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(54) Title: RENEWABLE MONOMER AND POLYMER THEREOF

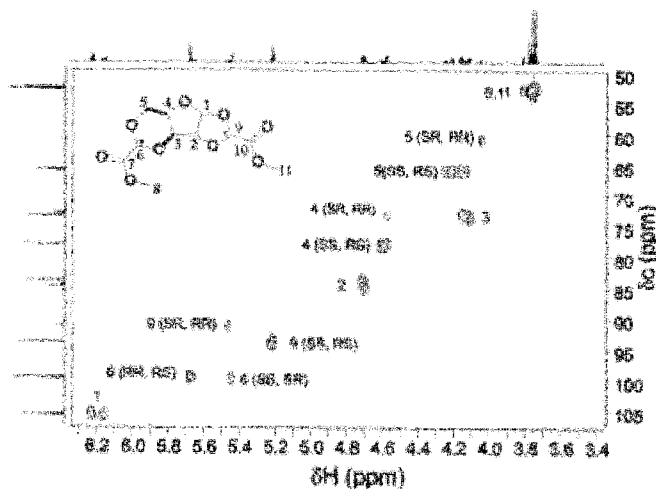
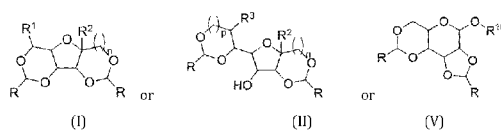


Figure 1

(57) Abstract: Described is a compound having the structure (I), (II) or (V), Formulae(I), (II), (V), wherein R<sup>1</sup> is -H, -CH<sub>2</sub>OH or -CH(OH)CH<sub>2</sub>OH; R<sup>2</sup> is -H, -OH, or -CH<sub>2</sub>OH; R<sup>3</sup> is -H, -OH, or -CH<sub>2</sub>OH; n is 0 or 1; p is 0 or 1; R<sup>10</sup> is hydrogen or a hydrocarbon moiety with 1 to 20 carbon atoms, wherein each hydrogen atom of the hydrocarbon moiety may optionally be substituted with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom; R is either -Z-F or Y and wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group and wherein Y is hydrogen or a linear, branched or cyclic organic residue having 1 to 20 carbon atoms with the proviso that if R is Y and n is 0



SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN,  
TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

**(84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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## Renewable Monomer and Polymer thereof

### BACKGROUND

Plastic has become a ubiquitous consumable in our daily lives. Global plastic  
5 production has increased to over 380 million tons per year in 2015 with a compound  
annual growth rate of 8.5 %. Global life-cycle greenhouse gas emissions from  
production of these plastics were 1.7 Gt of CO<sub>2</sub>-equivalent (CO<sub>2</sub>e) in 2015, or 5% of  
total global greenhouse gas emissions, and is estimated to increase to 6.5 Gt CO<sub>2</sub>e by  
10 2050 if current trends continue (Zheng, J. & Suh, S. Strategies to reduce the global  
carbon footprint of plastics. *Nat. Clim. Chang.* **9**, 374–378 (2019). Also, more than a  
third of this plastic has an average lifetime of less than six months before it is  
discarded—the majority of which ends up in landfills or the environment (Geyer, R.;  
Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.*  
**2017**, 3 (7), e1700782). Not only are plastics produced from non-renewable and  
15 polluting fossil fuels, but they are also non-biodegradable and detrimental to the  
world's ecosystems.

To mitigate emissions and pollution from plastic production, research into biobased  
and biodegradable polymers is sorely needed. In 2018, 2.274 million tons of bioplastic  
20 were produced—amounting to less than 1% of global plastic production. Of this 2.274  
million tons, 38.7% consists of biodegradable polymers. However, with increasing  
consumer demand for renewable products, the bioplastics market is expected to  
expand considerably in the next decade (Biopolymers facts and statistics 2017 report.  
Institute for Bioplastics and Biocomposites).

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Polymers from renewable resources have been developed, but usually their  
mechanical properties and/or their processability come short of the properties of  
petroleum-based plastics. The frequently used polymers from renewable resources

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polylactic acid (PLA), polybutyl succinate (PBS), polyhydroxyalkonates (PHA) are not suitable replacements for packaging materials such as polyethylene terephthalate (PET), the most abundant polyester, which comprises 8% of the global polymer market (Muñoz-Guerra, S.; Lavilla, C.; Japu, C.; Martínez de Ilarduya, A. Renewable Terephthalate Polyesters from Carbohydrate-Based Bicyclic Monomers. *Green Chem.* **2014**, *16* (4), 1716–1739). This is due to their inferior mechanical properties and processability. Coca-Cola co. and DuPont have commercialized partially renewable PET through the use of renewably derived diols but still have not managed to find a renewable route to economically produce or replace the rigid diacid component, terephthalic acid (TPA).

A satisfying renewable replacement for PET has not been found yet. At the moment, the most promising sustainable replacement candidate for PET appears to be poly(ethylene furanoate) (PEF), which is manufactured from 2,5-furandicarboxylic acid. While PEF may be manufactured from renewable resources, the multi-step reaction sequence from glucose, combined with undesirable degradation products and the intensive separations required prior to polymerization, have limited its commercialization. Furthermore, there have been reports that PEF is non-biodegradable (Sajid et al., *Green Chem.* **2018**, *20* (24), 5427-5453).

20

Renewable polyesters have been prepared using dianhydrohexitols, such as the commercially available isosorbide, which are rigid, bicyclic diols derived from sugars. Polyesters containing these cyclic sugars also have good thermal and mechanical properties and show improved biodegradability (Zamora, F.; Hakkou, K.; Muñoz-Guerra, S.; Galbis, J. A. Hydrolytic Degradation of Carbohydrate-Based Aromatic Homo- and Co-Polyesters Analogous to PET and PEI. *Polymer Degradation and Stability* **2006**, *91* (11), 2654–2659). However, the major drawback of these sugars is their low reactivity—caused by the secondary nature of the alcohol groups, and in some cases, the different steric orientations of the hydroxyl groups with respect to the fused rings. In addition, isosorbide is normally obtained by acid catalyzed dehydration of the D-sorbitol. In order to obtain the required purity of the isosorbide monomer, laborious

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reaction steps including distillation, recrystallization from alcohols, recrystallization from the melt, or a combination of these methods are required. In addition, the synthesis is limited to the diol, and the manufacture of derivatives such as amines requires further synthetic steps.

5

A similar bicyclic, sugar-derived, diacid (2,3:4,5-di-O-methylene-galactarate) has also been synthesized via acetalization of galactaric acid with formaldehyde in an attempt to directly replace terephthalic acid (TPA). Although high molecular weight polymers with good thermal and mechanical properties and enhanced hydrobiodegradability were attained, the production of these precursors from biomass requires a laborious, multi-step reaction sequence using toxic paraformaldehyde, making commercial synthesis from renewable carbon currently impractical. For example, the production of the glucaric acid-based polymer, which is the most promising candidate for feasible production (as it is produced from glucose), requires the fermentation of glucose to gluconic acid, followed by oxidation of gluconic acid over a Pt/C catalyst to glucaric acid and lastly, reaction with toxic paraformaldehyde to achieve the final product (Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Benito, E.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. Carbohydrate-Based Polyesters Made from Bicyclic Acetalized Galactaric Acid. *Biomacromolecules* **2011**, *12* (7), 2642–2652; Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Benito, E.; García-Martín, M. G.; Galbis, J. A.; Muñoz-Guerra, S. Biodegradable Aromatic Copolyesters Made from Bicyclic Acetalized Galactaric Acid. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50* (16), 3393–3406).

Acetals of carbohydrates, such as acetals of glucose, have been prepared. For example, in US 6,294,666, a tricyclic compound prepared by acetalization of glucose is described. However, US 6,294,666 does not describe a polymerizable monomer. Also in WO 96/32434 A1, a tricyclic compound prepared by acetalization of glucose is described as a saccharide residue of polyethylene oxide used for pharmaceutical applications. Also, WO 96/32434 A1 does not describe a polymerizable monomer.

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Proceeding from the prior art elucidated hereinabove, it is an object of the invention to provide a monomer that can be polymerized or co-polymerized, in particular, to yield a fully renewable polymer, preferably with potential for biodegradability.

Ideally, the polymer or copolymer prepared from the monomer has good thermal and/or mechanical properties.

WO2011/021398 discloses pyranose derivatives and furanose derivatives having a polymerizable group that can be used for a photosensitive resin and a method for producing those pyranose derivatives and furanose derivatives.

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Other and more specific objects will in part be apparent and will in part appear hereinafter.

#### SUMMARY OF THE INVENTION

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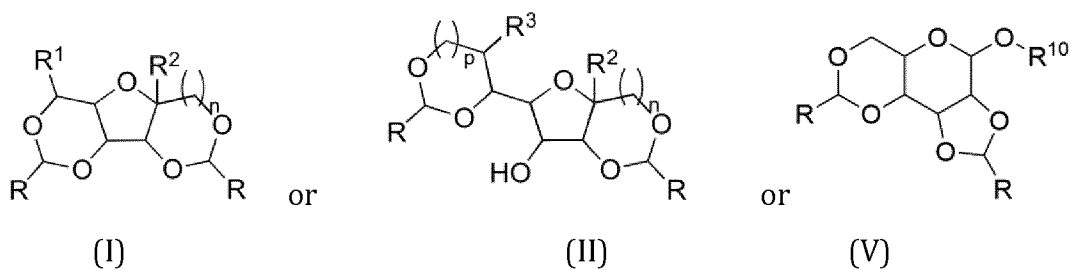
Some or all of these advantages are achieved according to the invention by the compound according to claim 1, the method according to claim 7, the polymer according to claim 13, the method according to claim 16, and the use according to claim 22.

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Further advantageous embodiments of the invention are specified in the dependent claims and are elucidated in detail herein below.

The invention provides for a compound having the structure (I) or (II), or (V)

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- 5 -

wherein

R<sup>1</sup> is -H, -CH<sub>2</sub>OH or -CH(OH)CH<sub>2</sub>OH;

R<sup>2</sup> is -H, -OH, or -CH<sub>2</sub>OH;

R<sup>3</sup> is -H, -OH, or -CH<sub>2</sub>OH;

5 R<sup>10</sup> is hydrogen or a hydrocarbon moiety with 1 to 20 carbon atoms, wherein each hydrogen atom of the hydrocarbon moiety may optionally be substituted with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom;

n is 0 or 1;

p is 0 or 1;

10 R is either -Z-F or Y, and wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, and

15 Y is a hydrogen or a linear, branched or cyclic organic residue having 1 to 20 carbon atoms,

wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and

R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group,

with the provision that

if R is Y and n is 0 at least one of R<sup>1</sup> or R<sup>2</sup> is different from hydrogen.

20

Preferably, if Z is a hydrocarbon moiety with 0 carbon atom, it is a covalent bond.

Preferably, R<sup>10</sup> can be a substituted or unsubstituted hydrocarbon moiety with 1 to 20 carbon atoms. The term "substituted hydrocarbon moiety with 1 to 20 carbon atoms" stands for a hydrocarbon moiety wherein one or more or all hydrogen atoms may be replaced (substituted) with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom. Each of the three hydrogen atoms of the terminal carbon atom of the hydrocarbon moiety can be substituted with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom. R<sup>10</sup> may be for example methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, 25 tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, fluoromethyl, difluoromethyl, trifluoromethyl, fluoroethyl, difluoroethyl, 1-fluoroisopropyl, 1,1- 30

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difluoroisopropyl, 1,1,1-trifluoroisopropyl, 1,1,1,2-tetrafluoro-isopropyl, pentafluoroisopropyl, hexafluoroisopropyl, and the like.

5 The  $-C_2H_3$  group represents a vinyl group. The  $-C_2H$  group represents an ethynyl group. The  $-N_3$  group represents an azide group.

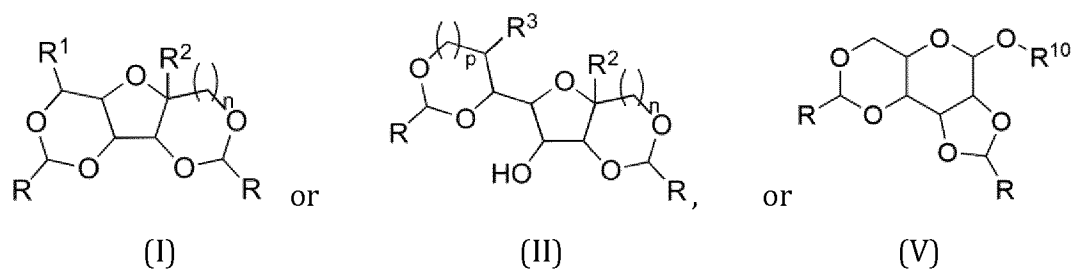
10 For chemical moieties, such as alkyl moieties or aromatic or aliphatic moieties, which are substituted, one of the hydrogen atoms in the moiety is replaced by the substituent. For example, a  $-C_6H_4-$  moiety that is substituted with a methyl group, corresponds to a  $-C_6H_3(CH_3)-$  moiety.

15 Surprisingly, it has been found that using a simple synthetic protocol, it is possible to prepare a polymerizable monomer from renewable resources such as biomass. By using established acetalization chemistry, the compounds reported herein can be obtained. Depending on the additional functional group connected to the aldehyde, monomers with different functionalities can be obtained. In the alternative, acetalization can be conducted using an aldehyde with the functional group that can be easily transformed into other functional groups including, but not limited to, vinyl, alcohol, amine, and azide groups. Accordingly, polyesters, polyamides, or other types of polymers can be prepared from the compounds reported herein. Without wishing to be bound by scientific theory, the fused rings in the structures (I), (II) and (V) are believed to provide polymers prepared from the compounds described herein with good thermal and/or mechanical properties. These properties are found in PET and PEF, which are made from terephthalic acid and furandicarboxylic acid. Thus, the present invention provides for the first-time monomers from renewable resources using biodegradable carbohydrates, which can be manufactured in a simple process directly from biomass.

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30 The invention also provides for a method for the preparation of the compound according to the invention or a composition comprising at least two different compounds according to the invention, having one of the structures (I), (II) or (V)

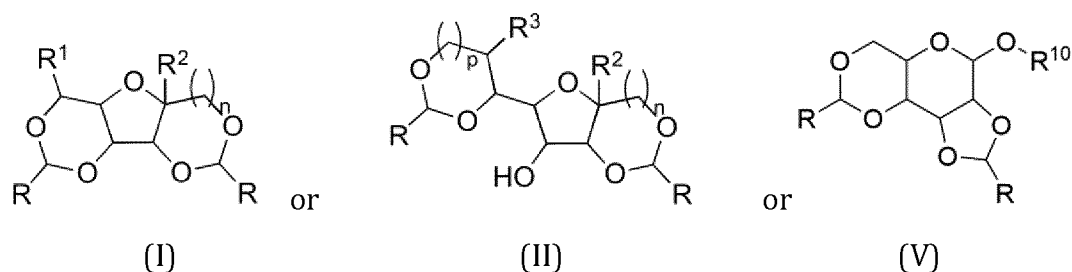


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wherein

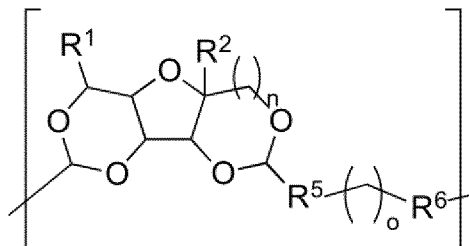
- 5 R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined herein, comprising the steps of
- providing a carbohydrate or a lignocellulose-containing composition;
  - adding an aldehyde optionally comprising at least one functional group selected from the group consisting of carboxylic acid, carboxylic amide, ether, alkyne, alkene, aldehyde, chloride, hydroxyl, and azide, carboxylic acid ester,
  - 10 aldehyde, vinyl, and amine to the carbohydrate or to the lignocellulose-containing composition to obtain a mixture;
  - heating the mixture under acidic conditions and
  - separating, in particular isolating, the compound according to the invention or the composition comprising at least two different compounds
  - 15 according to the invention, having one of the structures (I), (II) or (V)

wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined herein.

- 20 Preferably, said at least one functional group is selected from the group consisting of carboxylic acid, carboxylic amide, ether, aldehyde, chloride, and hydroxyl.

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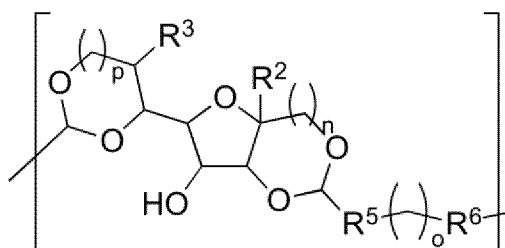
The invention also provides for a polymer comprising as repeat unit



(III)

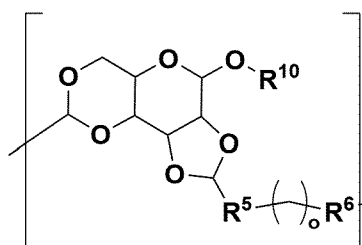
5

and/or



(IV)

and/or



(VI)

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wherein

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined herein; and

R<sup>5</sup> is -Z-F<sup>1</sup>- or Y<sup>1</sup> and R<sup>6</sup> is -F<sup>2</sup>-Z- or Y<sup>1</sup>, wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and wherein F<sup>1</sup> is -C(=O)O-, -OC(=O)-, -C(=O)NR<sup>8</sup>-, -R<sup>8</sup>NC(=O)-, or a covalent bond, and F<sup>2</sup> is -OC(=O)-, -C(=O)O-, -R<sup>8</sup>NC(=O)-, -C(=O)NR<sup>8</sup>-, or a covalent bond;

wherein R<sup>8</sup> is H or a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and

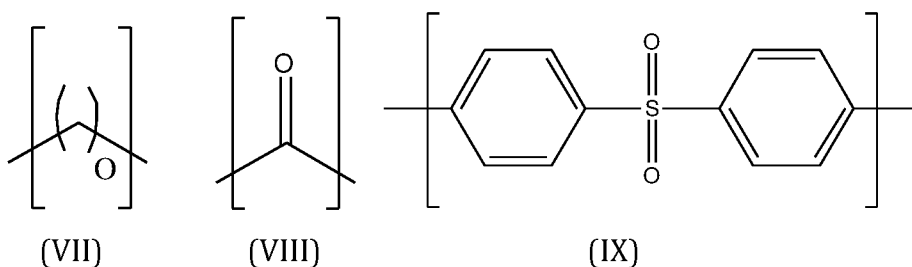
o is an integer from 2 to 10, in particular from 2 to 4; and

Y<sup>1</sup> is a linear, branched or cyclic organic residue having 1 to 20 carbon atoms with the proviso that if R<sup>5</sup> and R<sup>6</sup> are Y<sup>1</sup> and n is 0 at least one of R<sup>1</sup> or R<sup>2</sup> is different from hydrogen.

5

The invention also provides for a method for the preparation of a polymer according to the invention, wherein at least one compound according to the invention is subjected to a reaction, optionally with a compound with the formula R<sup>9</sup>-L-R<sup>9A</sup>, wherein

10 L is selected from the group consisting of (CH<sub>2</sub>)<sub>o</sub> (VII), CO (VIII) and diphenyl sulfone (IX)



R<sup>9</sup> and R<sup>9A</sup> are independently selected from the group consisting of -OR<sup>11</sup>, -OH, -NR<sup>8</sup>,  
15 COOH, COOR<sup>4</sup> and a halogen atom;

wherein R<sup>11</sup> is selected from the group consisting of aryl and alkyl or R<sup>11</sup> of residue R<sup>9</sup> and R<sup>11</sup> of residue R<sup>9A</sup> form together a ring system;

wherein the halogen atom is selected from the group consisting of fluorine, chlorine, bromine and iodine; and

20 wherein R<sup>4</sup>, R<sup>8</sup> and o are as defined herein.

Lastly, the invention also provides for the use of the polymer according to the invention for the manufacture of sheets, fibers or molded objects, in particular as a replacement for poly(ethylene terephthalate).

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Fig. 1 shows a 2D HSQC NMR spectrum of dimethylglyoxylate xylose (DMGX) isomers in DMSO-d<sub>6</sub>.

Fig. 2 shows a  $^{13}\text{C}$  NMR spectrum of DMGX isomers in DMSO-d<sub>6</sub>.

Fig. 3 shows a gas chromatography chromatogram (GC) of purified DMGX isomers.

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Fig. 4 shows a mass spectrum (MS) and fragmentation of DMGX isomers from GC-MS.

10

Fig. 5 shows a 2D HSQC NMR spectrum of poly(ethylene dimethylglyoxylate xylose) (PEDMGX).

Fig. 6 shows a reflector positive MALDI spectrum of PEDMGX.

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Fig. 7 shows a GPC chromatograms of three PEDMGX samples synthesized at various temperatures and durations.

Fig. 8 shows a differential scanning calorimetry (DSC) curve of PEDMGX heating from 30°C to 250°C and cooling back down to 30°C.

20

Fig. 9 shows a thermogravimetric analysis (TGA) curve of PEGDMX.

## PREFERRED EMBODIMENTS

### The Compound according to the Invention

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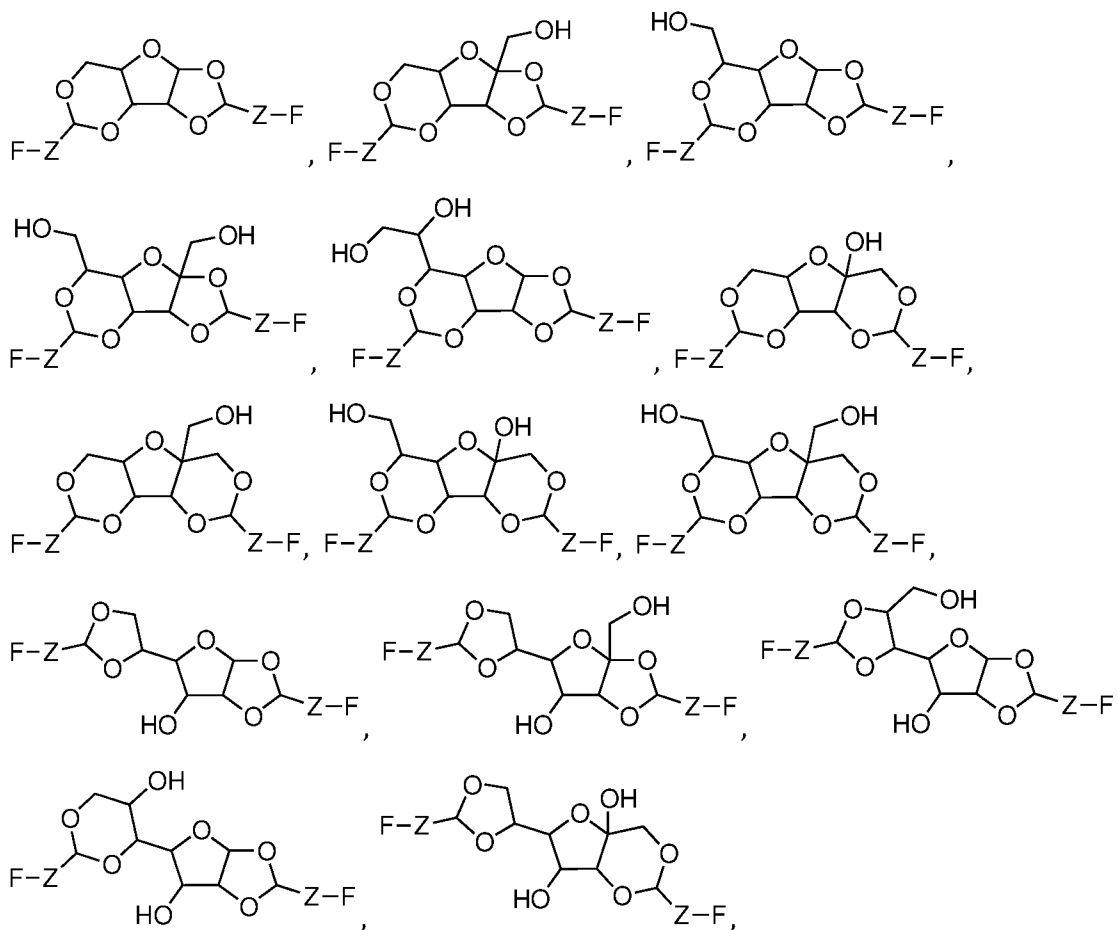
The structures (I), (II) and (V) are preferably obtained from carbohydrates such as aldoses or ketoses by reaction with an aldehyde. The skilled person is aware about the implications this has on the stereochemistry of the compounds and polymers reported herein.

30

The residues R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>10</sup> particularly differ depending on the type of carbohydrate from which the structures (I), (II) or (V) have been obtained. If the structures (I), (II) or (V) have been obtained from aldoses, R<sup>1</sup> may be -H, -CH<sub>2</sub>OH or -CH(OH)CH<sub>2</sub>OH, R<sup>2</sup> may be -H, and R<sup>3</sup> may be -H, -OH, or -CH<sub>2</sub>OH. If the structures (I), (II) or (V) have been obtained from ketoses, R<sup>1</sup> may be -H or -CH<sub>2</sub>OH, R<sup>2</sup> may be -OH or -CH<sub>2</sub>OH, and R<sup>3</sup> may be -H.

