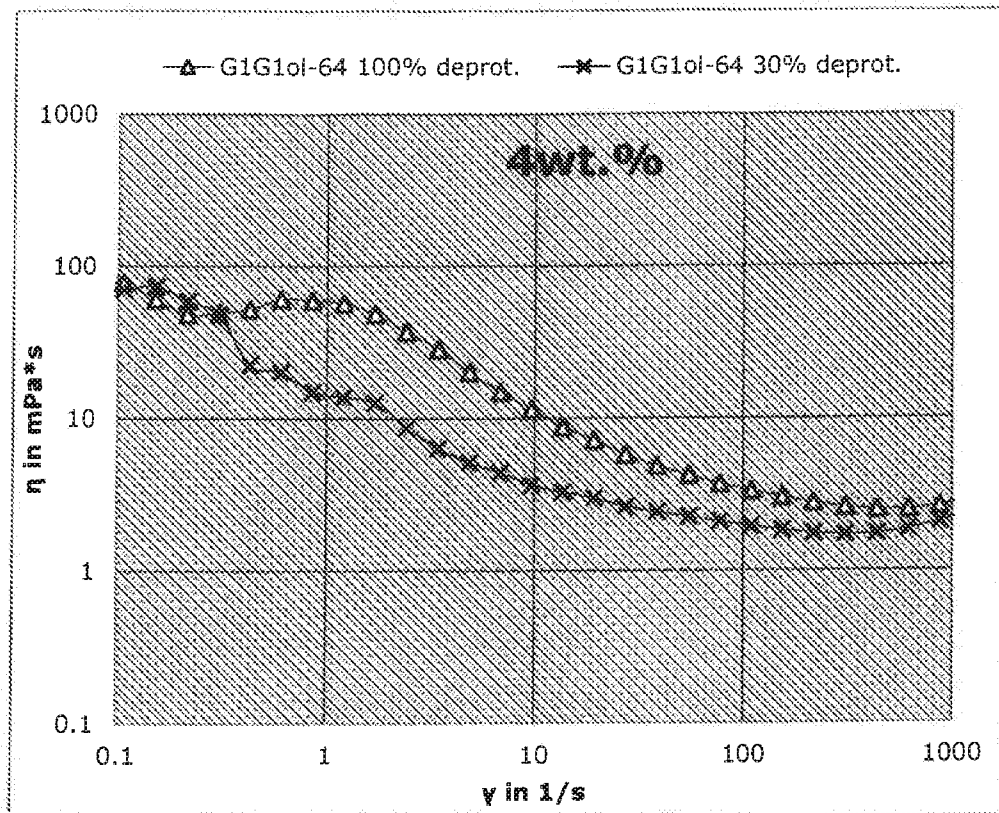


Figure 8

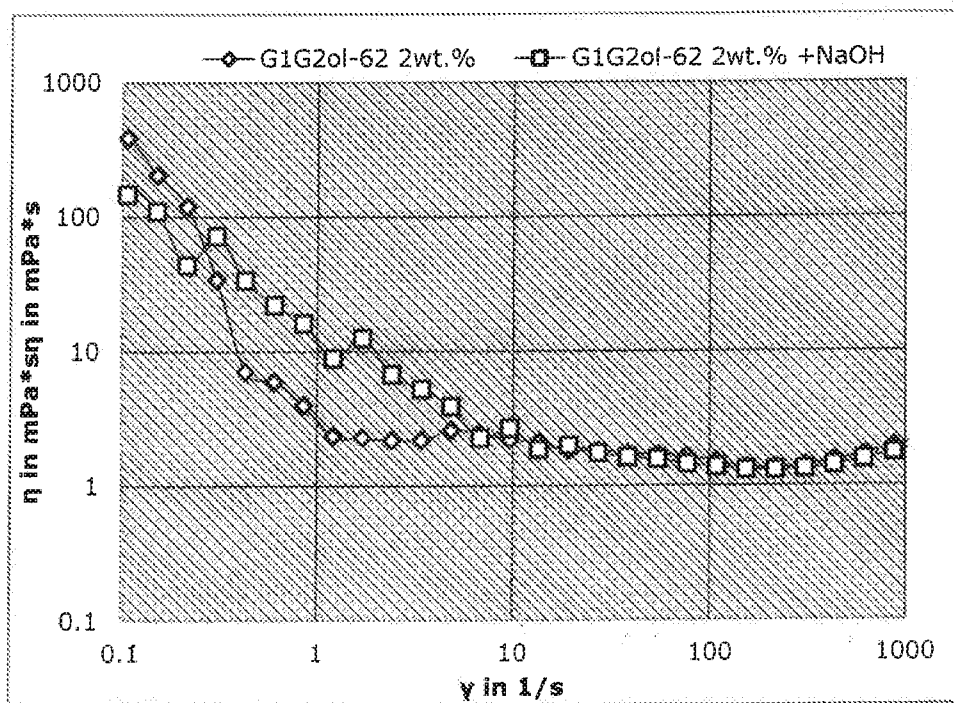
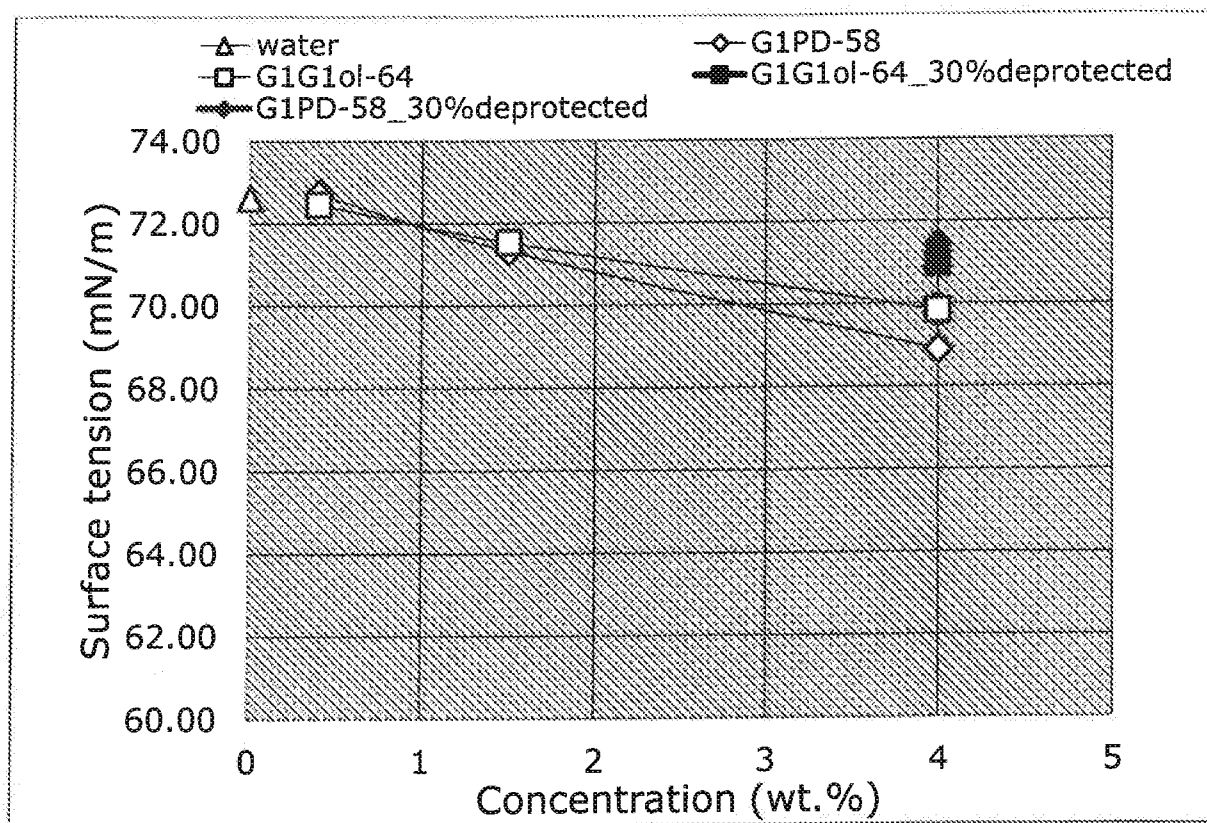


Figure 9



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2018/050211

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G63/42 C08G63/66 C08G63/672 C08G63/78 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C08G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, COMPENDEX, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 083 187 A (STUART FRANK A ET AL) 26 March 1963 (1963-03-26) column 1, lines 10-16 claim 1	1-16
A	----- DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; 11 July 2011 (2011-07-11), LAVILLA C ET AL: "Carbohydrate-based polyesters made from bicyclic acetalized galactaric acid", XP002773535, Database accession no. E20112914149949 the whole document -/--	1-16
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 15 May 2018		Date of mailing of the international search report 24/05/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Bezard, Stéphane

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2018/050211

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	-& LAVILLA C ET AL: "Carbohydrate-based polyesters made from bicyclic acetalized galactaric acid", BIOMACROMOLECULES, vol. 12, no. 7, 11 July 2011 (2011-07-11), pages 2642-2652, XP002773794, AMERICAN CHEMICAL SOCIETY USA DOI: 10.1021/bm200445w the whole document ----- FR 3 024 733 A1 (COATEX SAS [FR]) 12 February 2016 (2016-02-12) page 1, lines 4-9 claim 1; example 1 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2018/050211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3083187	A	26-03-1963	NONE

FR 3024733	A1	12-02-2016	BR 112016028511 A2 22-08-2017
			CN 106488939 A 08-03-2017
			EP 3177661 A1 14-06-2017
			FR 3024733 A1 12-02-2016
			US 2017101544 A1 13-04-2017
			WO 2016066910 A1 06-05-2016