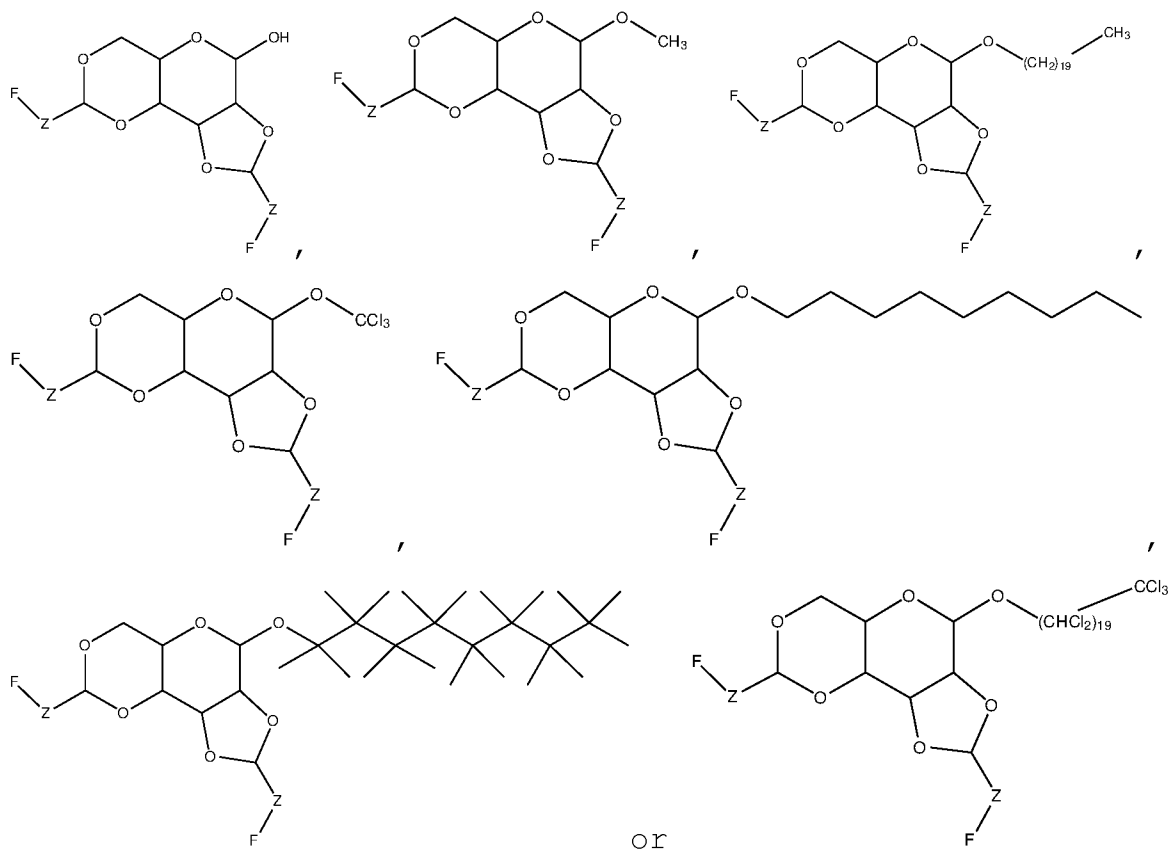
Accordingly, the compound according to the invention may preferably have one of the following structures:

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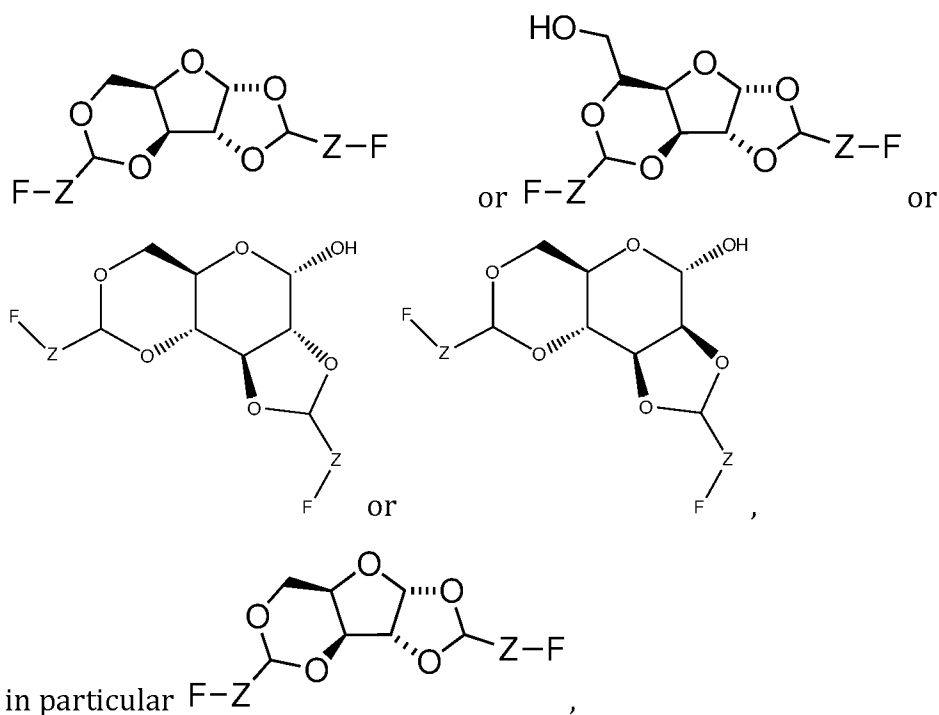
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- 12 -



- 5 wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group.
- 10 More preferably, the compound according to the invention has the structure

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- 5 wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group.

10

Z is preferably -(CH<sub>2</sub>)<sub>m</sub>-, wherein m is an integer from 0 to 10, in particular from 0 to 4; -C<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or -C<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups. F is preferably -COOH, -COOR<sup>4</sup>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, or -N<sub>3</sub>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group.

15

Preferably, R<sup>2</sup> is -H. More preferably, R<sup>2</sup> is H, R<sup>1</sup> is H or CH<sub>2</sub>OH, and R<sup>3</sup> is -H.

In the structures (I) and (II), n is preferably 0. This is particularly the case when the structures (I) or (II) have been obtained from aldoses.

20

Preferably, the compound has the structure (I). Compounds with the structure (I) are rigid monomers that impart good thermal and/or mechanical properties to the polymer.

- 5 Very good results have been obtained when the compound has the structure (I), R<sup>2</sup> is H and R<sup>1</sup> is H or CH<sub>2</sub>OH, in particular R<sup>1</sup> is H.

In the structures (I), (II) and (V), R may comprise a hydrocarbon moiety and a functional group. Advantageously, the hydrocarbon moiety is an alkylene moiety with  
 10 0 to 10, preferably 0 to 4, carbon atoms. The hydrocarbon moiety may also be an aromatic ring system with 5 to 10, preferably 6, carbon atoms. The hydrocarbon moiety may also be a cyclic aliphatic ring system with 5 to 10, preferably 6, carbon atoms. The functional group that may be comprised in R may be selected from the group consisting of -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -NH<sub>2</sub>, -  
 15 C<sub>2</sub>H, -N<sub>3</sub>, -NHR<sup>7</sup>, -OH, and -CH(CH<sub>2</sub>OH)<sub>2</sub>, preferably from the group consisting of -COOH, -COOR<sup>4</sup>, -NH<sub>2</sub>, -NHR<sup>7</sup>, and -OH, more preferably from the group consisting of -COOH and -COOR<sup>4</sup>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group. R may also consist of one of the aforementioned functional groups.

20 As described, in the structures (I), (II) and (V), R is -Z-F, wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group

25

According to an embodiment of the invention, in the structures (I), (II) and (V), R is preferably

30 -(CH<sub>2</sub>)<sub>m</sub>COOH; -C<sub>6</sub>H<sub>4</sub>COOH, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>COOH, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(COOH)<sub>2</sub>; -(CH<sub>2</sub>)<sub>m</sub>COOR<sup>4</sup>; -C<sub>6</sub>H<sub>4</sub>COOR<sup>4</sup>, wherein the aromatic ring is optionally substituted with



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1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>COOR<sup>4</sup>, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(COOR<sup>4</sup>)<sub>2</sub>;  
 -(CH<sub>2</sub>)<sub>m</sub>CHO; -C<sub>6</sub>H<sub>4</sub>CHO, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>CHO, wherein the aliphatic ring is  
 5 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(CHO)<sub>2</sub>;  
 -(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H<sub>3</sub>; -C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>3</sub>, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>C<sub>2</sub>H<sub>3</sub>, wherein the aliphatic ring is  
 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(C<sub>2</sub>H<sub>3</sub>)<sub>2</sub>;  
 -(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H; -C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H, wherein the aromatic ring is optionally substituted with 1 to 4  
 10 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>C<sub>2</sub>H, wherein the aliphatic ring is  
 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;  
 -(CH<sub>2</sub>)<sub>m</sub>N<sub>3</sub>; -C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>, wherein the aromatic ring is optionally substituted with 1 to 4  
 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>, wherein the aliphatic ring is  
 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;  
 15 -(CH<sub>2</sub>)<sub>m</sub>NH<sub>2</sub>; -C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, wherein the aromatic ring is optionally substituted with 1 to 4  
 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>NH<sub>2</sub>, wherein the aliphatic ring is  
 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(NH<sub>2</sub>)<sub>2</sub>;  
 -(CH<sub>2</sub>)<sub>m</sub>NHR<sup>7</sup>; -C<sub>6</sub>H<sub>4</sub>NHR<sup>7</sup>, wherein the aromatic ring is optionally substituted with 1  
 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>NHR<sup>7</sup>, wherein the aliphatic  
 20 ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(NHR<sup>7</sup>)<sub>2</sub>;  
 -(CH<sub>2</sub>)<sub>m</sub>OH; -C<sub>6</sub>H<sub>4</sub>OH, wherein the aromatic ring is optionally substituted with 1 to 4  
 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>OH, wherein the aliphatic ring is  
 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or  
 -(CH<sub>2</sub>)<sub>m</sub>CH(CH<sub>2</sub>OH)<sub>2</sub>,  
 25 wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group;  
 R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and  
 m is an integer from 0 to 10, in particular from 0 to 4.

More preferably, in the structures (I), (II) and (V), R is  
 30 -(CH<sub>2</sub>)<sub>m</sub>COOH; -C<sub>6</sub>H<sub>4</sub>COOH, wherein the aromatic ring is optionally substituted with 1  
 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>COOH, wherein the aliphatic

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ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;  $-(\text{CH}_2)_m\text{CH}(\text{COOH})_2$ ;  
 $-(\text{CH}_2)_m\text{COOR}^4$ ;  $-\text{C}_6\text{H}_4\text{COOR}^4$ , wherein the aromatic ring is optionally substituted with  
 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms;  $-\text{C}_6\text{H}_{10}\text{COOR}^4$ , wherein the aliphatic  
 ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;  $-(\text{CH}_2)_m\text{CH}(\text{COOR}^4)_2$ ,

5 wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and

m is an integer from 0 to 10, in particular from 0 to 4.

Very good results have been obtained when R is  $-(\text{CH}_2)_m\text{COOR}^4$ ;  $-\text{C}_6\text{H}_4\text{COOR}^4$ , wherein  
 10 the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;  $-\text{C}_6\text{H}_{10}\text{COOR}^4$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl  
 groups; or  $-(\text{CH}_2)_m\text{CH}(\text{COOR}^4)_2$ , wherein m is 0 to 4, and R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group.  
 Preferably, R is  $-\text{COOMe}$ .

15 The aforementioned hydrocarbon moieties are normally part of easily accessible  
 aldehydes. In case these aldehydes are not available, the compounds can be obtained  
 by functional group transformations, for example reductive amination or  
 hydroaminations. Further, the aforementioned functional groups of the residues R  
 allow to prepare polymers from the compounds with structures (I) and (II) with good  
 20 thermal and/or mechanical properties. In particular, the thermal and/or mechanical  
 properties can be tailored by choosing particular hydrocarbon moieties such as a  
 cyclic aromatic or aliphatic ring system for more rigid polymers, or an alkylene moiety  
 for more flexible polymers. The aforementioned functional groups provide access to a  
 range of different types of polymers such as polyesters, polyamides, or polyethers.  
 25 Polyesters have the particular advantage that they are very often biodegradable.

According to an embodiment of the invention, R is  $-(\text{CH}_2)_m\text{COOH}$ ,  $-(\text{CH}_2)_m\text{CH}(\text{COOH})_2$ ,  
 $-(\text{CH}_2)_m\text{COOR}^4$ ,  $-(\text{CH}_2)_m\text{CH}(\text{COOR}^4)_2$ ,  $-(\text{CH}_2)_m\text{CHO}$ ,  $-(\text{CH}_2)_m\text{CH}(\text{CHO})_2$ ;  $-(\text{CH}_2)_m\text{C}_2\text{H}_3$ ,  $-\text{C}_6\text{H}_4\text{C}_2\text{H}_3$ ,  
 $-(\text{CH}_2)_m\text{CH}(\text{C}_2\text{H}_3)_2$ ,  $-(\text{CH}_2)_m\text{C}_2\text{H}_4$ ,  $-(\text{CH}_2)_m\text{N}_3$ ,  $-(\text{CH}_2)_m\text{NH}_2$ ,  $-(\text{CH}_2)_m\text{CH}(\text{NH}_2)_2$ ,  $-\text{C}_6\text{H}_4\text{NH}_2$ ,  
 30  $-(\text{CH}_2)_m\text{NHR}^7$ ,  $-(\text{CH}_2)_m\text{OH}$ , or  $-(\text{CH}_2)_m\text{CH}(\text{CH}_2\text{OH})_2$ , wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group,

preferably a -CH<sub>3</sub> group; R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and m is an integer from 0 to 10, preferably from 0 to 4, more preferably 0.

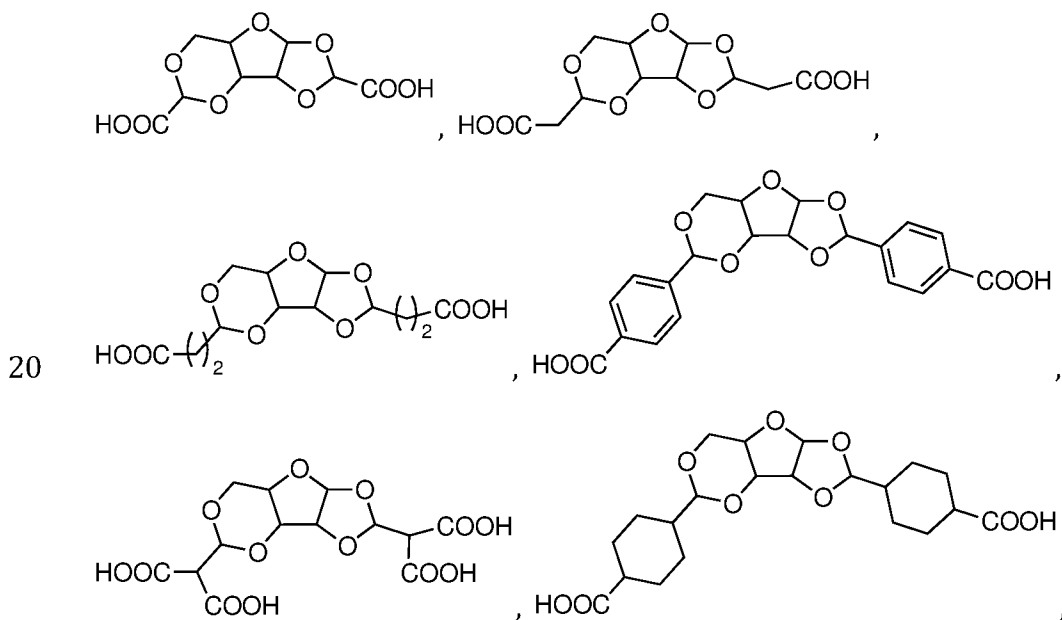
Optimal results have been obtained when the compound has the structure (I), R is -  
 5 (CH<sub>2</sub>)<sub>m</sub>COOH, -(CH<sub>2</sub>)<sub>m</sub>CH(COOH)<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>COOR<sup>4</sup>, -(CH<sub>2</sub>)<sub>m</sub>CH(COOR<sup>4</sup>)<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>CHO, -  
 (CH<sub>2</sub>)<sub>m</sub>CH(CHO)<sub>2</sub>; -(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H<sub>3</sub>, -(CH<sub>2</sub>)<sub>m</sub>CH(C<sub>2</sub>H<sub>3</sub>)<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H, -(CH<sub>2</sub>)<sub>m</sub>N<sub>3</sub>, -  
 (CH<sub>2</sub>)<sub>m</sub>NH<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>CH(NH<sub>2</sub>)<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>NHR<sup>7</sup>, -(CH<sub>2</sub>)<sub>m</sub>OH, or -(CH<sub>2</sub>)<sub>m</sub>CH(CH<sub>2</sub>OH)<sub>2</sub>,  
 wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group, preferably a -CH<sub>3</sub> group; R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group;  
 and m is 0. More preferably, R<sup>2</sup> is H and R<sup>1</sup> is H or CH<sub>2</sub>OH, in particular R<sup>1</sup> is H.

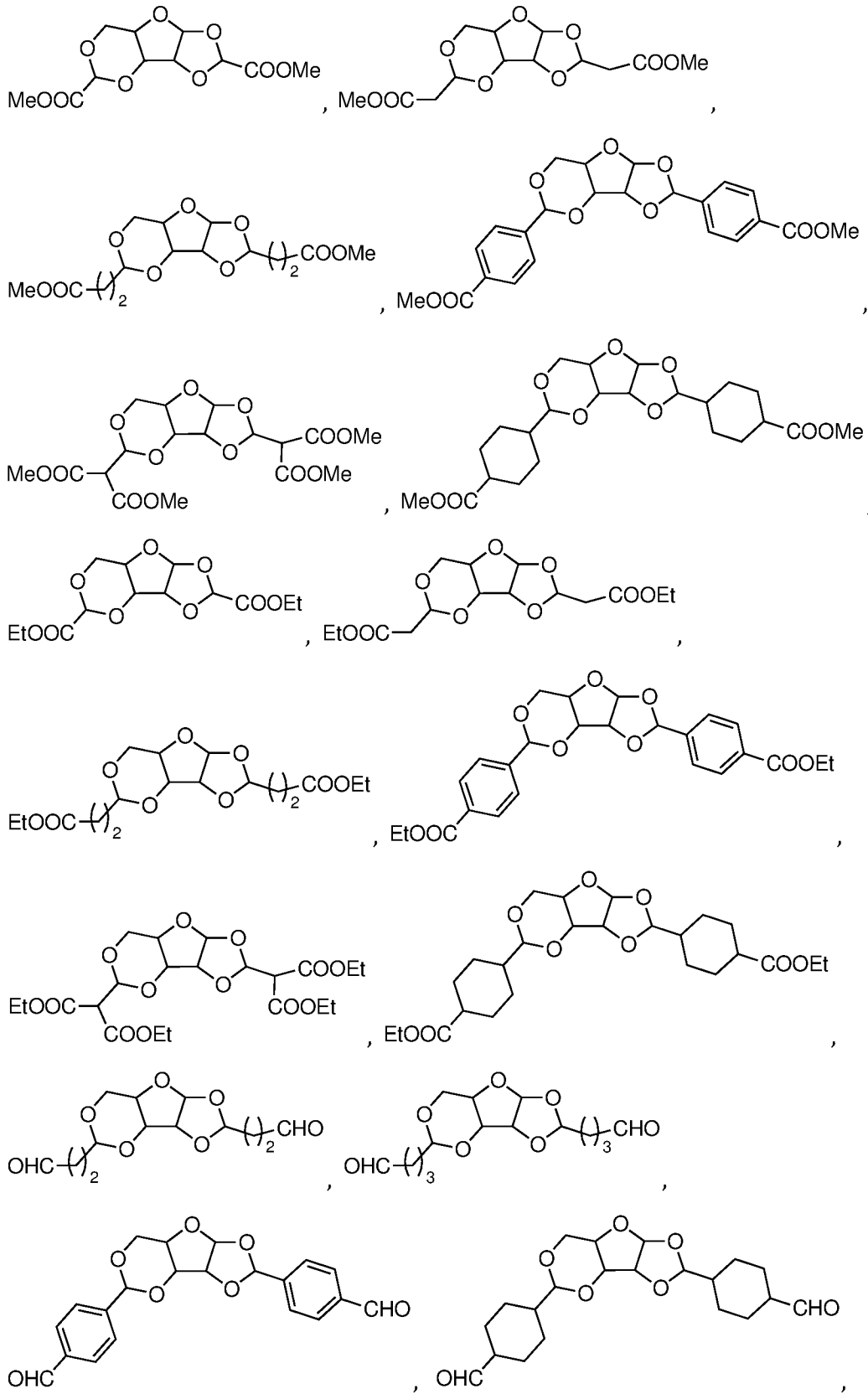
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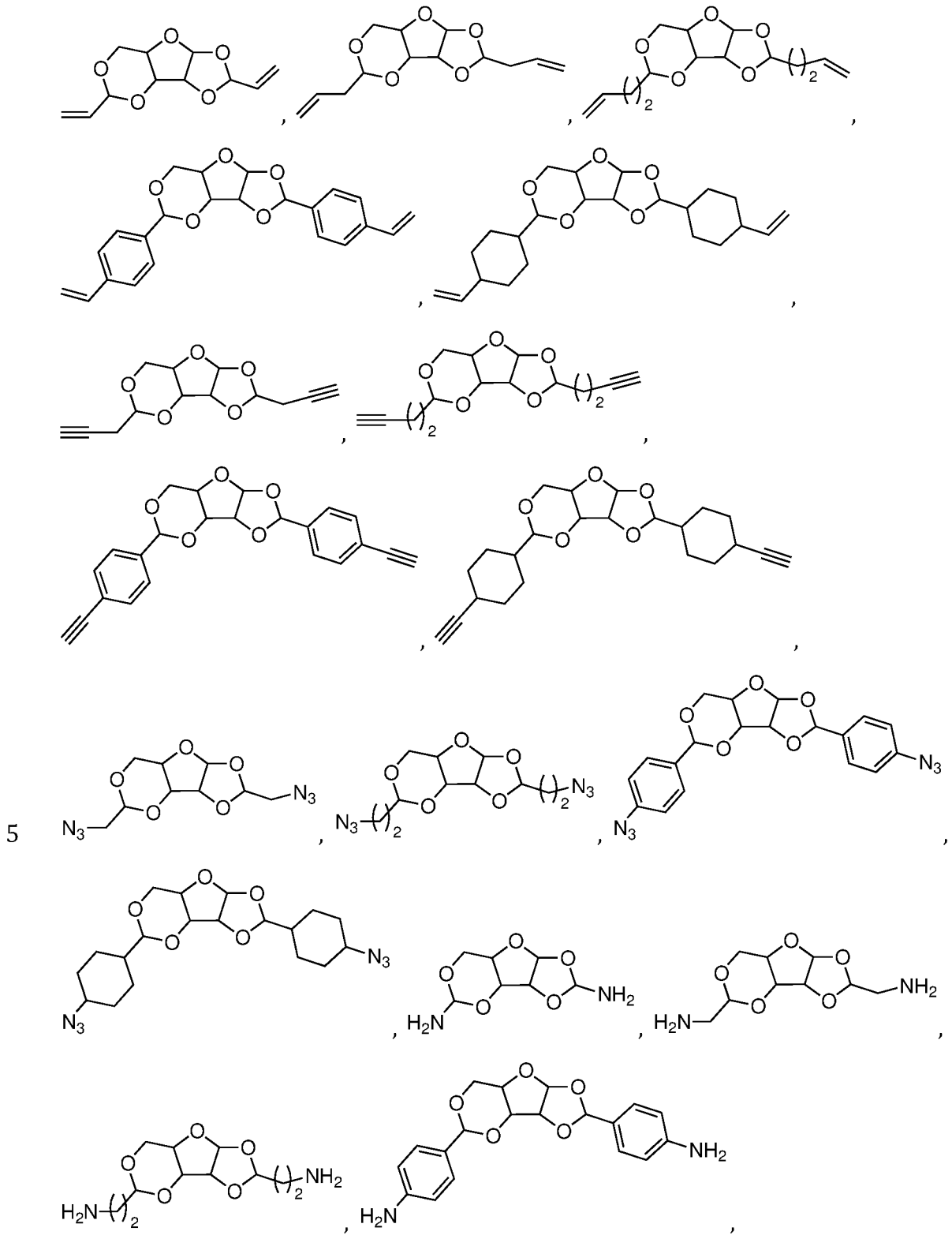
In a preferred embodiment of the invention good results have been obtained when Y is hydrogen or a linear or branched organic residue with 1 to 10 carbon atoms, more preferably 1 to 7 carbon atoms, most preferably 1 to 3 carbon atoms, that is, for example a hydrocarbon moiety such as methylene, ethylene, propylene.

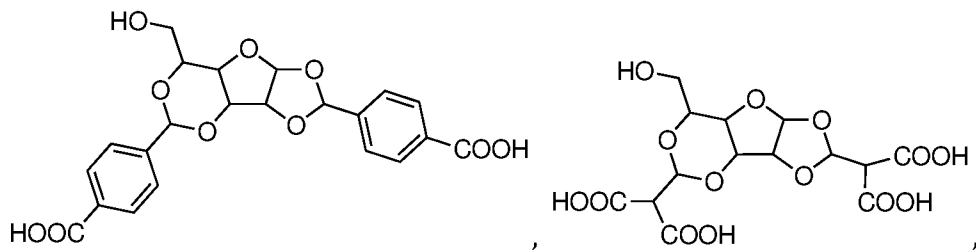
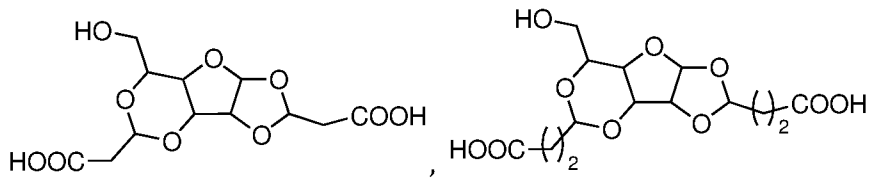
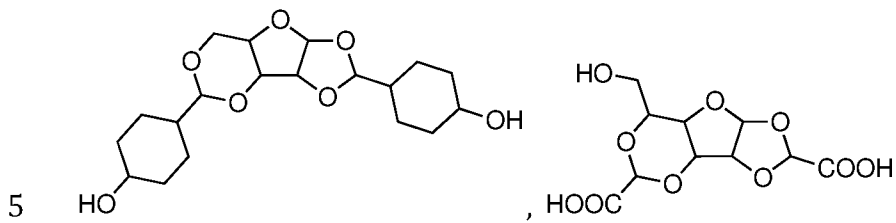
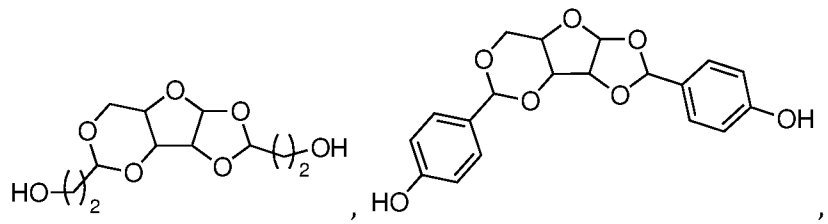
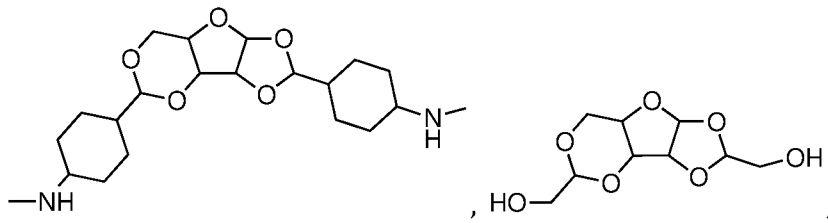
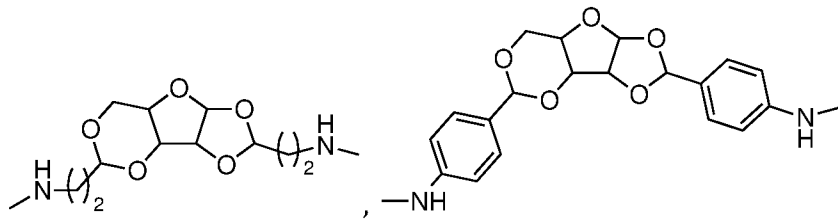
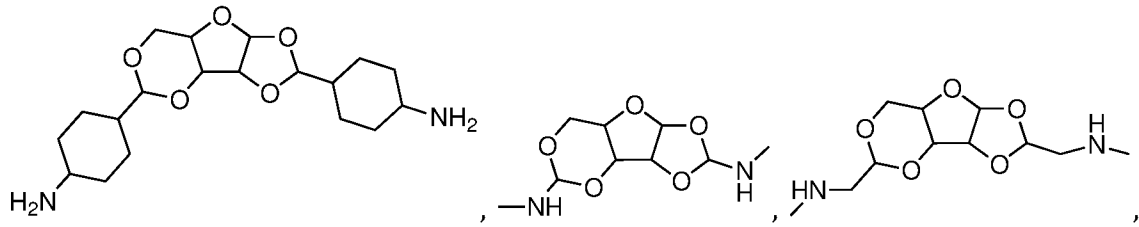
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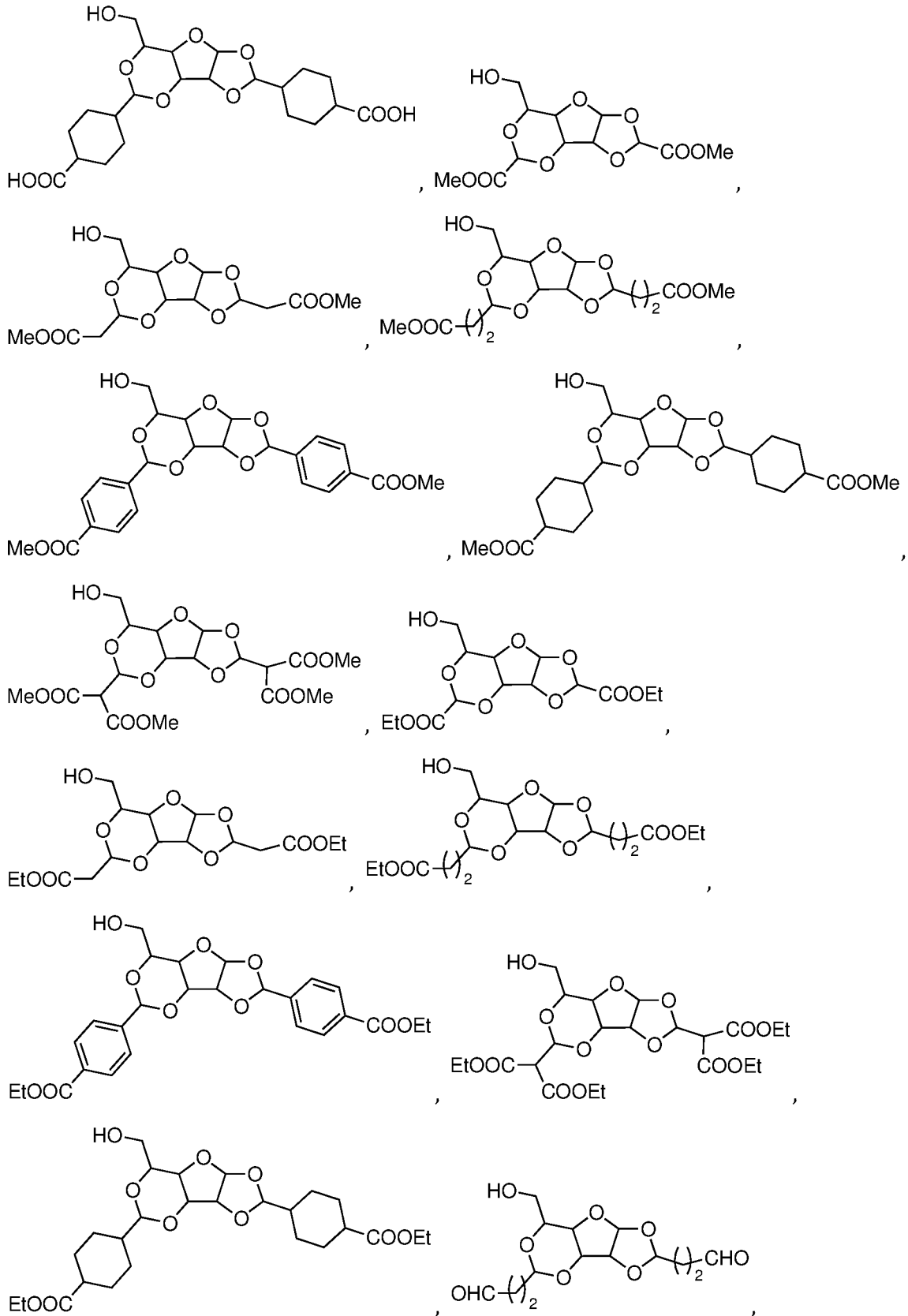
Thus, preferably, the compound according to the invention has one of the following structures:



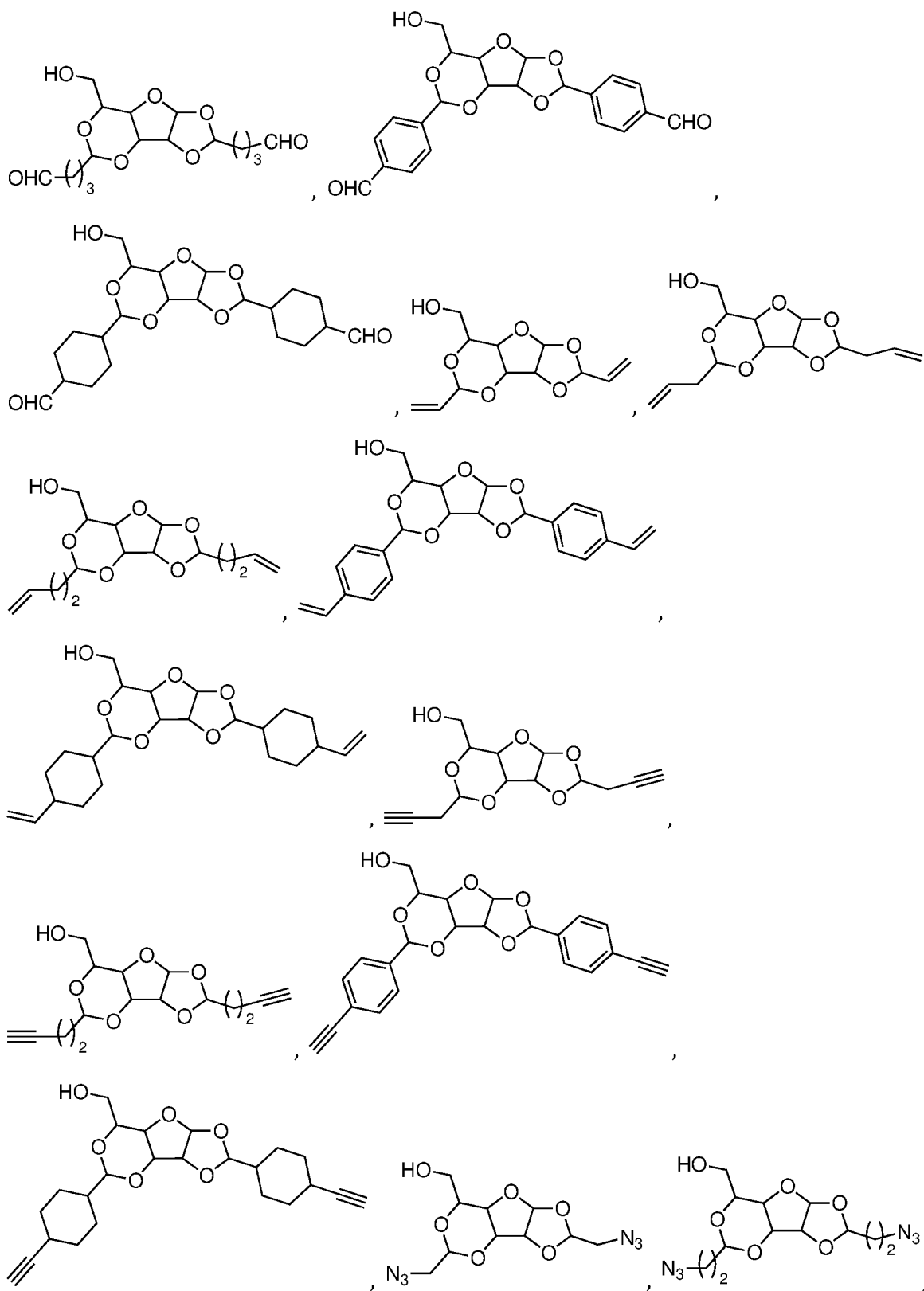




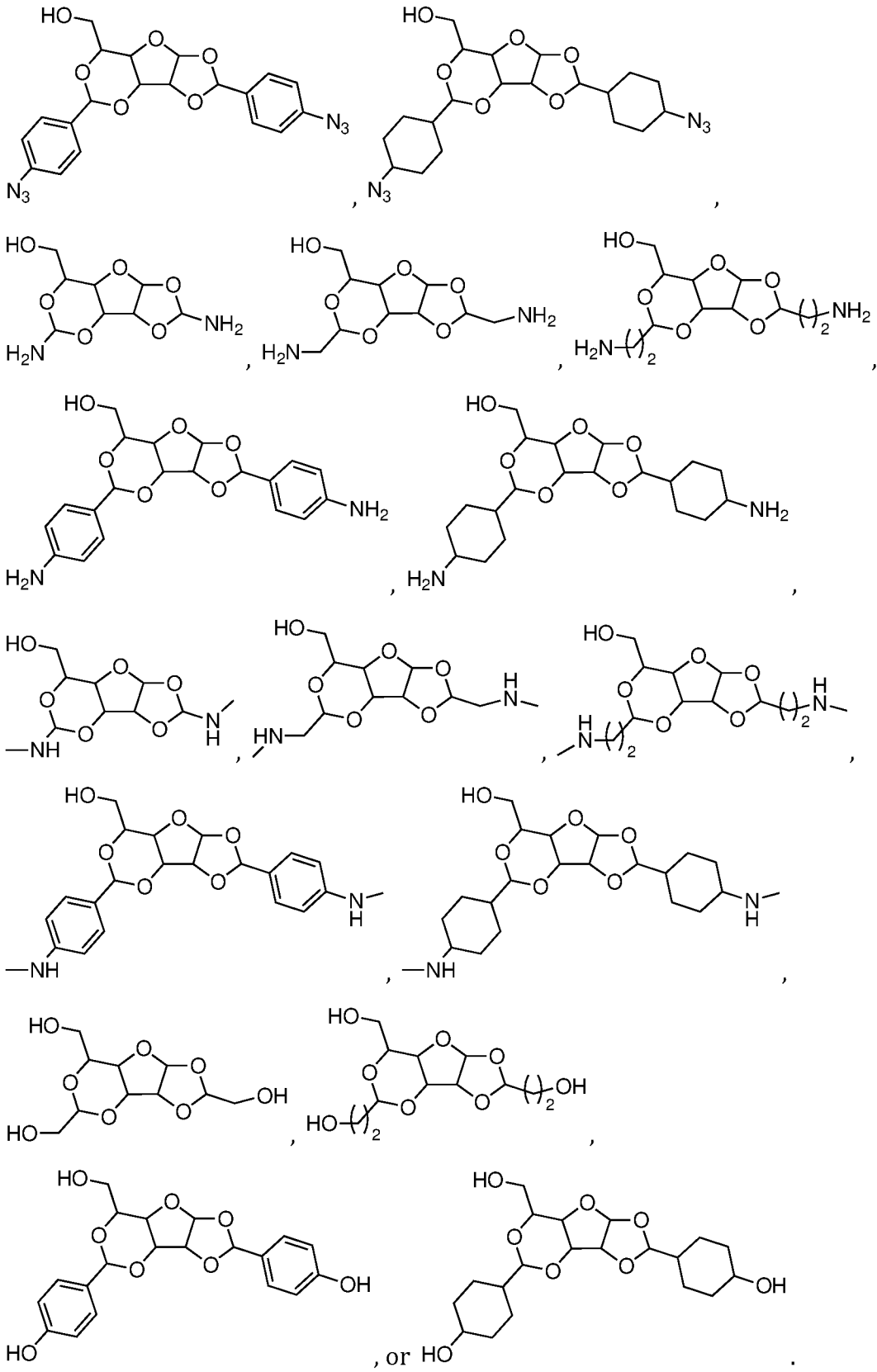


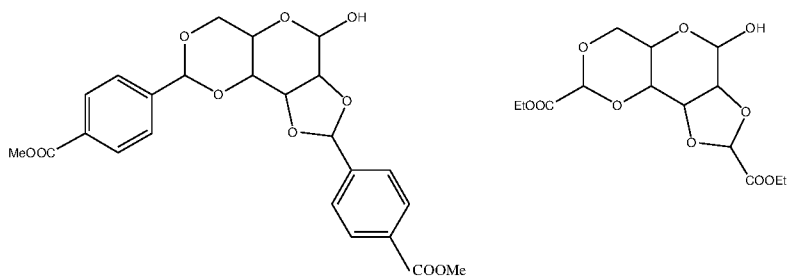
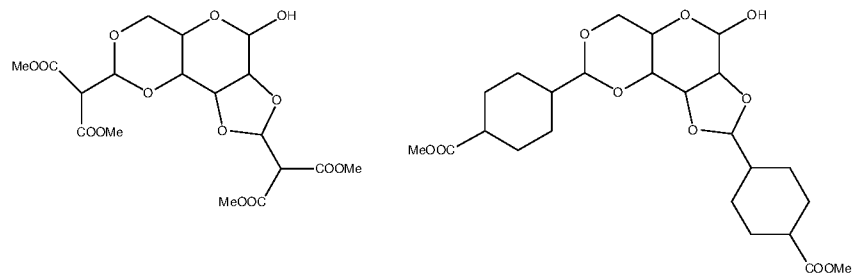
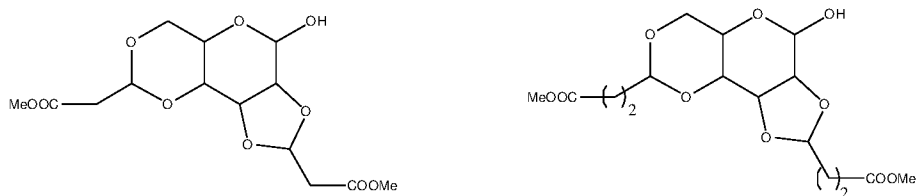
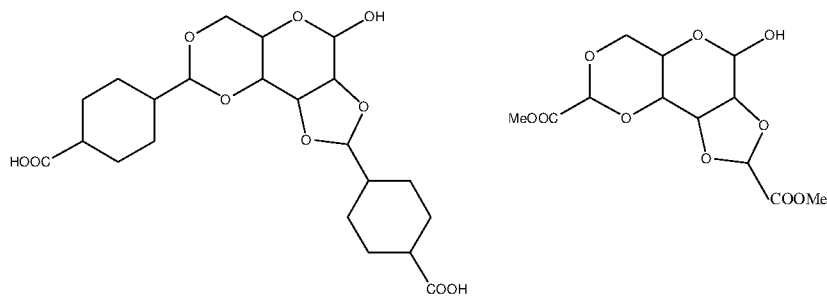
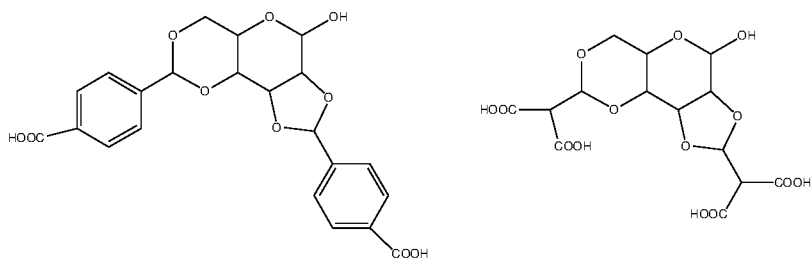
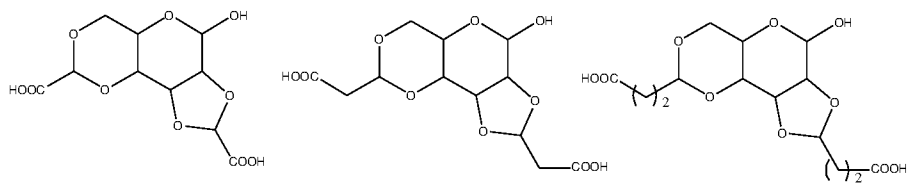


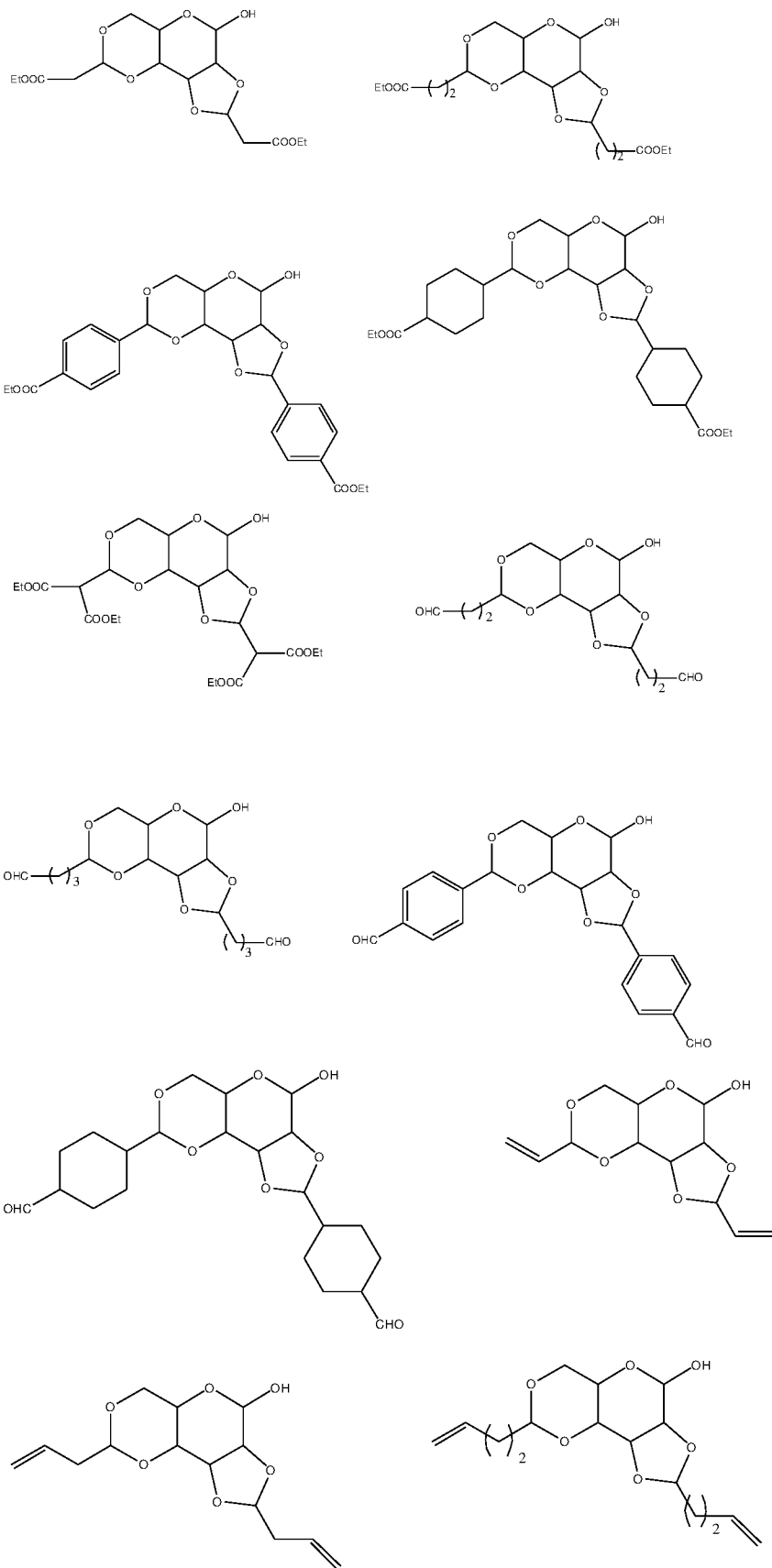
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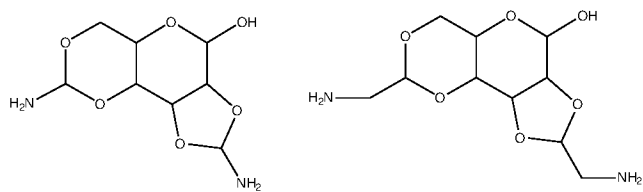
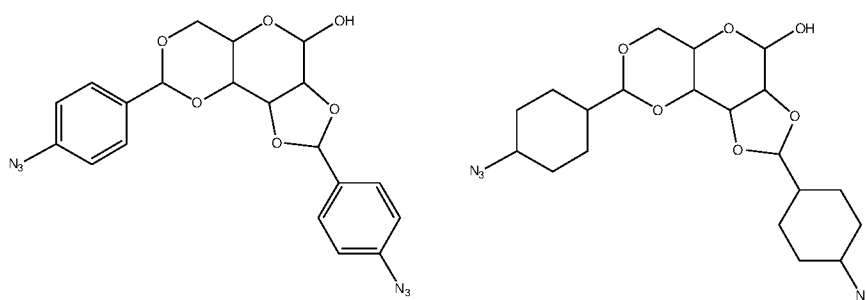
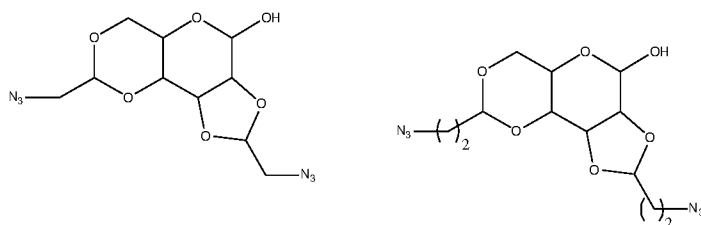
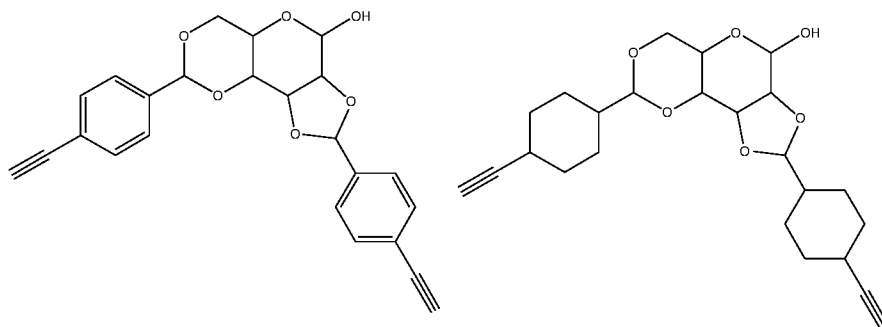
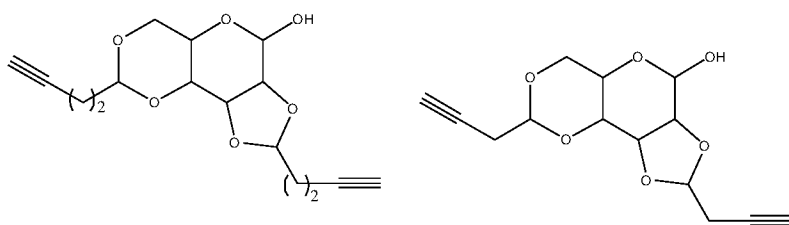
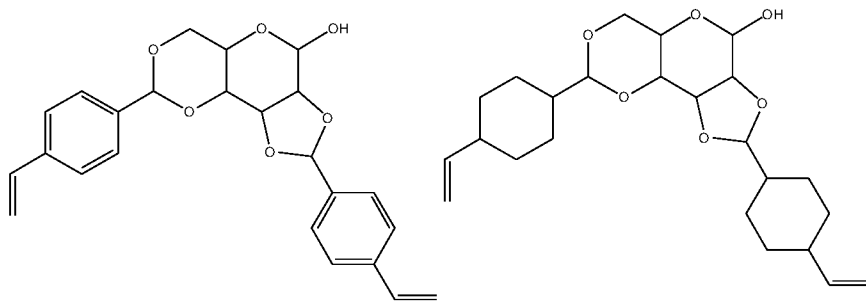


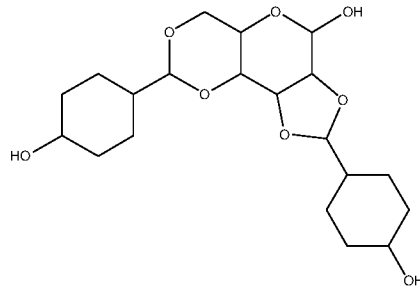
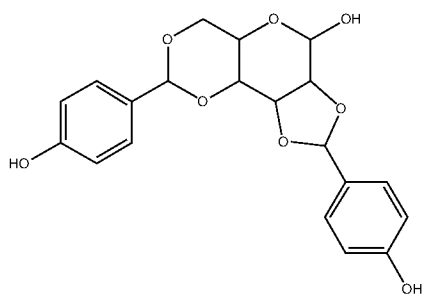
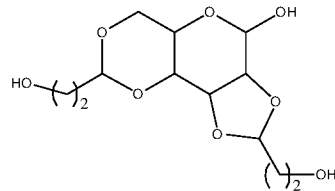
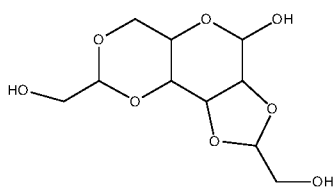
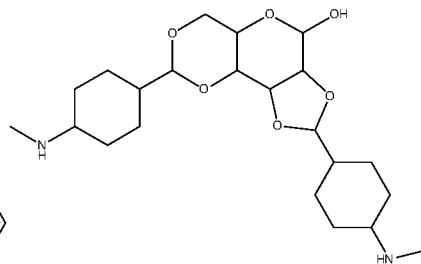
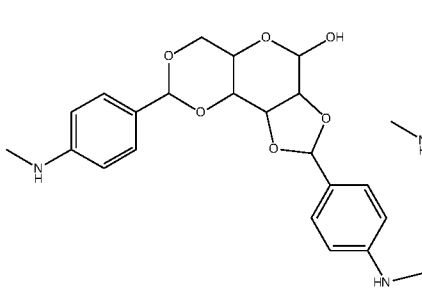
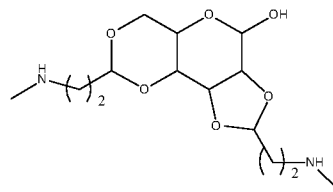
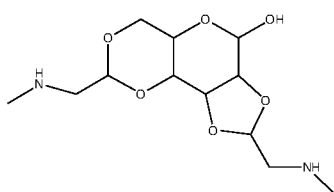
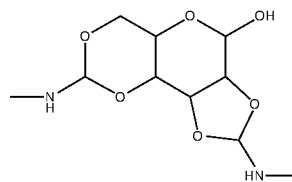
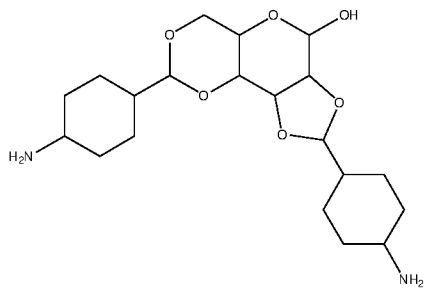
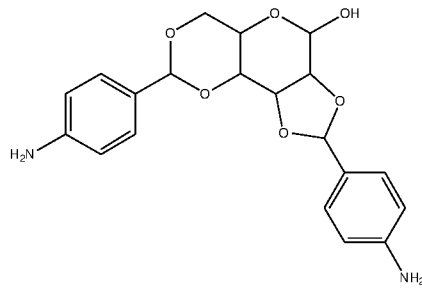
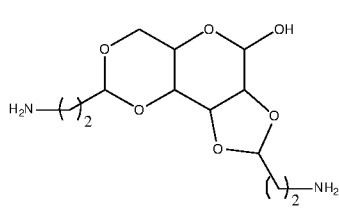




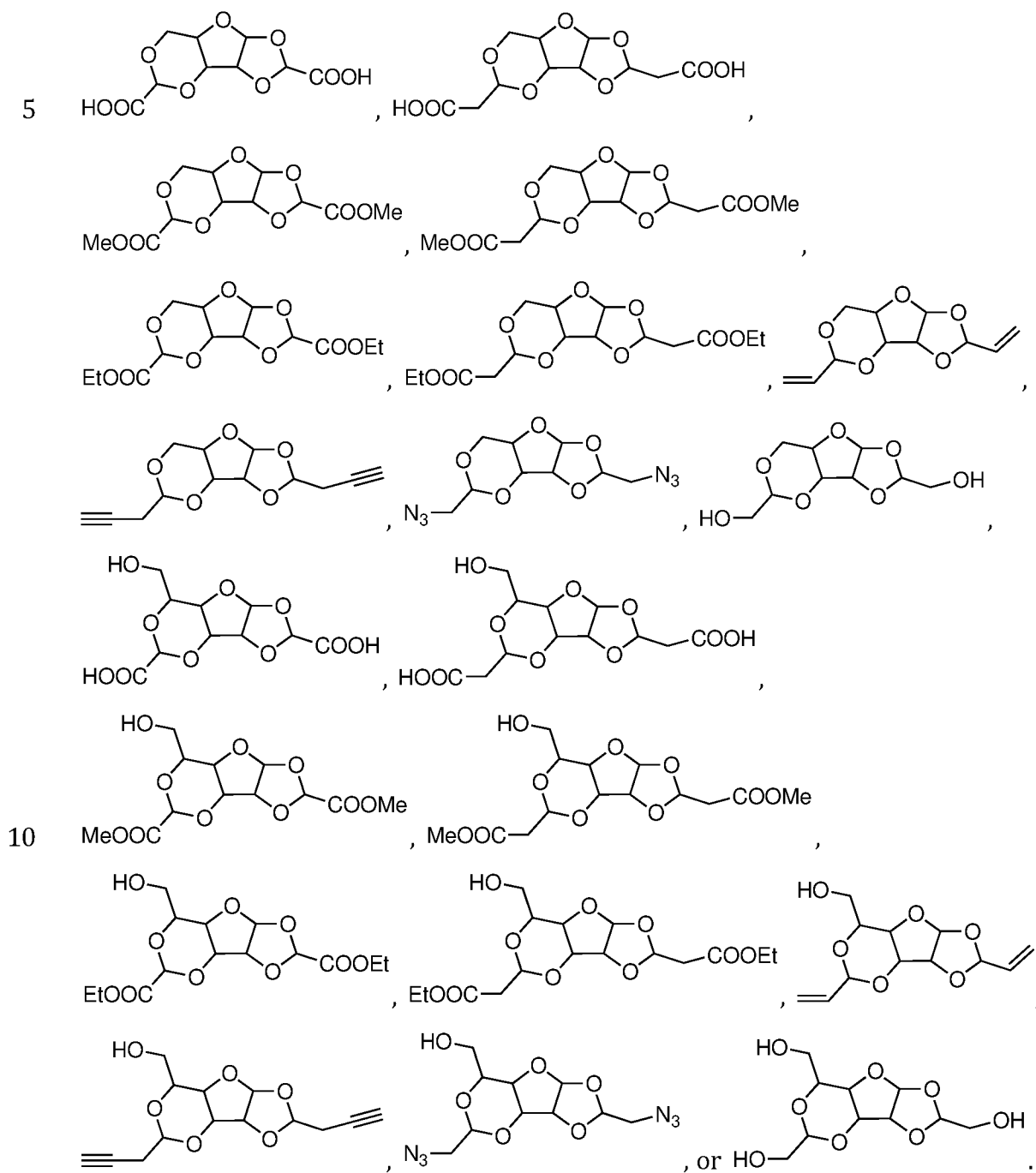




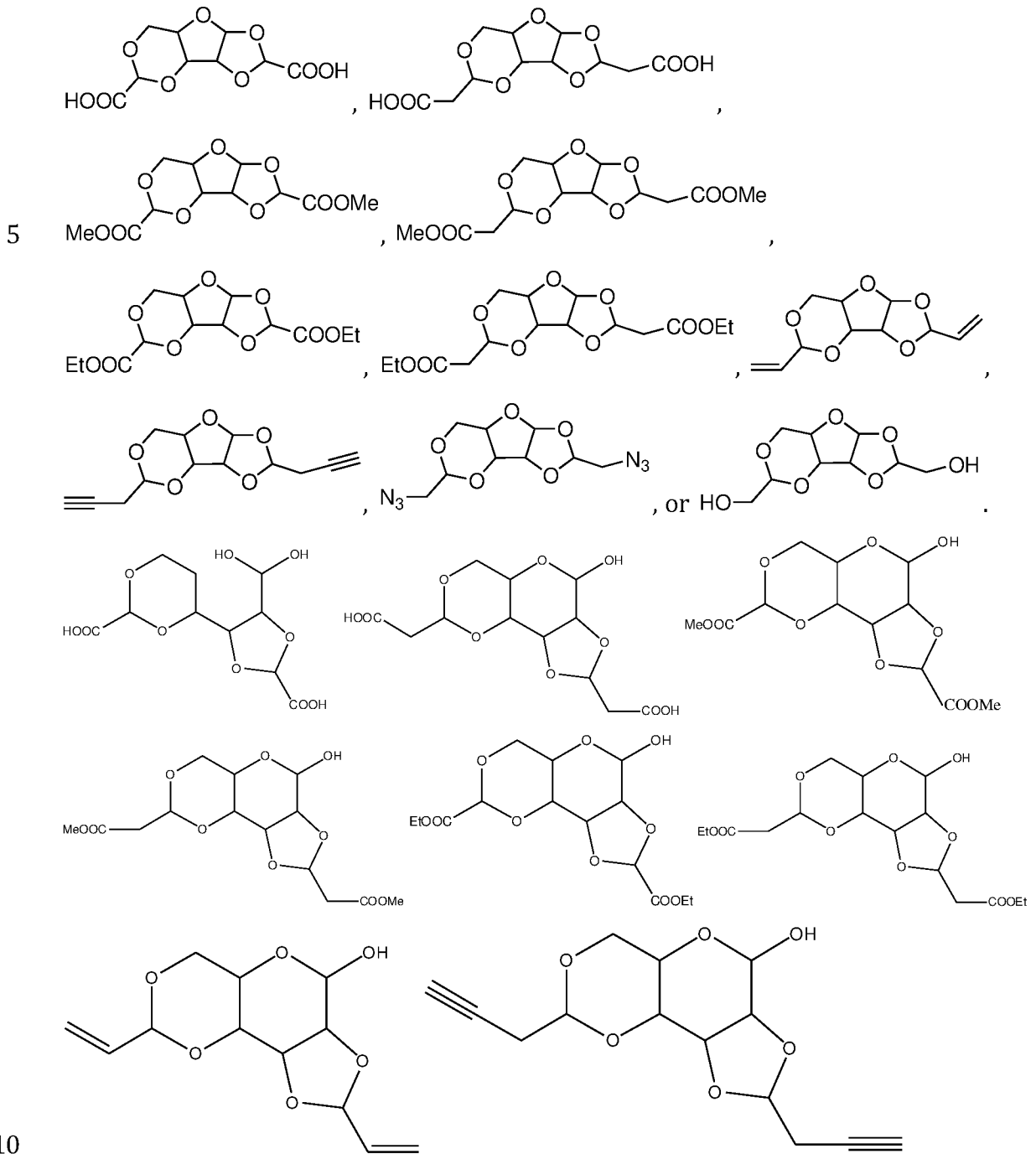




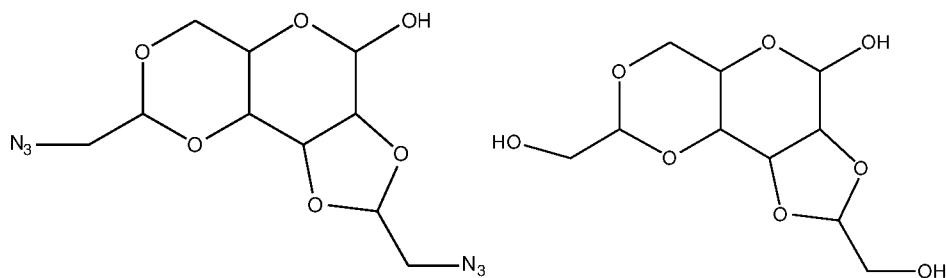
More preferably, the compound according to the invention has one of the following structures:



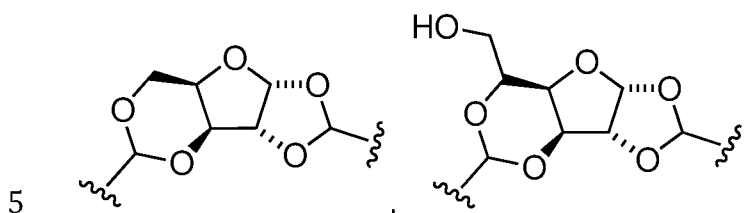
Still more preferably, the compound according to the invention has one of the following structures:



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In the structures shown above, the ring systems preferably have the following stereochemistry:



#### The Method for the Preparation of the Compound

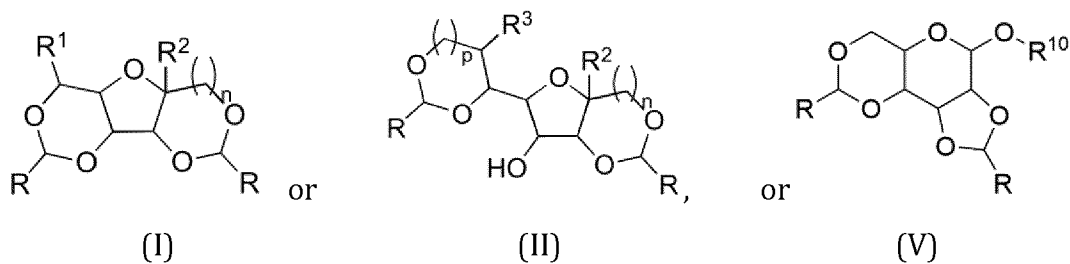
- 10 The invention also provides for a method for the preparation of the compound according to the invention having the structure (I), (II) or (V). The method according to the invention comprises providing a carbohydrate and adding an aldehyde to the carbohydrate. If a mixture of carbohydrates is employed, a mixture of compounds having the structure (I), (II) or (V), in particular a mixture of compounds according to
- 15 the invention having the structure (I), (II) or (V), may be obtained.

Thus, the invention provides for a method for the preparation of a compound according to the invention or a composition comprising at least two different compounds according to the invention, having one of the structures (I), (II) or (V),

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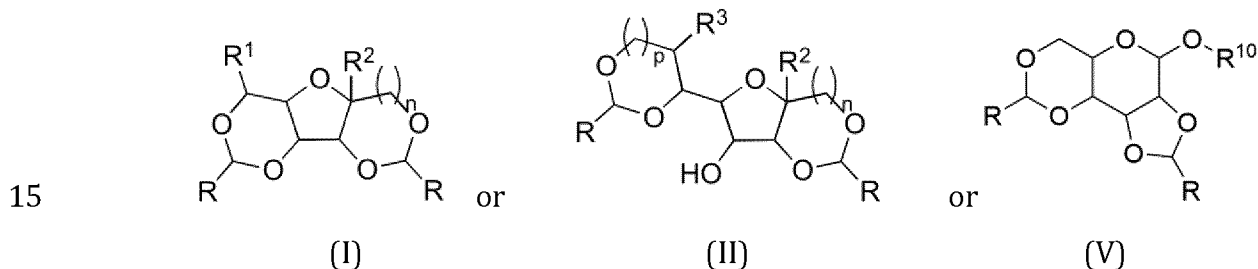
- 31 -



wherein

R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined herein, comprising the steps of

- 5 a. providing a carbohydrate or a lignocellulose-containing composition;
- b. adding an aldehyde optionally comprising at least one functional group selected from the group consisting of carboxylic acid, carboxylic amide, ether, alkyne, alkene, aldehyde, chloride, hydroxyl, azide, carboxylic acid ester, aldehyde, vinyl, and amine to the carbohydrate or to the lignocellulose-
- 10 containing composition to obtain a mixture;
- c. heating the mixture under acidic conditions; and
- d. separating, in particular isolating, the compound according to the invention or the composition comprising at least two different compounds according to the invention, having one of the structures (I), (II) or (V)

wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined herein.

In a preferred embodiment of the invention good results have been obtained when the

20 aldehyde of step b) is selected from a group consisting of acetaldehyde, propionaldehyde, isobutyraldehyde, glyoxylic acid, dialdehyde,

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cyclopropanecarboxaldehyde, isobutyraldehyde, pivaldehyde, tolualdehyde, and benzaldehyde.

Different carbohydrates can be employed as carbohydrates in the method for the preparation of the compound according to the invention. The carbohydrate may be an  
5 aldose or a ketose. The carbohydrate may be a pentose, a hexose, or a heptose. Preferably, the carbohydrate is an aldopentose, an aldohexose, an aldoheptose, a ketohexose, a ketoheptose or a mixture thereof. More preferably, the carbohydrate is an aldopentose, an aldohexose, an aldoheptose, or a mixture thereof, in particular an  
10 aldopentose, an aldohexose, or a mixture thereof.

Advantageously, the carbohydrate is selected from the group consisting of ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, glucoheptose, mannoheptose, psicose, fructose, sorbose, tagatose,  
15 sedoheptulose, mannoheptulose, taloheptulose, alloheptulose, and mixtures thereof. Preferably, the carbohydrate is selected from the group consisting of ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, glucoheptose, mannoheptose, or mixtures thereof, more preferably selected from the group consisting of ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose,  
20 gulose, idose, galactose, or mixtures thereof. Most preferably, the carbohydrate is xylose, glucose, or a mixture thereof.

In the method for the preparation of the compound according to the invention, a lignocellulose-containing composition may be employed.

25 Lignocellulose is considered to be the most abundantly available raw material (biomass) on earth. Lignocellulosic biomass can be classified into virgin biomass, waste biomass and energy crops. Virgin lignocellulosic biomass includes all naturally occurring terrestrial plants such as trees, bushes and grass. Waste lignocellulosic  
30 biomass is produced as a low valuable byproduct of various industrial sectors, such as

agriculture (corn stover, sugarcane bagasse, straw etc.) and forestry (sawmill and paper mill discards).

Lignocellulose comprises hemicellulose, cellulose and lignin. Hemicellulose and  
5 cellulose can both be regarded as carbohydrate polymers. The carbohydrate polymers contain five and six carbon sugar monomers and are bound to lignin.

Lignin can be regarded as an aromatic polymer. Said aromatic polymer contains methoxylated phenyl-propane subunits such as guaiacyl and syringyl subunits.

10

Xylan is a polysaccharide which belongs to the hemicelluloses, wherein the main monomer unit of xylan is D-xylose. Cellulose can be regarded as a polysaccharide, wherein the main monomer unit is D-glucose which is linked via  $\beta$ -1-4 bindings.

15 Preferably, the lignocellulose-containing composition is biomass, in particular, lignocellulosic biomass, preferably virgin lignocellulosic biomass, for example wood. The lignocellulosic biomass is preferably derived from trees, such as birch, beech, poplar, cedars, Douglas firs, cypresses, firs, junipers, kauri, larches, pines, hemlocks, redwoods, spruces, and yews. The most preferred wood is hardwood such as oak,  
20 poplar, maple, eucalyptus, birch and/or beach as lignocellulose-containing composition.

The lignocellulose-containing composition may also be derived from energy crops. Energy crops are crops with high yields of lignocellulosic biomass. In addition, energy  
25 crops are fast growing such that the lignocellulosic biomass is available already within a short period of time for example after a couple of months. Examples of energy crops include giant reed, big bluestem, Chinese tallow, camelina, duckweed, purging nut, millettia pinnata, switchgrass, and elephant grass.

30 According to an embodiment, the lignocellulose-containing composition is derived from corn cobs.

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It is preferred that the lignocellulose-containing composition is solid at a temperature of 23°C. Preferably, the lignocellulose-containing composition is air dried at temperatures  $\leq 60$  °C. For example, the lignocellulose-containing composition is air  
5 dried for storage to remove excessive water. The air-dried lignocellulose-containing composition preferably comprises less than 50 wt.%, more preferably less than 30 wt.%, and in particular from 0 to 10 wt.% water.

The lignocellulose-containing composition may have a lignin content of 1 to 50 wt.%,  
10 preferably 10 to 30 wt.%, based on the total weight of the lignocellulose-containing composition. The lignin is preferably determined as Klason lignin.

For the determination of Klason lignin, the Klason lignin test is applied. In this test, wood particles (0.25 to 0.50 g) are loaded into 50 mL beaker with the addition of 7.5  
15 mL of a 72 wt.% sulfuric acid solution. The mixture is left at room temperature for 2 hours and stirred with a glass rod every 10 minutes. Afterwards the slurry is transferred into a round bottom flask and 290 mL of water are added to reach a sulfuric acid concentration of 3 wt.%. The glass bottle is sealed with the screw cap and sterilized at 120°C for 1 hour in an autoclave. The resulting solution is filtered, and the  
20 precipitate is washed with water, dried at 105°C, and weighed to determine the Klason lignin content.

The content of Klason lignin can be determined by the following equation:

25 Content of Klason lignin [%] =  $KL/LCC \times 100\%$ , wherein

KL is the amount of Klason lignin in g, LCC is the amount of lignocellulose-containing composition in g.

30 Different aldehydes may be used in the method for the preparation of a compound according to the invention. Preferably, the aldehyde has the formula R-CHO, wherein

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R is as defined herein. More preferably, the aldehyde has the formula CHO-(CH<sub>2</sub>)<sub>m</sub>COOH; CHO-C<sub>6</sub>H<sub>4</sub>COOH, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; CHO-C<sub>6</sub>H<sub>10</sub>COOH, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or CHO-(CH<sub>2</sub>)<sub>m</sub>CH(COOH)<sub>2</sub>.

5

The lignocellulose-containing composition may be mixed with a solvent for example ethereal solvent such as dioxane, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, tetrahydrofuran, or  $\gamma$ -valerolactone, glyme, or diglyme.

- 10 To produce the monomers, the mixture containing the substrate (sugars or lignocellulose) and aldehyde may be heated at various temperatures in step c. Advantageously, the mixture is heated at 50 to 120 °C, preferably at 60 to 110 °C, more preferably at 60 to 100 °C, most preferably at 60 to 85 °C. It was found that at temperature below 50 °C, the reaction proceeds very slowly. At all temperatures, the  
15 reaction can be accelerated by the presence of an acid catalyst. At temperatures above 120 °C, it was found that undesired by-products are formed.

Heating of the mixture may also be conducted under various pressures depending on the feedstock. For carbohydrates, the heating is advantageously conducted at a  
20 pressure below 150 mbar. In particular, the reaction may be conducted at a pressure of 70 to 130 mbar, preferably at 80 to 120 mbar, more preferably at 90 to 110 mbar. It was found that the reaction proceeds faster at reduced pressures.

For carbohydrates, very good results are obtained, when the mixture is heated at 50 to  
25 120 °C, preferably at 60 to 110 °C, more preferably at 60 to 100 °C, most preferably at 60 to 85 °C and at a pressure of 70 to 130 mbar, preferably at 80 to 120 mbar, more preferably at 90 to 110 mbar. Under these conditions, water produced in the course of the reaction can be removed from the reaction which aids in obtaining high yields of the desired products and also aids in accelerating the reaction.

30

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According to an embodiment, for biomass, steps a. to c. are advantageously conducted in a solvent that is preferably a polar aprotic solvent, and even more preferably ethereal, most preferably dioxane,  $\gamma$ -valerolactone, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, or tetrahydrofuran. According to this embodiment, steps a. to c. are preferably conducted for 0.5 to 72 hours, more preferably 1 to 24 hours, and most preferably 2 to 4 hours. According to this embodiment, steps a. to c. are advantageously conducted at temperatures of 50 to 120 °C, preferably at 60 to 110 °C, more preferably at 60 to 100 °C, and most preferably at 60 to 85 °C. The cellulose is then preferably removed by filtration from the reaction mixture. Also the solvent is then preferably removed by evaporation at reduced pressure such as 1 mbar to 150 mbar from the reaction mixture. The lignin is then preferably removed by precipitation in a solvent followed by filtration of the precipitation mixture yielding a filtrate solution. The resulting filtrate solution is then preferably concentrated and an acid is added followed by heating and reducing the pressure as described for the carbohydrates above.

Acidic conditions of the mixture may be effected by various means. Advantageously, an acid is added to the mixture. Different acids can be used for this purpose. Examples of suitable acids are sulfuric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, perchloric acid, phosphoric acid, nitric acid, formic acid, acetic acid, trifluoroacetic acid, methanesulfonic acid, and toluenesulfonic acid. The acids are preferably used at a concentration of 0.1 to 1 M, more preferably 0.2 to 0.6 M. Preferably, sulfuric acid is added to the mixture. An acidic aldehyde such as, but not limited to glyoxylic acid can self-catalyze the reaction.

The method for the preparation of the compound according to the invention may comprise additional steps. Advantageously, the method according to the invention comprises the step of adding an alcohol. In particular, an alcohol may be added if the aldehyde comprises a carboxylic acid group, more particularly if the aldehyde has the formula  $\text{CHO}-(\text{CH}_2)_m\text{COOH}$ ;  $\text{CHO}-\text{C}_6\text{H}_4\text{COOH}$ , wherein the aromatic ring is optionally substituted with 1 to 4  $\text{C}_1$ - $\text{C}_4$ -alkyl groups;  $\text{CHO}-\text{C}_6\text{H}_{10}\text{COOH}$ , wherein the aliphatic ring is optionally substituted with 1 to 4  $\text{C}_1$ - $\text{C}_4$ -alkyl groups; or  $\text{CHO}-$

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$(\text{CH}_2)_m\text{CH}(\text{COOH})_2$ , wherein  $m$  is an integer from 0 to 10, preferably from 0 to 4. The alcohol is preferably added after the mixture is heated under acidic conditions.

Preferably, the alcohol is a  $\text{C}_1$ - $\text{C}_4$ -alkylalcohol, more preferably methanol.

- 5 Advantageously, the aldehyde has the formula  $\text{CHO}-(\text{CH}_2)_m\text{COOH}$ ;  $\text{CHO}-\text{C}_6\text{H}_4\text{COOH}$ , wherein the aromatic ring is optionally substituted with 1 to 4  $\text{C}_1$ - $\text{C}_4$ -alkyl groups;  $\text{CHO}-\text{C}_6\text{H}_{10}\text{COOH}$ , wherein the aliphatic ring is optionally substituted with 1 to 4  $\text{C}_1$ - $\text{C}_4$ -alkyl groups; or  $\text{CHO}-(\text{CH}_2)_m\text{CH}(\text{COOH})_2$ , wherein  $m$  is an integer from 0 to 10, preferably from 0 to 4, and wherein the method comprises the additional step of
- 10 adding a  $\text{C}_1$ - $\text{C}_4$ -alkylalcohol, preferably methanol, after step c. and before step d.

The alcohol such as the  $\text{C}_1$ - $\text{C}_4$ -alkylalcohol, preferably methanol, may be added to the mixture at a ratio of 1:1 volume of alcohol to mass of reaction mixture to 20:1 volume of alcohol to mass of reaction mixture, preferably 5:1 volume of alcohol to mass of

15 reaction mixture to 15:1 volume of alcohol to mass of reaction mixture, more preferably 10:1 volume of alcohol to mass of reaction mixture.

The mixture containing the  $\text{C}_1$ - $\text{C}_4$ -alkylalcohol, preferably methanol, may then be heated, preferably to the boiling temperature of the mixture. The heating may be

20 continued for 1 to 10 hours, preferably for 2 to 5 hours, more preferably for 2 to 4 hours.

Step d. may comprise a neutralization step. Neutralization is preferably conducted using a weak base. Examples for suitable weak bases are bicarbonates such as sodium

25 bicarbonate or potassium bicarbonate, preferably as aqueous solutions.

Separating, in particular isolating, of the compound according to the invention or the composition comprising at least two different compounds according to the invention may comprise several steps. Separating may comprise dissolving the compound or the

30 compounds according to the invention with an organic solvent. Separating may also comprise one or more filtration and/or drying steps, preferably before dissolving the

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compound or the compounds according to the invention in an organic solvent. Examples for suitable organic solvents are diethyl ether, tetrahydrofuran, ethyl acetate, glyme, diglyme, dichloromethane, chloroform and tetrachloromethane, in particular diethyl ether, tetrahydrofuran, ethyl acetate, and dichloromethane, more particularly ethyl acetate or dichloromethane. Separating may also comprise one or more washing steps, for example with aqueous solutions such as aqueous sodium bicarbonate solution and/or aqueous sodium chloride solution. Separating may also comprise a purification step, for example distilling. Distilling is preferably conducted as the last purification step. Alternatively, crystallization can be carried out as a final purification step before polymerization. For example, for dimethylglyoxylate xylose, cyclopentylmethyl ether, toluene, or alcohols can be used for crystallization. By carrying out a temperature-controlled crystallization it is even possible to obtain chiral resolution of the isomers.

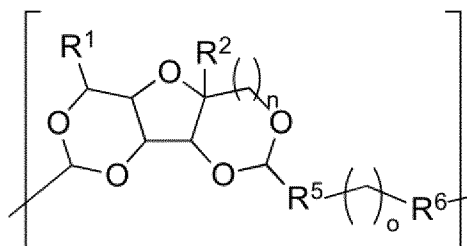
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### The Polymer according to the invention

The compounds according to the invention can be used for the preparation of polymers. For example, the compounds according to the invention can be used as monomers for the preparation of polyesters or polyamides.

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Accordingly, the invention also provides for a polymer comprising as repeat unit



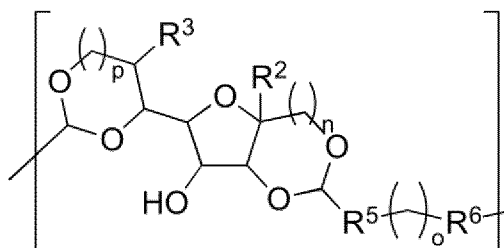
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(III)

and/or

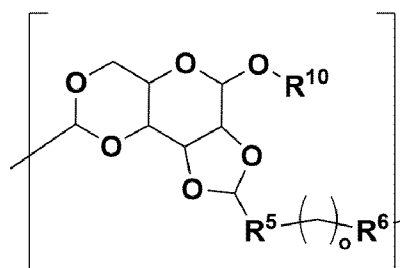


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(IV)

and/or



(VI)

5

wherein

$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^{10}$ ,  $n$ , and  $p$  are as defined herein; and

$R^5$  is  $-Z-F^1-$  and  $R^6$  is  $-F^2-Z-$ , wherein  $Z$  is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4  $C_1$ - $C_4$ -alkyl groups or 1 to 4 halogen atoms, and wherein  $F^1$  is  $-C(=O)O-$ ,  $-OC(=O)-$ ,  $-C(=O)NR^8-$ ,  $-R^8NC(=O)-$ , or a covalent bond,

10

and  $F^2$  is  $-OC(=O)-$ ,  $-C(=O)O-$ ,  $-R^8NC(=O)-$ ,  $-C(=O)NR^8-$ , or a covalent bond;

wherein  $R^8$  is H or a  $C_1$ - $C_4$ -alkyl group; and

$o$  is an integer from 2 to 10, in particular from 2 to 4.

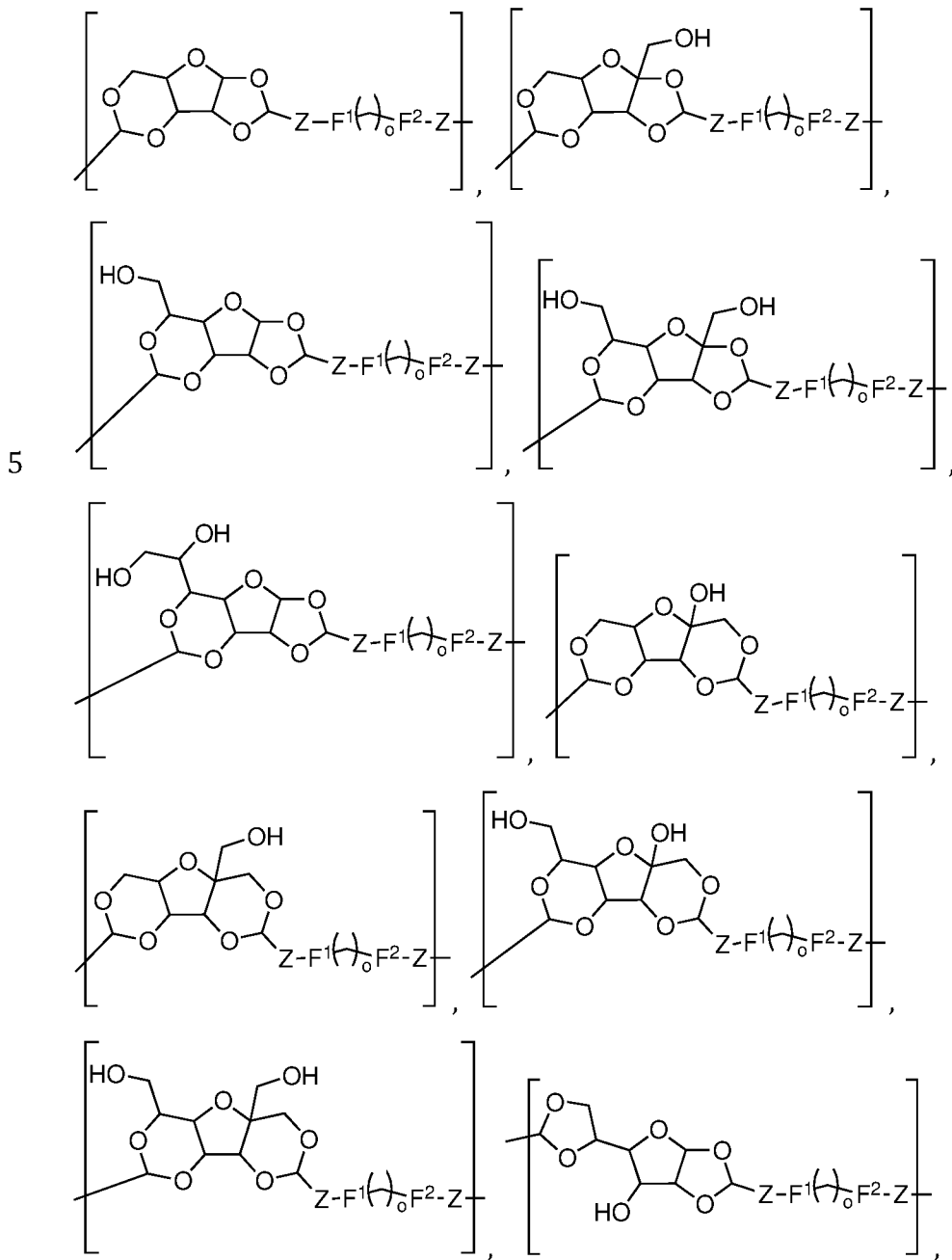
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The residues  $R^1$ ,  $R^2$ , and  $R^3$  differ depending on the type of carbohydrate from which the monomers used in the preparation of the polymer according to the invention have been obtained. If the monomers have been obtained from aldoses,  $R^1$  may be  $-H$ ,  $-CH_2OH$  or  $-CH(OH)CH_2OH$ ,  $R^2$  may be  $-H$ , and  $R^3$  may be  $-H$ ,  $-OH$ , or  $-CH_2OH$ . If the monomers have been obtained from ketoses,  $R^1$  may be  $-H$  or  $-CH_2OH$ ,  $R^2$  may be  $-OH$

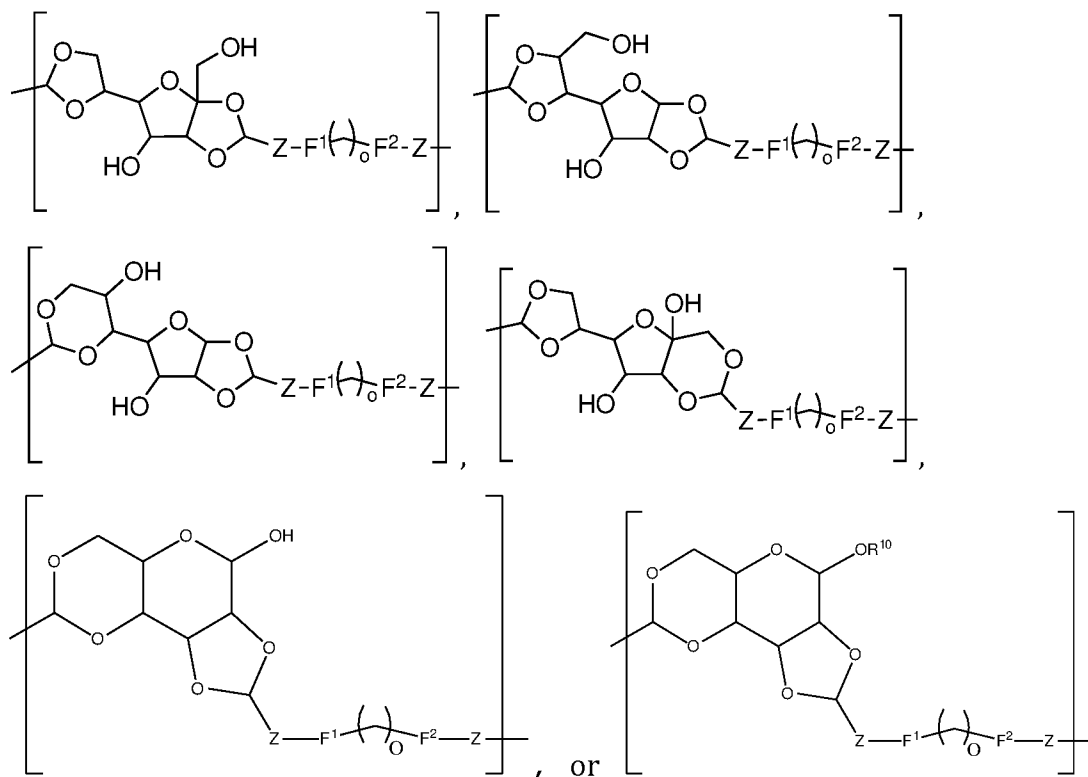
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or  $-CH_2OH$ , and  $R^3$  may be  $-H$ .

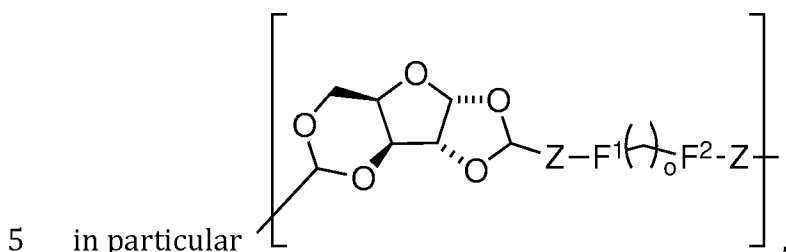
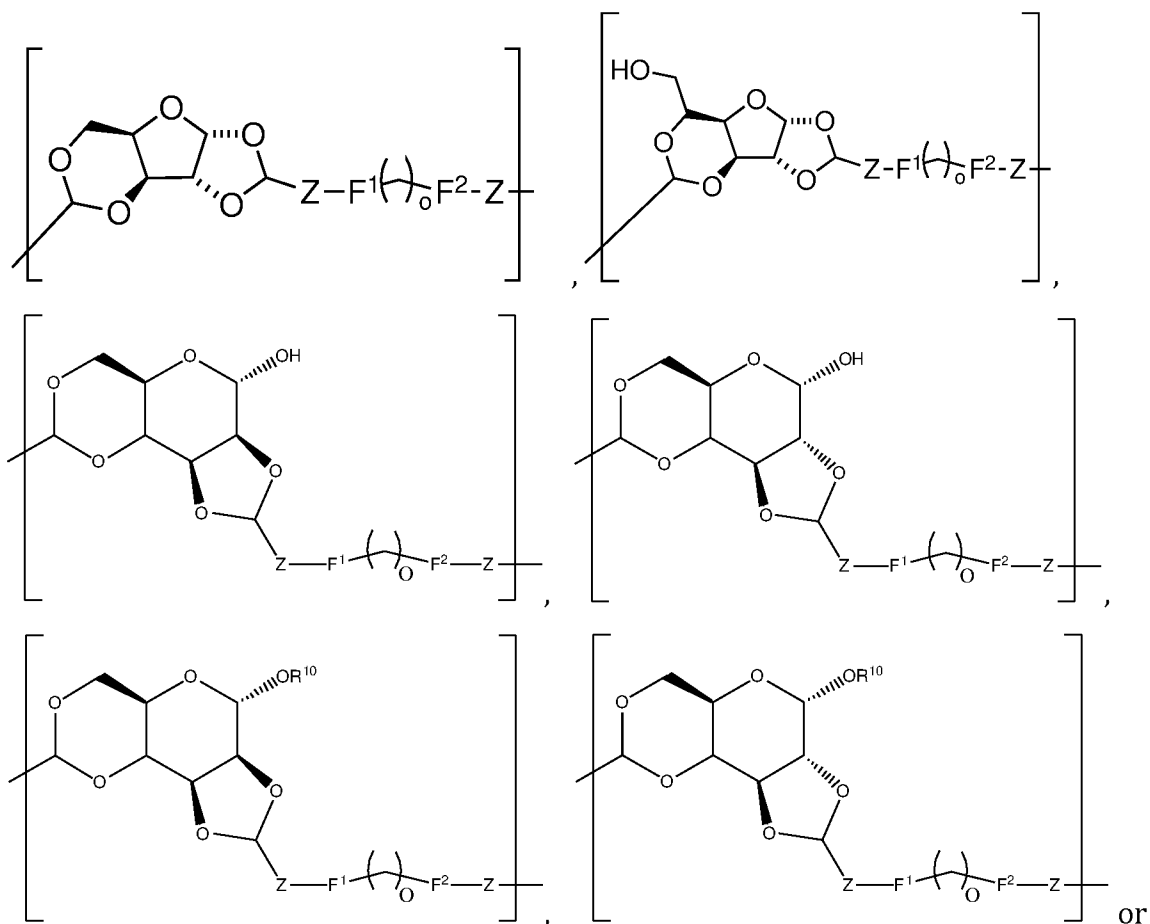
Accordingly, the polymer according to the invention preferably comprises as repeat unit at least one of the following structures:



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- 5 wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and wherein F<sup>1</sup> is -C(=O)O-, -OC(=O)-, -C(=O)NR<sup>8</sup>-, -R<sup>8</sup>NC(=O)-, or a covalent bond, and F<sup>2</sup> is -OC(=O)-, -C(=O)O-, -R<sup>8</sup>NC(=O)-, -C(=O)NR<sup>8</sup>-, or a covalent bond;  
wherein R<sup>8</sup> is H or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;
- 10 R<sup>10</sup> is hydrogen or a hydrocarbon moiety with 1 to 20 carbon atoms, wherein each hydrogen atom of the hydrocarbon moiety may optionally be substituted with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom; and  
o is an integer from 2 to 10, in particular from 2 to 4.
- 15 More preferably, the polymer according to the invention comprises as repeat unit at least one of the following structures:



wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and wherein F<sup>1</sup> is -C(=O)O-, -OC(=O)-, -C(=O)NR<sup>8</sup>-, -R<sup>8</sup>NC(=O)-, or a covalent bond, and F<sup>2</sup> is -OC(=O)-, -C(=O)O-, -R<sup>8</sup>NC(=O)-, -C(=O)NR<sup>8</sup>-, or a covalent bond;

wherein R<sup>8</sup> is H or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

R<sup>10</sup> is hydrogen or a hydrocarbon moiety with 1 to 20 carbon atoms, wherein each

hydrogen atom of the hydrocarbon moiety may optionally be substituted with a C1-C4-alkyl group or a halogen atom;

and

o is an integer from 2 to 10, in particular from 2 to 4.

5

Z may also be an alkylene moiety with 0 to 10, preferably 0 to 4, carbon atoms.

Further, Z may also be an aromatic ring system with 5 to 10, preferably 6, carbon atoms. Even further, Z may be a cyclic aliphatic ring system with 5 to 10, preferably 6, carbon atoms.

10

Z is preferably  $-(CH_2)_m-$ , wherein m is an integer from 0 to 10, in particular from 0 to 4;  $-C_6H_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C1-C4-alkyl groups or 1 to 4 halogen atoms; or  $-C_6H_{10}-$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C1-C4-alkyl groups. F is preferably  $-COOH$ ,  $-COOR^4$ ,  $-C_2H_3$ ,

15

wherein  $R^4$  is a C1-C4-alkyl group.

Preferably,  $R^2$  is  $-H$ . More preferably,  $R^2$  is H,  $R^1$  is H or  $CH_2OH$ , and  $R^3$  is  $-H$ .

In the structures (III) and (IV), n is preferably 0. This is particularly the case when the structures (III) or (IV) have been obtained from aldoses.

20

As described, in the structures (I), (II) and (V), R is  $-Z-F$ , wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C1-C4-alkyl groups or 1 to 4 halogen atoms, and F is  $-COOH$ ,  $-CH(COOH)_2$ ,  $-COOR^4$ ,  $-CHO$ ,  $-CH(CHO)_2$ ,  $-C_2H_3$ ,  $-NH_2$ ,  $-NHR^7$ ,  $-OH$ ,  $-CH(CH_2OH)_2$ , wherein  $R^4$  is a C1-C4-alkyl group; and  $R^7$  is a C1-C4-alkyl group.

25

According to an embodiment of the invention, in the structures (III), (IV) and (VI),  $R^5$  is preferably  $-(CH_2)_mC(=O)O-$  and  $R^6$  is  $-OC(=O)(CH_2)_m-$ ; or

30

$R^5$  is  $-C_6H_4C(=O)O-$  and  $R^6$  is  $-OC(=O)C_6H_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C1-C4-alkyl groups or 1 to 4 halogen atoms; or

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R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>C(=O)O- and R<sup>6</sup> is -OC(=O)C<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is -(CH<sub>2</sub>)<sub>m</sub>OC(=O)- and R<sup>6</sup> is -C(=O)O(CH<sub>2</sub>)<sub>m</sub>-; or

5 R<sup>5</sup> is -C<sub>6</sub>H<sub>4</sub>OC(=O)- and R<sup>6</sup> is -C(=O)OC<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or

R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>OC(=O)- and R<sup>6</sup> is -C(=O)OC<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is -(CH<sub>2</sub>)<sub>m</sub>C(=O)NR<sup>8</sup>- and R<sup>6</sup> is -R<sup>8</sup>NC(=O)(CH<sub>2</sub>)<sub>m</sub>-; or

10 R<sup>5</sup> is -C<sub>6</sub>H<sub>4</sub>C(=O)NR<sup>8</sup>- and R<sup>6</sup> is -R<sup>8</sup>NC(=O)C<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or

R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>C(=O)NR<sup>8</sup>- and R<sup>6</sup> is -R<sup>8</sup>NC(=O)C<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is -(CH<sub>2</sub>)<sub>m</sub>R<sup>8</sup>NC(=O)- and R<sup>6</sup> is -C(=O)NR<sup>8</sup>(CH<sub>2</sub>)<sub>m</sub>-; or

15 R<sup>5</sup> is -C<sub>6</sub>H<sub>4</sub>R<sup>8</sup>NC(=O)- and R<sup>6</sup> is -C(=O)NR<sup>8</sup>C<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or

R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>R<sup>8</sup>NC(=O)- and R<sup>6</sup> is -C(=O)NR<sup>8</sup>C<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;

wherein R<sup>8</sup> is H or a C<sub>1</sub>-C<sub>4</sub>-alkyl group; and

m is an integer from 0 to 10, in particular from 0 to 4.

20

More preferably, in the structures (III), (IV) and (VI), R<sup>5</sup> is preferably -(CH<sub>2</sub>)<sub>m</sub>C(=O)O- and R<sup>6</sup> is -OC(=O)(CH<sub>2</sub>)<sub>m</sub>-; or

R<sup>5</sup> is -C<sub>6</sub>H<sub>4</sub>C(=O)O- and R<sup>6</sup> is -OC(=O)C<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or

25 R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>C(=O)O- and R<sup>6</sup> is -OC(=O)C<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is -(CH<sub>2</sub>)<sub>m</sub>OC(=O)- and R<sup>6</sup> is -C(=O)O(CH<sub>2</sub>)<sub>m</sub>-; or

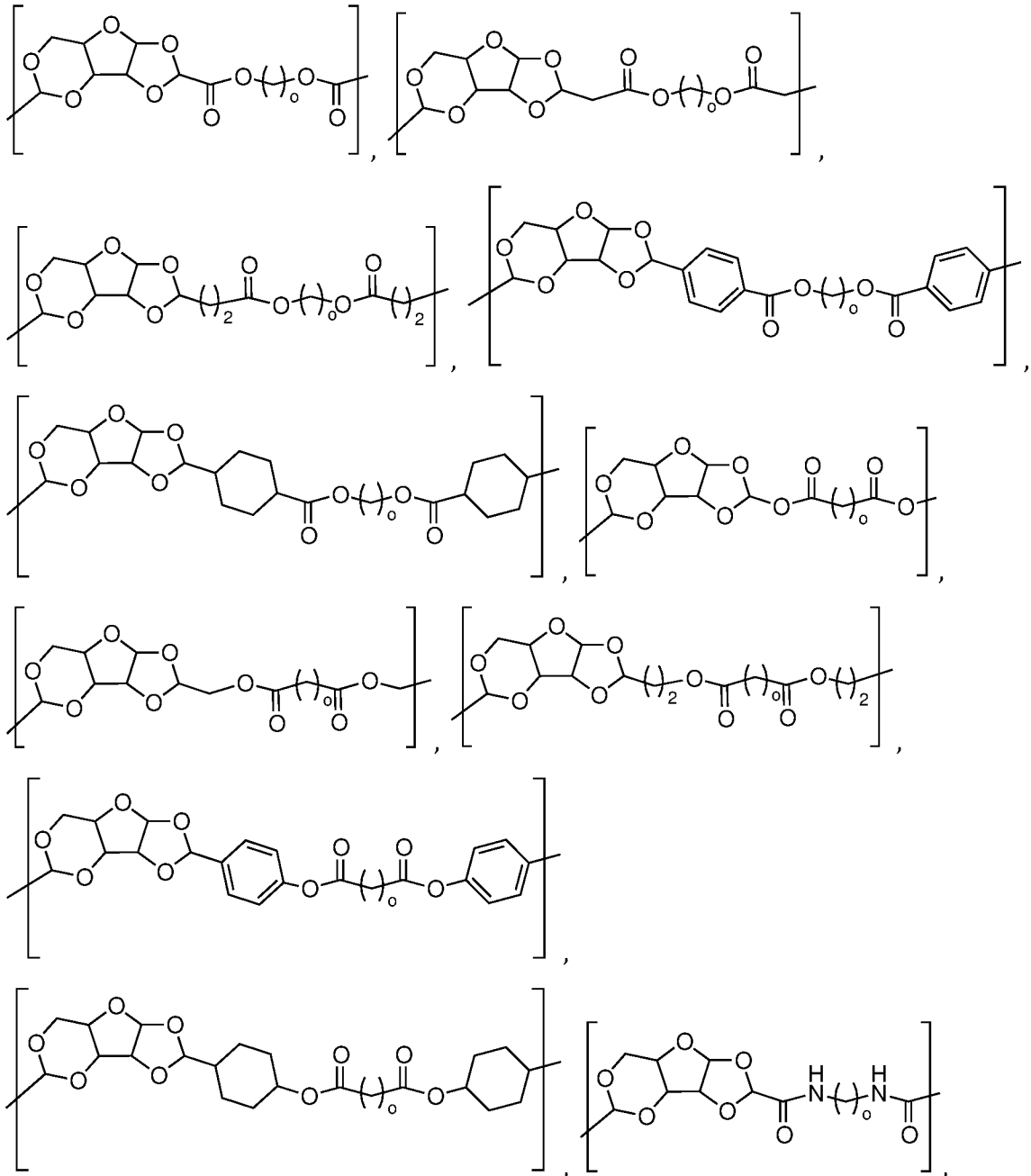
R<sup>5</sup> is -C<sub>6</sub>H<sub>4</sub>OC(=O)- and R<sup>6</sup> is -C(=O)OC<sub>6</sub>H<sub>4</sub>-, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; or

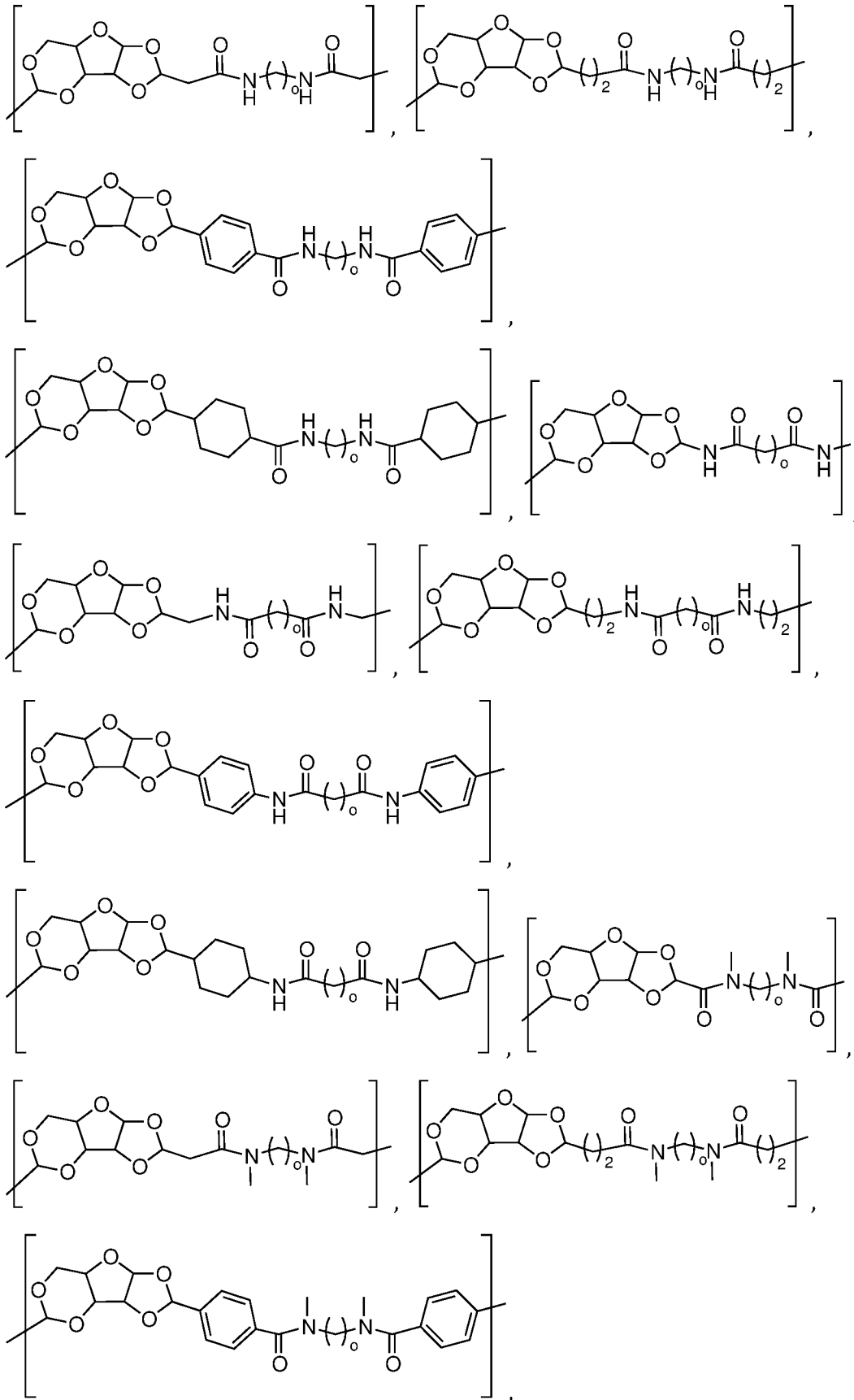
30 R<sup>5</sup> is -C<sub>6</sub>H<sub>10</sub>OC(=O)- and R<sup>6</sup> is -C(=O)OC<sub>6</sub>H<sub>10</sub>-, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;

wherein m is an integer from 0 to 10, in particular from 0 to 4.

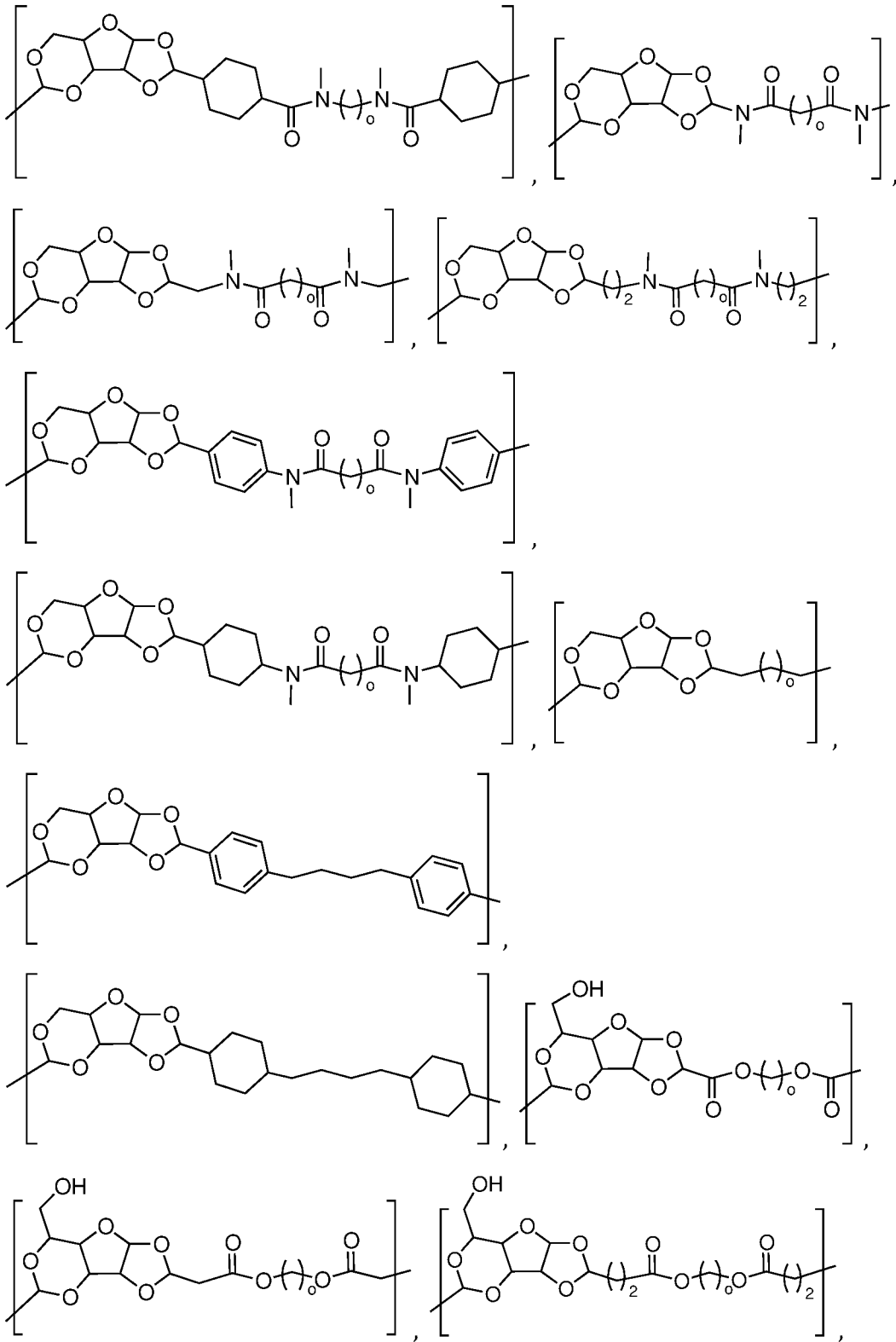
Thus, preferably, the polymer according to the invention comprises as repeat unit at least one of the following structures:

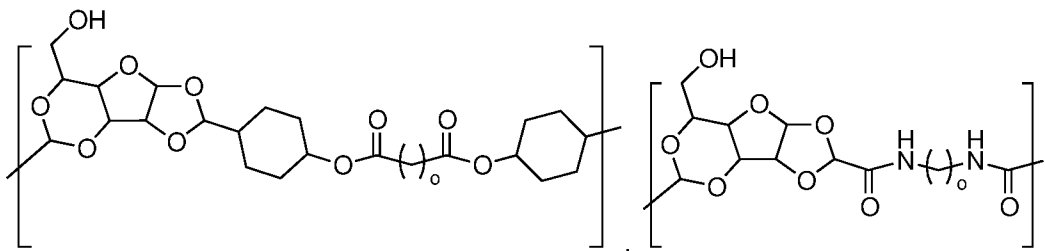
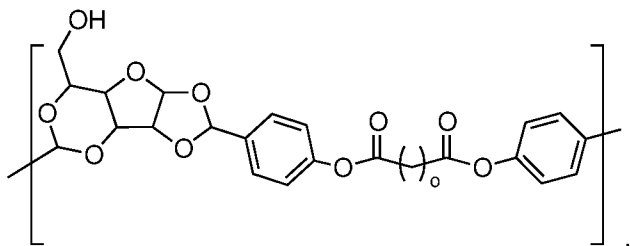
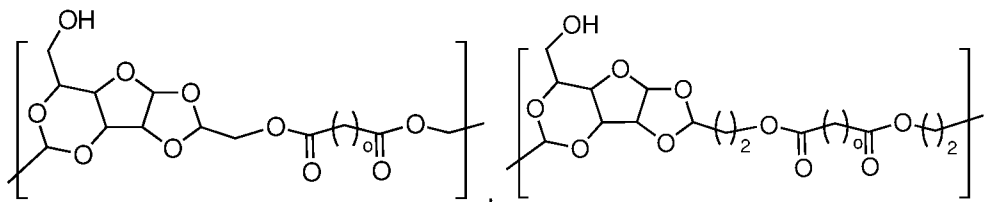
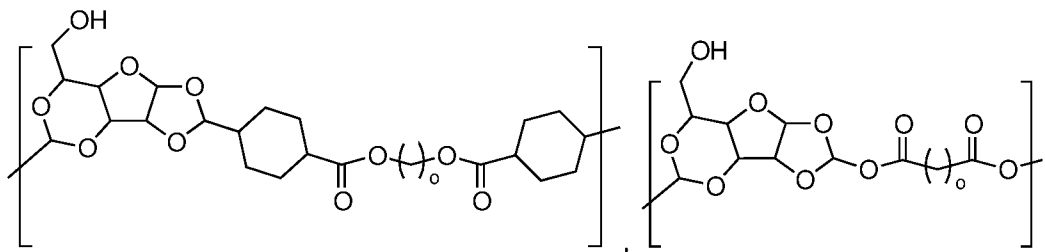
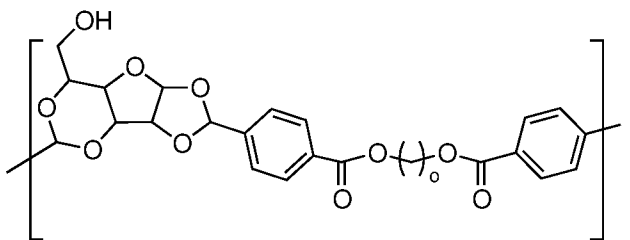
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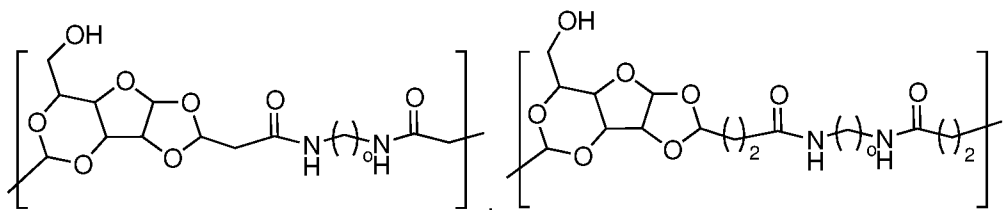


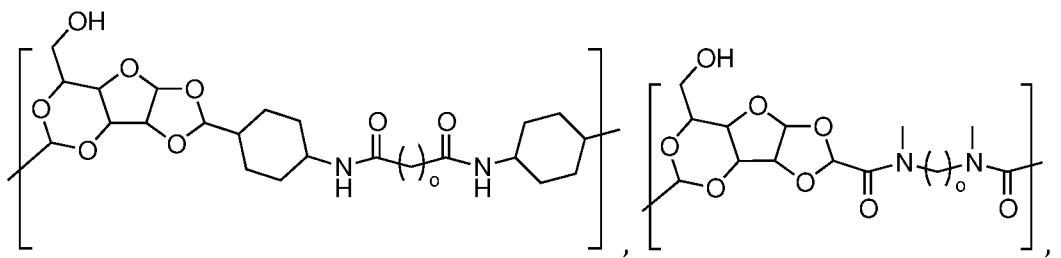
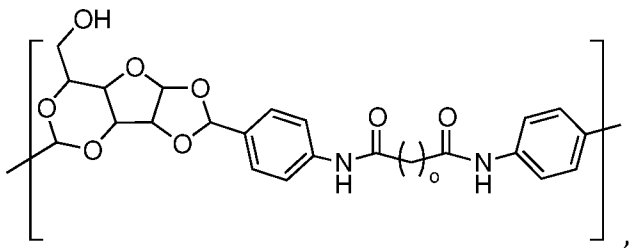
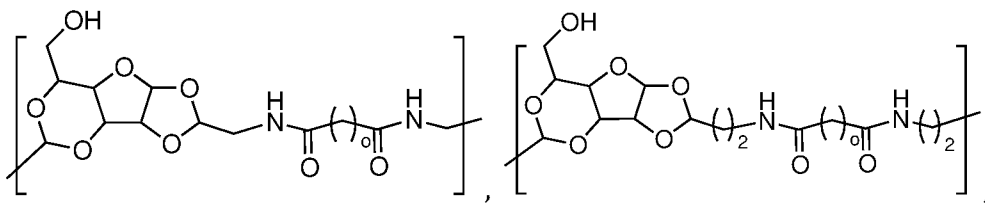
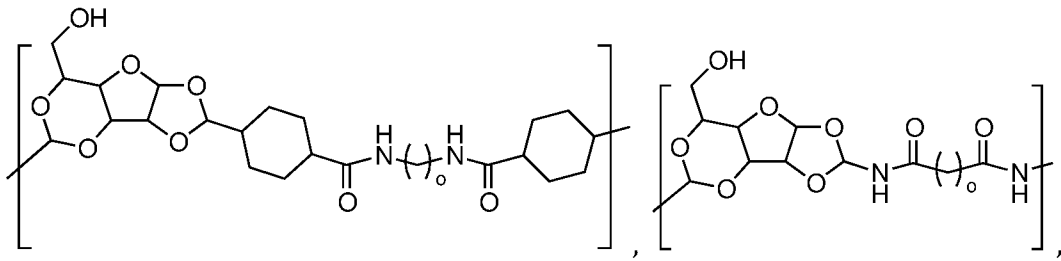
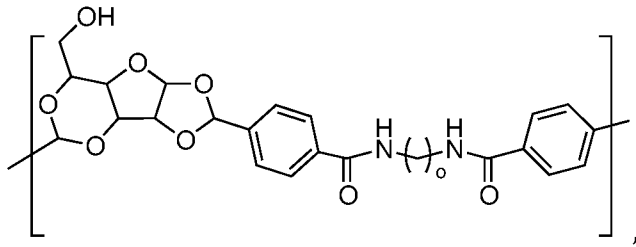




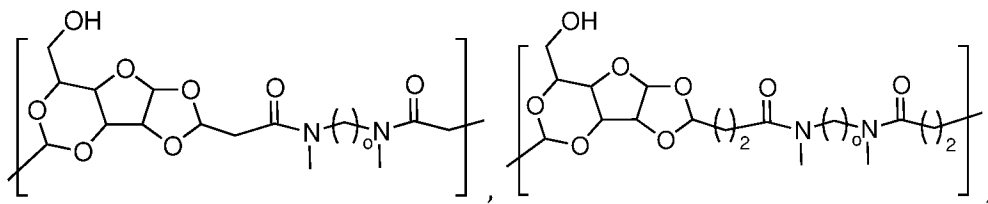


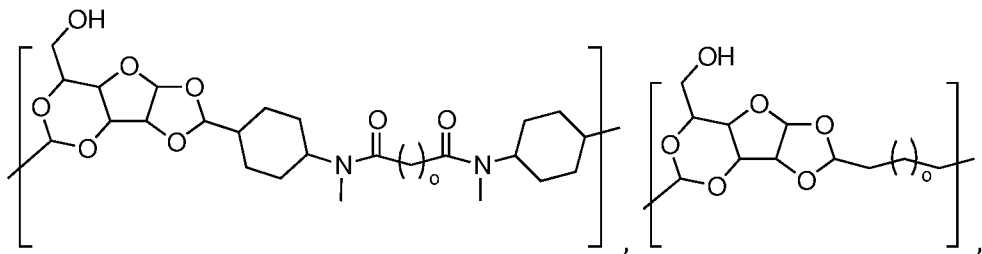
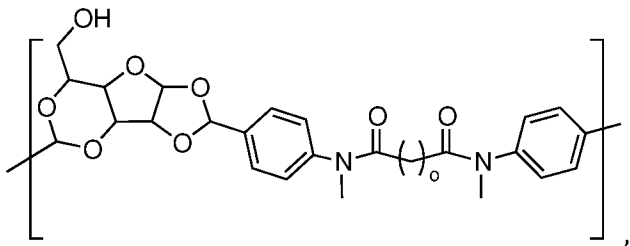
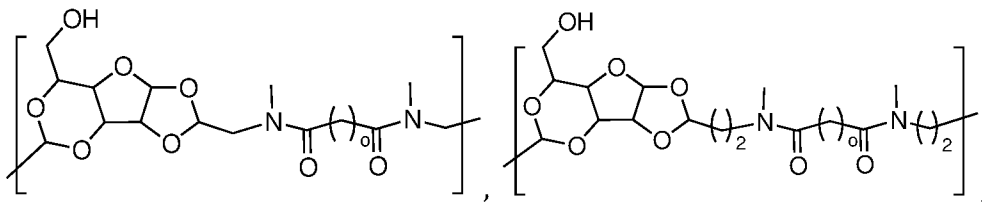
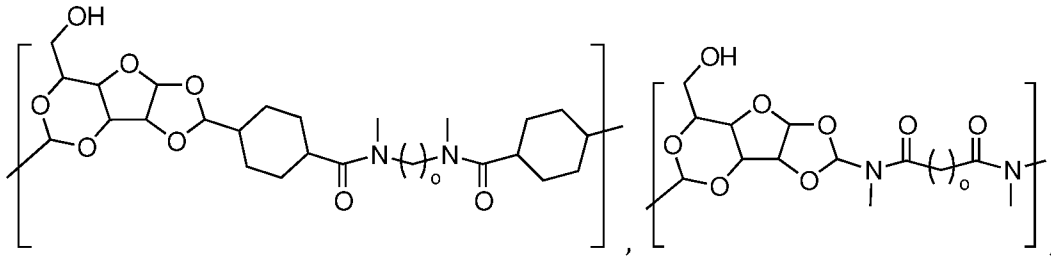
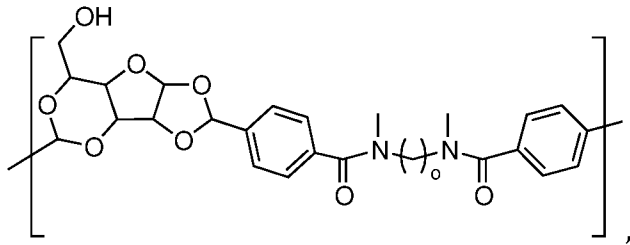
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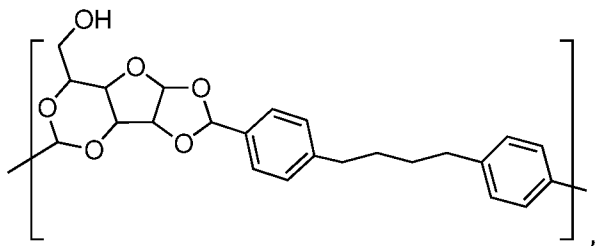


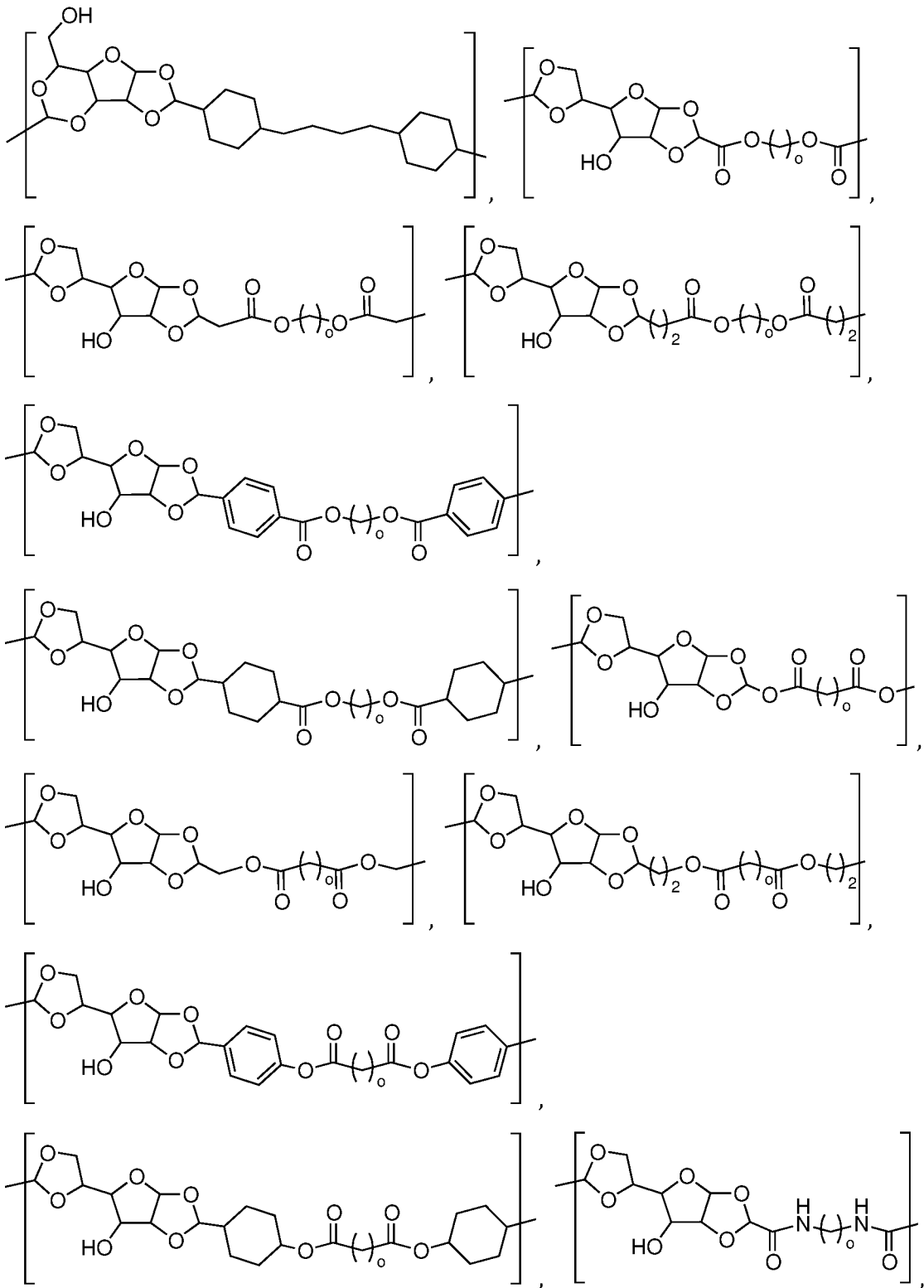
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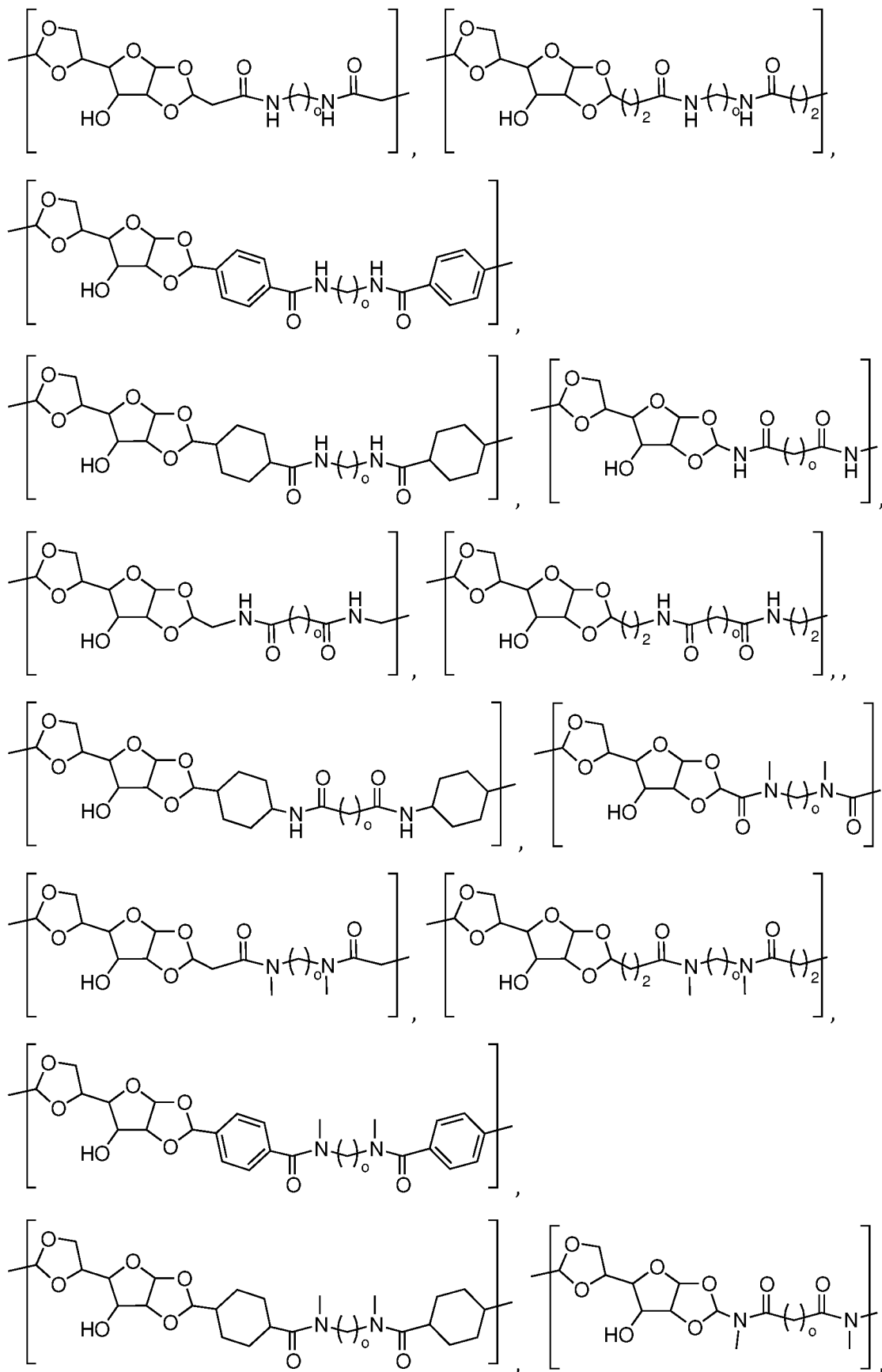




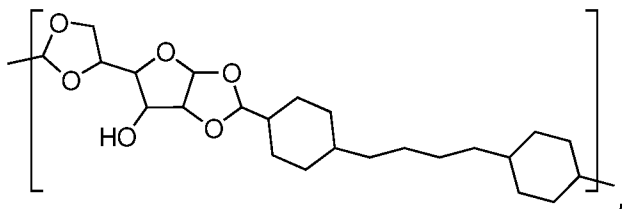
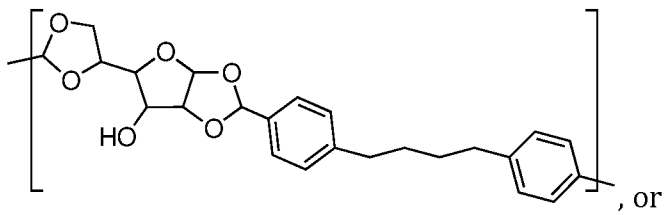
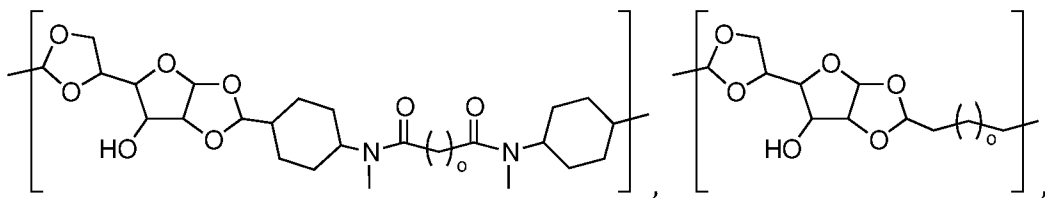
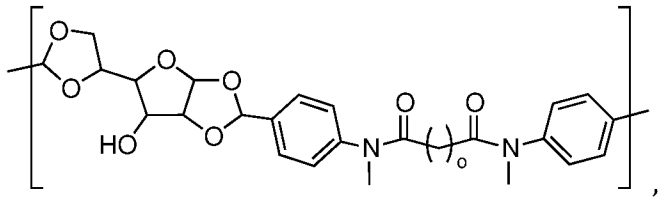
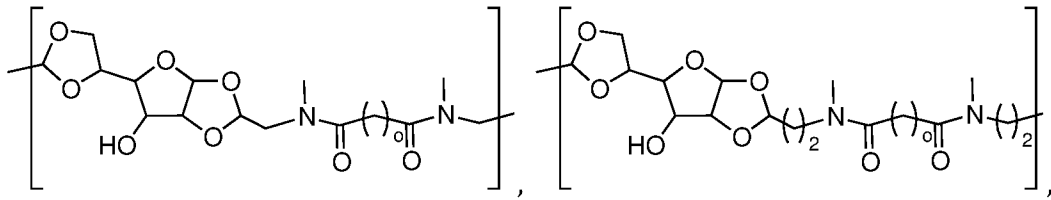
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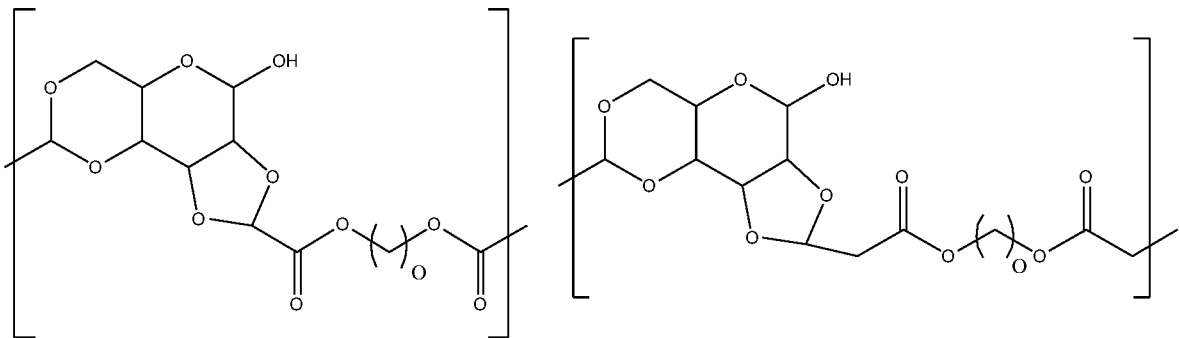


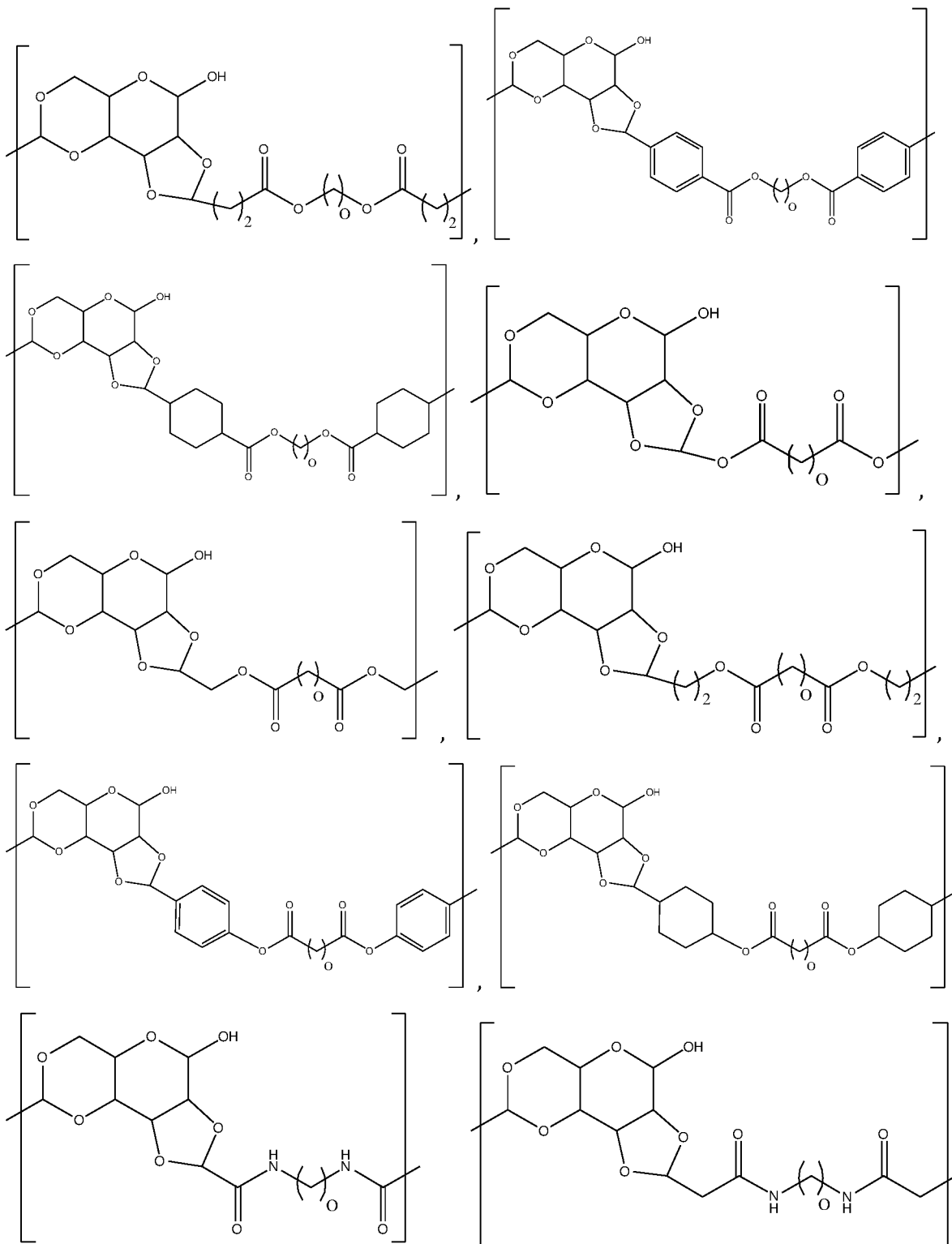


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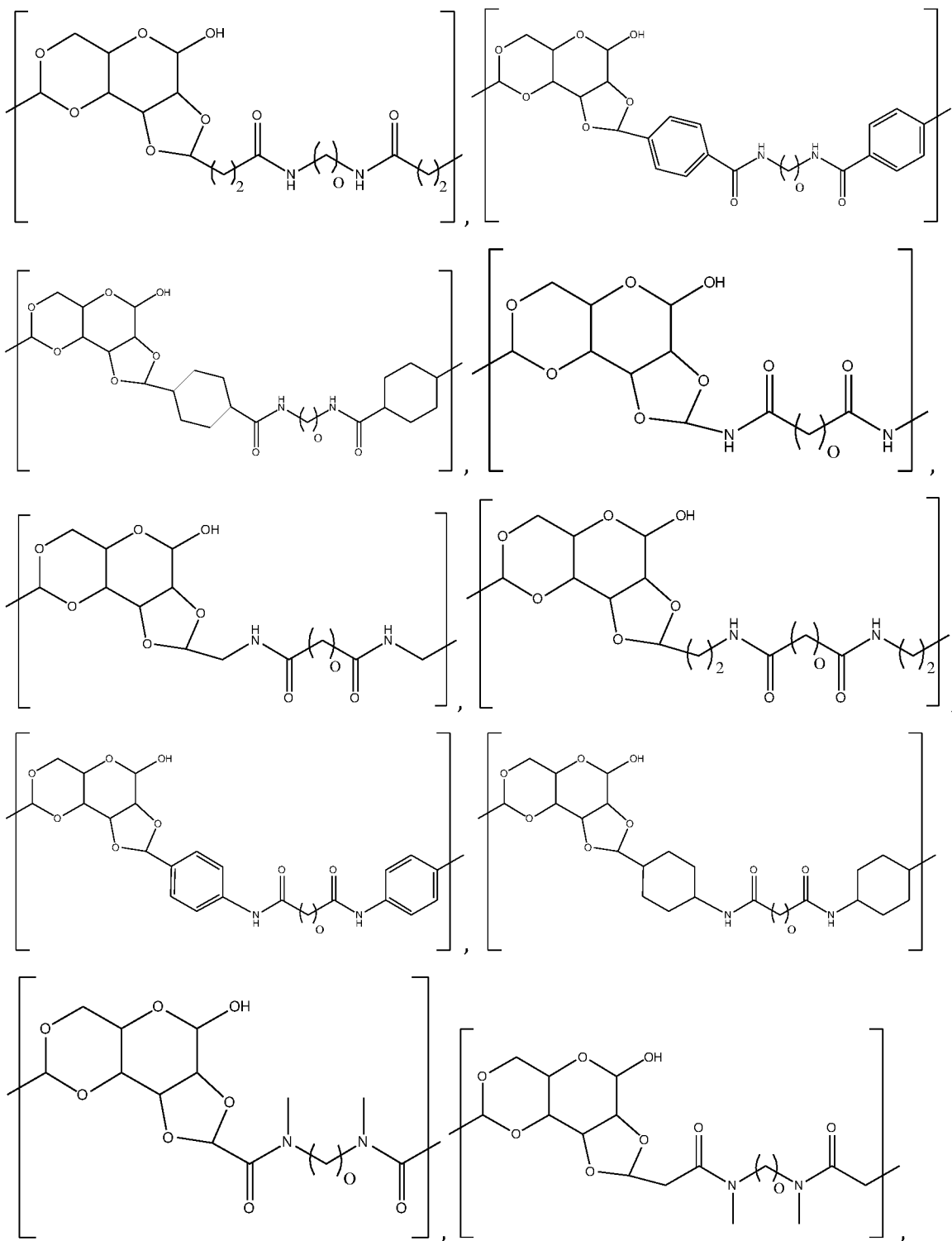


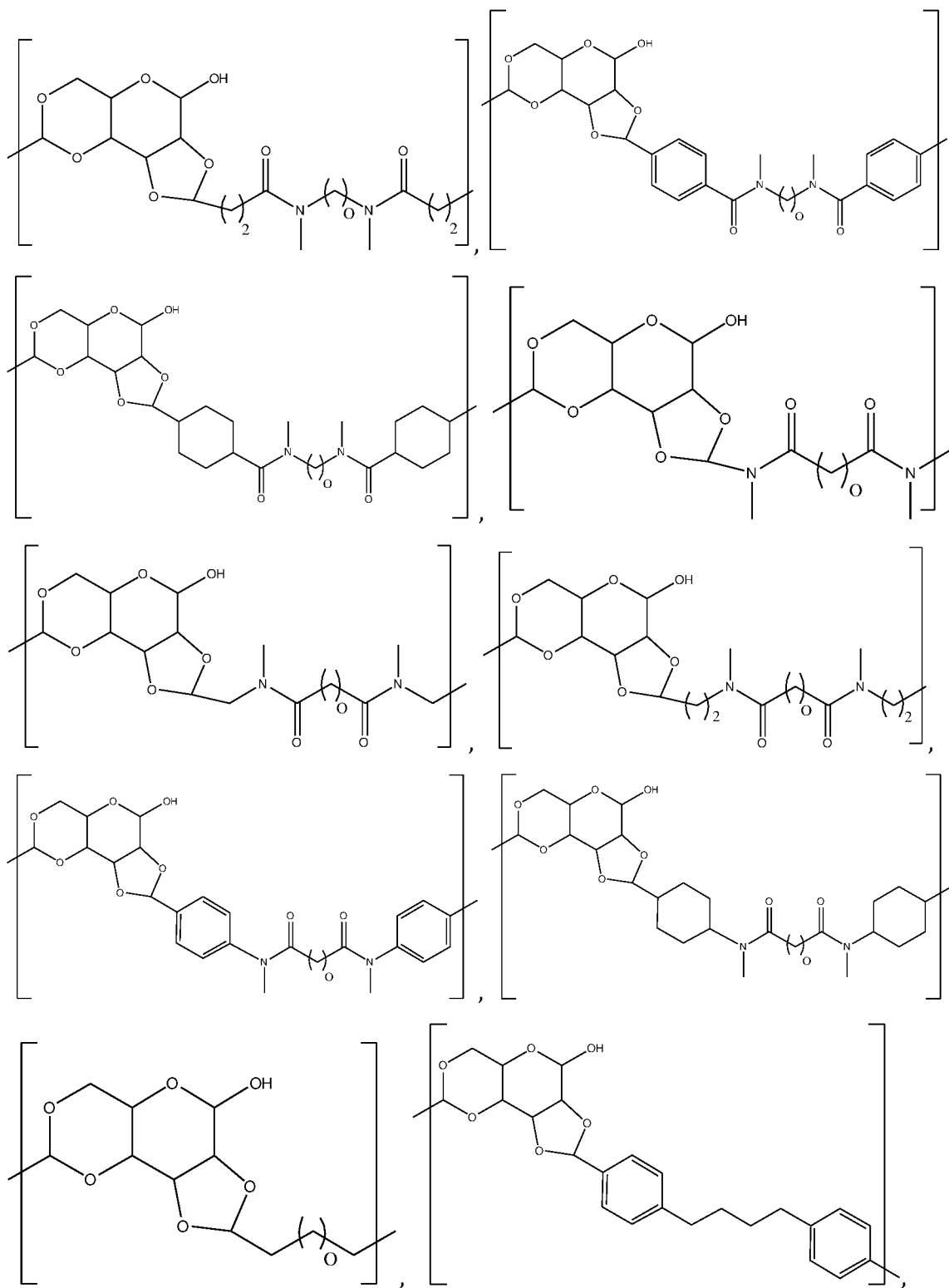
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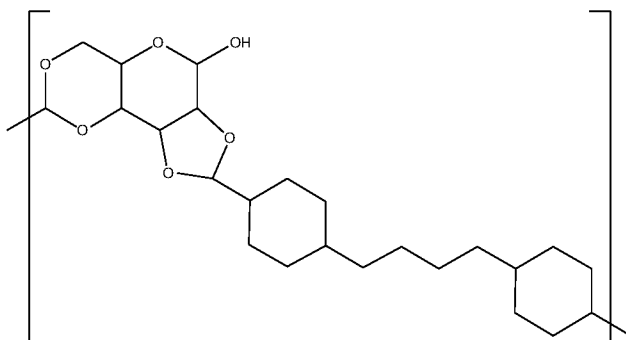












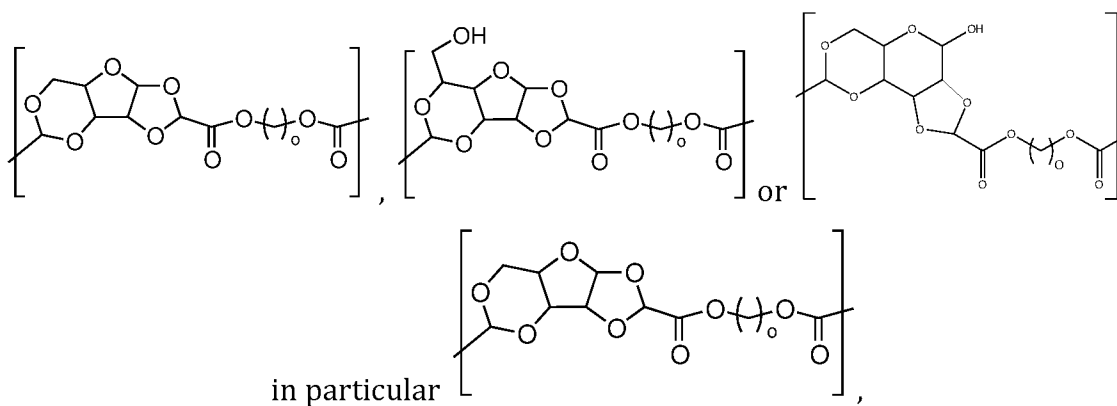
wherein o is an integer from 2 to 10, in particular from 2 to 4.

- 5 Preferably, the polymer according to the invention comprises the repeat unit with the structure (III), wherein n is 0 and R<sup>2</sup> is -H and R<sup>1</sup> is H or CH<sub>2</sub>OH, in particular R<sup>1</sup> is H, and m is 0.

10 According to an embodiment of the invention, the polymer does not comprise the repeat unit with the structure (IV).

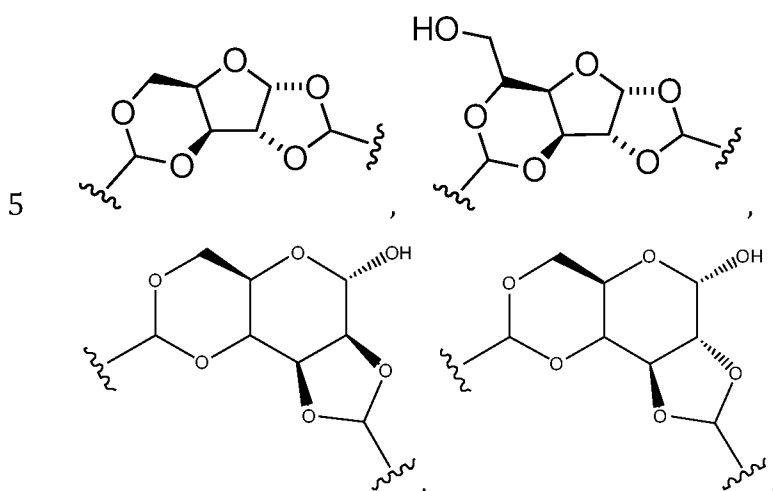
Very good results have been obtained, when in the structures (III), (IV) and (VI), R<sup>5</sup> is -C(=O)O- and R<sup>6</sup> is -OC(=O)- and o is 2.

- 15 Most preferably, the polymer according to the invention comprises as repeat unit



- 20 wherein o is 2; and does not comprise the repeat unit with the structure (IV).

In the structures shown above, the ring systems preferably have the following stereochemistry:



It was found that polymers comprising the aforementioned repeat units, in particular the repeat unit derived from xylose, show good thermal and/or mechanical properties. Moreover, these polymers can be easily prepared from cheap and abundant resources in a simple process.

10

#### The Method for the Preparation of the Polymer

15 The present invention also provides for a method for the preparation of a polymer according to the invention, wherein at least one compound according to the invention is subjected to a reaction, optionally with a compound with the formula R<sup>9</sup>-L-R<sup>9A</sup>, wherein R<sup>9</sup> and R<sup>9A</sup> are independently selected from the group consisting of -OR<sup>11</sup>, -OH, -NHR<sup>8</sup>, -COOH, -COOR<sup>4</sup> and a halogen atom;

20 wherein R<sup>11</sup> is selected from the group consisting of aryl and alkyl or R<sup>11</sup> of residue R<sup>9</sup> and R<sup>11</sup> of residue R<sup>9A</sup> form together a ring system;

wherein the halogen atom is selected from the group consisting of fluorine, chlorine, bromine and iodine;

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wherein R<sup>4</sup>, R<sup>8</sup>, and o are as defined herein. This means that R<sup>9</sup> and R<sup>9A</sup> can be the same or different from each other.

Very good results have been obtained in a preferred embodiment of the invention,  
5 wherein R<sup>9</sup> and R<sup>9A</sup> are identical.

In another preferred embodiment of the invention good results have been obtained when L is (CH<sub>2</sub>)<sub>0</sub>.

10 In a further preferred embodiment of the invention good results have been obtained when R<sup>9</sup>-L-R<sup>9A</sup> is a bis-(4-halogenphenyl) sulfone, in particular bis-(4-chlorophenyl) sulfone or a bis-(4-fluorophenyl) sulfone.

In a further preferred embodiment of the invention good results have been obtained  
15 when R<sup>9</sup>-L-R<sup>9A</sup> is an organic carbonate that is L CO of formula (VIII) and R<sup>9</sup> and R<sup>9A</sup> are the same or different and OR<sup>11</sup>, wherein R<sup>11</sup> is selected from the group consisting of aryl and alkyl or R<sup>11</sup> of residue R<sup>9</sup> and R<sup>11</sup> of residue R<sup>9A</sup> form together a ring system, i.e. forming a cyclic carbonate. For example, the organic carbonate can be a dialkyl carbonate, a diaryl carbonate or a cyclic carbonate. Examples for dialkyl carbonate are  
20 dimethyl carbonate, diethyl carbonate or methylethyl carbonate. Examples for diaryl carbonate are diphenyl carbonate or dimethylphenyl carbonate. Examples for cyclic carbonate are ethylene carbonate or trimethylene carbonate.

Preferably, the reaction is a polymerization reaction.  
25

The at least one compound according to the invention and the compound with the formula R<sup>9</sup>-L-R<sup>9A</sup> may be provided in different ratios, for example from 1:10 to 10:1. Preferably, the at least one compound according to the invention and the compound with the formula R<sup>9</sup>-L-R<sup>9A</sup> are provided in a ratio of from 1:1 to 1:10, more preferably  
30 from 1:1 to 1:8, most preferably from 1:1 to 1:5.

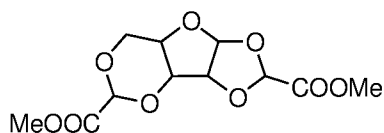
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Preferably, the reaction is conducted in the presence of a catalyst. A non-exhaustive list of polycondensation catalysts that can be used include: antimony trioxide, titanium isopropoxide, titanium butoxide, dibutyltin oxide, and zinc acetate.

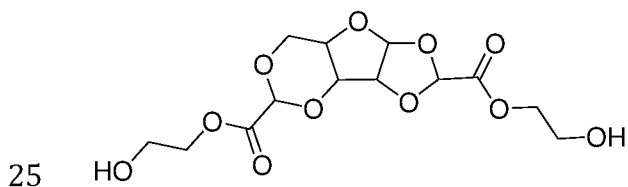
- 5 The reaction may also be conducted in the presence of an initiator, in particular a radical initiator. This is particularly the case when the compound according to the invention contains a vinyl group.

The reaction may be carried out at different temperatures. Preferably, the reaction is carried out at a temperature of 30 to 250 °C, more preferably at a temperature of 50 to 230 °C, most preferably at a temperature of 100 to 220 °C. If the reaction is conducted in the presence of a radical initiator, the temperature is preferably adjusted in view of the radical initiator, in particular in view of the half-life of the initiator. Examples for suitable radical initiators are peroxides such as benzoyl peroxide or azo initiators such as azoisobutyronitrile.

The reaction in the method for the preparation of a polymer according to the invention may also contain several steps. According to an embodiment of the method for the preparation of a polymer according to the invention, in a first step, the compound according to the invention and the compound with the formula  $R^9-L-R^{9A}$  may be reacted to yield an intermediate. For example, a compound with the structure

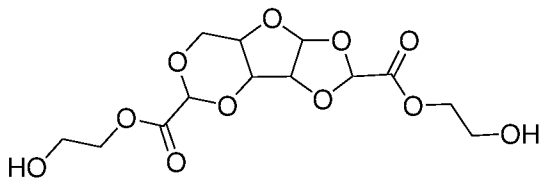


may be reacted with ethanediol to yield as intermediate the corresponding transesterification intermediate containing two ethanediol units:



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In a second step, the intermediate may then be polymerized to yield the polymer according to the invention. For example, the intermediate with the structure



may be polymerized in a second step.

5

The first and the second step may be conducted at different temperatures. For example, the first step may be conducted at a temperature of from 100°C to 200°C, preferably from 120°C to 160°C, most preferably from 130°C to 150°C. Further, the second step may be conducted at a temperature of from 150°C to 250°C, preferably from 170°C to 230°C, most preferably from 180°C to 220°C.

10

The steps of the reaction may be conducted for various periods of times. For example, the first step of the reaction may be conducted for 1 to 15 hours, preferably for 1 to 10 hours, more preferably for 1 to 7 hours. The second step of the reaction may be conducted for 2 to 15 hours, preferably for 3 to 10 hours, more preferably for 3 to 8 hours.

15

In order to achieve high yields and also high molecular weights in the first and second step, in particular in the case of transesterification reactions, the pressure may be reduced. For example, in the transesterification reaction with ethanediol as a reagent described above, the reaction may be conducted first at normal pressure, then the pressure may be reduced. However, this may also be applied in the preparation of amides, polyesters, or polyamides.

20

Preferably, during the first step, the pressure is reduced to 100 mbar or less, more preferably 50 mbar or less, most preferably 10 mbar or less. Advantageously, during the second step, the pressure is reduced to 100 mbar or less, more preferably 50 mbar or less, more preferably 10 mbar or less, most preferably 1 mbar or less. By reducing

25

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the pressure during the reaction, in particular during the first and/or second step, higher yields and/or higher molecular weights of the polymers can be achieved.

The method according to the invention may also contain a purification step. The  
5 polymer may be purified by precipitation, extraction, and/or column chromatography. Preferably, the polymer is purified by precipitation.

The polymers according to the invention are promising candidates to replace  
10 poly(ethylene terephthalate). Therefore, the invention also provides for the use of the polymer according to the invention for the manufacture of sheets, fibers or molded objects, in particular as a replacement for poly(ethylene terephthalate).

Hereinafter, examples are described that are in no way meant to be limiting.

## 15 EXAMPLES

### Methods

MALDI-TOF: Matrix-assisted laser desorption/ionization time-of-flight mass  
20 spectrometry (MALDI-TOF-MS) spectra of the synthesized polymers were acquired using a Bruker AutoFlex Speed instrument (Bremen, Germany). Samples were prepared by dissolving the polymers in 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) at a concentration of 1 mg·mL<sup>-1</sup>. A solution of 10 mg of 2,5-dihydroxybenzoic acid and 10 µL of trifluoroacetic acid (TFA) in 1 ml of THF was prepared. Subsequently, 0.5 µL of the  
25 polymer/HFIP solution was deposited on the steel analysis plate followed by 0.5 µL of the DHB/TFA solution. The laser power was set between 60-90% for the different polymer samples in order to achieve the optimal signal.

Gel Permeation Chromatography: The number- and weight-average molecular  
30 weights,  $M_n$  and  $M_w$ , of the synthesized polymers were determined via gel permeation chromatography (GPC). An Agilent 1100 GPC/SEC was equipped with one PFG linear



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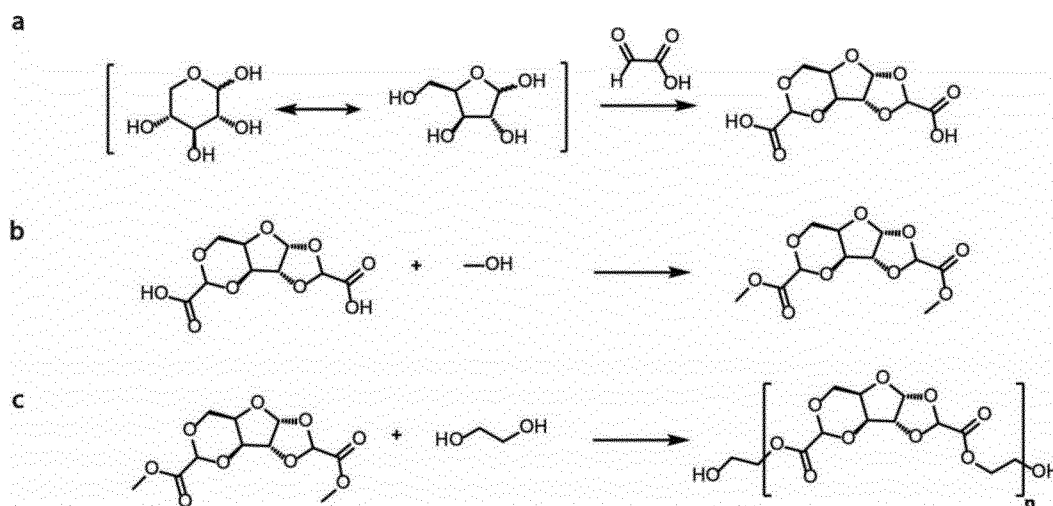
M column (PSS) and attached to an Agilent 1100 VWD/UV detector operated at 294 nm, a DAWN HELEOS II multi-angle laser light scattering (MALS) detector (Wyatt Technology Europe) and an Optilab TrEX RI detector (Wyatt). Samples were eluted in HFIP with 0.03 M K-TFAc at 1 mL min<sup>-1</sup> at room temperature. Each polymer sample was analyzed twice to ensure precision of the instrument. To measure accurate molecular weight, polymethylmethacrylate (PMMA) standards purchased from PSS Polymer Standards Service, Germany were used to build a calibration curve that was applied to our data.

10 GC-MS Analysis: Gas chromatography-mass spectrometry spectra were obtained using an Agilent 7890B series GC equipped with a HP5-MS capillary column and an Agilent 5977A series Mass Spectroscopy detector. The GC-MS method was performed as follows: an injection temperature of 250°C, a column temperature program beginning at 50°C for 1 min, followed by a ramp of 15°C/min to 300°C, a hold at 300°C for 7 min, and a detection temperature of 290°C.

NMR Analysis: All NMR spectra were acquired using a Bruker Avance III 400 MHz spectrometer.

## 20 Syntheses

General Reaction Scheme:



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For the preparation of the monomer, glyoxylic acid, which is produced at commercial scale and can be readily produced from renewable ethylene glycol, was reacted with D-xylose (step a in the scheme above). The glyoxylic acid protected xylose was then esterified with methanol to enhance polycondensation rates and facilitate separation of the protected sugar (step b in the scheme above). Finally, the diester protected xylose, dimethylglyoxylate xylose (DMGX), was polymerized with ethylene glycol to form the fully renewable polyester, poly(ethylene dimethylglyoxylate xylose) (PEDMGX) (step c in the scheme above).

10

Synthesis of dimethyl glyoxylate xylose from xylose.

D-xylose (200 g, 1.33 mol, 1.00 equiv.) was combined with glyoxylic acid monohydrate (500 g, 5.43 mol, 4.08 equiv.) in a 2 L, round-bottom flask and heated at 95 °C on a rotary evaporator. After dissolution of the xylose in the molten glyoxylic acid, 98 wt/wt% sulfuric acid (28.57 g, 270.8 mmol, 0.2 equiv.) was added dropwise. The pressure on the rotary evaporator was then slowly reduced to 20 mbar to continuously pull off the water that is produced as a by-product of the reaction. The reaction was stopped after yields of diglyoxylic acid protected xylose exceeded 93% (~3 h), as determined by. Methanol (1 L) was then added to the reaction mixture and the resulting solution was heated to reflux using an oil bath at 80 °C until yields of the dimethyl ester of the diglyoxylic acid-protected xylose exceeded 95% (~1 h) as determined by GC-FID. The reaction was then cooled to room temperature and neutralized with sodium hydroxide. The resulting salts were removed by filtration and the filtrate was concentrated *in vacuo* on a rotavap at 45 °C and 100 mbar. The residue was then dissolved in DCM (0.6 L) and transferred to a (2 L) separatory funnel. The organic phase was then washed with deionized water (1 L) three times to remove darkly coloured sugar degradation products and unreacted carboxylates. The organic phase was then extracted once with brine (1 L) and then transferred to a 1 L, round-bottom flask and concentrated *in vacuo*. The resulting residue was distilled using a distillation bridge at a pressure of 0.02 mbar and an oil bath temperature of 80-180 °C. The distillate containing methyl glyoxylates and residual solvent obtained during the ramp between 80°C and 180°C was discarded. A second flask was equipped and a

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second fraction was collected, which contains the product. This viscous, yellow oil that was dissolved in DCM (0.5 L) and treated with activated carbon (30 g). After stirring at 700 RPM using a PTFE coated stir-bar for 4 h, the solution was filtered through a 0.2  $\mu\text{m}$  nylon membrane filter to remove the activated carbon and concentrated *in vacuo* to afford the dimethylglyoxylate xylose as a viscous-colourless oil (205 g, 53%). This oil is a mixture of four stereoisomers. Alternatively, crystallization can be used instead of activated carbon treatment to remove yellow impurities. Crystallization was successfully performed in methanol, cyclopentylmethyl ether, and toluene. Also, by using controlled-temperature crystallization we have managed to selectively crystallize the most abundant isomer, leaving the other 3 isomers in the mother liquor.

Fig. 1 to 4 show analytical data for DMGX. Fig. 1 shows a 2D HSQC NMR showing the successful synthesis of DMGX isomers. The different isomers of DMGX give rise to different sets of peaks in the NMR spectrum. The letters in parentheses next to the peaks indicate the stereochemistry at carbons 6 and 9, respectively. Fig. 2 shows the  $^{13}\text{C}$  NMR spectrum of DMGX isomers alone. The letters in parentheses next to the peaks indicate the stereochemistry at carbons 6 and 9, respectively. In Fig. 3, the different retention times in gas chromatography of the purified DMGX isomers become apparent. Fig. 4 shows the corresponding GC-MS mass peaks of the DMGX isomers as well as fragmentation products.

#### Exemplary synthesis of Poly(ethylene dimethylglyoxylatexylose)

In a 2-neck round bottom flask, 1 molar equivalent of dimethyl glyoxylatexylose was charged with an excess of freshly distilled ethanediol (2.2 eq) and 0.4 wt% of antimony trioxide. The reaction vessel was attached to a distillation tube and was purged with nitrogen three times prior to heating. The vessel was heated to 140°C in a sand bath with continuous stirring under a steady nitrogen flow for 2 h with methanol being pulled off by distillation. The bath was then brought to 200°C for 2 h under continuous nitrogen flow. Vacuum was then applied at a pressure of 0.1 mbar and the reaction was allowed to continue for an additional 3 h with ethylene glycol being distilled off to drive the transesterification forward. The reaction was allowed to cool

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to room temperature and was subsequently dissolved in the minimum volume of 1,1,1,3,3,3-hexafluoro-2-propanol and precipitated by dropwise addition to methanol while stirring. The polymer was filtered out of solution and washed with methanol followed by drying under vacuum. Various transesterification catalysts, reaction  
5 times, and temperature can be used to produce the same polymer of various molecular weights.

Fig. 5 to 9 show analytical data for PEDMGX. Fig. 5 shows a 2D HSQC NMR spectrum showing the successful synthesis of PEDMGX. The letters in parentheses next to the  
10 peaks indicate the stereochemistry at carbons 6 and 9, respectively. Fig. 6 shows a reflector positive MALDI spectrum of PEDMGX. The distances between prominent peaks correspond to the molecular weight of the repeat unit. Fig. 7 shows the GPC chromatograms of three different PEDMGX samples synthesized at various temperatures and durations (not all of them described herein). Each polymer sample  
15 was analyzed twice to ensure precision of the instrument. For the measurements, polymethylmethacrylate (PMMA) molecular weight standards from PSS Polymer Standards Service, Germany, were used as external standards for molecular weight determination. Molecular weights ranging from 10 to 50 kDa were achieved, which is well within the commercial range of PET (20 to 60 kDa). Fig. 8 shows a DSC curve of  
20 PEDMGX heating from 30°C to 250°C and cooling back down to 30°C. DSC reveals a glass transition of 125°C, which is 45 to 55°C higher than that of PET and 30°C higher than that of PEF. This would enable the polyester to be used for significantly higher temperature applications without it losing its properties, notably including those that require contact with boiling water. Fig. 9 shows a TGA curve of PEDMGX. TGA  
25 indicates a degradation temperature of approximately 348°C, which is lower than the 400°C degradation temperature of PET, but it is still well above the processing and end-use temperatures of the polymer.

### General Procedure for the Preparation of DMGX-based Polyesters

The following polymers have been synthesized using the following method: Poly(ethylene dimethylglyoxylatexylose), Poly(propylene dimethylglyoxylatexylose), Poly(butylene dimethylglyoxylatexylose), Poly(pentylene dimethylglyoxylatexylose), Poly(hexylene dimethylglyoxylatexylose) by polymerizing DMGX with ethanediol, 5 propanediol, butanediol, pentanediol, and hexanediol, respectively.

Dimethylglyoxylate xylose (10 g, 34.4 mmol, 1.0 equiv.) was combined with diol (86 mmol, 2.5 equiv.), the re-esterification catalyst: zinc acetate (2 mg, 0.011 mmol, 0.00032 equiv), antioxidants: pentaerythritol tetrakis(3,5-di-tert-butyl-4- 10 hydroxyhydrocinnamate) (13 mg, 0.011 mmol, 0.00032 equiv.) and triphenyl phosphite (13 mg, 0.042 mmol, 0.0012 equiv.) in a 250 mL, 2-neck, round-bottom flask. The reaction vessel was then equipped with a distillation bridge, a vacuum adapter, a valve for nitrogen flow, and a 250 mL collection flask and connected to a Schlenk line. The reaction vessel was back filled with nitrogen three times. Under a steady stream of 15 nitrogen, the reaction mixture was then heated with stirring to 140 °C with an oil bath. Over the course of the reaction, the methanol by-product was distilled from the reaction mixture and collected in the collection flask. Conversion was monitored by <sup>1</sup>H-NMR and once complete re-esterification was observed (~1-4 h), the transesterification catalyst, antimony trioxide (2 mg, 0.0069 mmol, 0.0002 equiv), was 20 added to the reaction mixture as a suspension in the diol (0.5 mL) under a positive nitrogen pressure. The reaction mixture was then heated to 190 °C and slowly over the course of 30 min the reaction vessel was evacuated to a pressure of 0.02 mbar to distil the diol reaction by-product and drive the polycondensation reaction. The reaction was monitored by <sup>1</sup>H-NMR and the reaction was halted once the desired molecular weight 25 was observed by end group analysis (high molecular weight ~ 8-14 h). Polymers derived from the mixture of 4 DMGX isomers were typically orange in color. Polymers synthesized from the most abundant DMGX isomer were generally highly transparent, and colorless. The reaction was cooled to room temperature and dissolved in a minimum volume of 1,1,1,3,3,3-hexafluoroisopropanol (250 mL). The resulting solution was added 30 dropwise to a stirred solution of isopropanol (1 L) for the butanediol, pentanediol and hexanediol polymers and methanol (1L) for the shorter chain diols, precipitating the

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polymer. The polymer was collected by filtration, washed with isopropanol, followed by diethyl ether, and dried *in vacuo* overnight at 60 °C and 0.02 mbar to afford the product as a brilliant-white powder. For the polymerizations with ethanediol and propanediol, where high molecular weights were more difficult to achieve, a more active  
5 transesterification catalyst, dibutyltin oxide (45 mg, 0.184 mmol, 0.0053 equiv.), was used in place of zinc acetate and antimony trioxide.

#### Synthesis of Dimethylglyoxylate xylose from Lignocellulosic Biomass

Biomass (extractives free and dried, 90.0 g) was massed into a tared, 1 L reagent  
10 bottle. To the bottle was then added the glyoxylic acid monohydrate (60.753 g, 660 mmol, 3.3 equiv.), 1,4-dioxane (250 mL), hydrochloric acid (37 wt%, 16.7 mL, 200 mmol, 1.0 equiv.), and two large PTFE coated stir bars. The flask was sealed with a GL 45 cap and placed in a shaking incubator for 24 hours at 300 RPM. Once completed, the reaction was cooled to room temperature (~23-30 °C). A filtration apparatus was  
15 assembled consisting of a 2 L filter flask, neoprene adapter, and a Buchner funnel with a piece of qualitative filter paper. The reaction was filtered through the Buchner funnel washing with dioxane (250 mL) to remove the cellulose-rich solids. The filtrate was then transferred to a 29/32, 2 L round-bottom flask and concentrated on a  
20 rotavap with a bath temperature of 45 °C and an ultimate pressure of 10 mbar. Into the concentrated lignin solution was then added an oval-type PTFE coated stir-bar followed by de-ionized water (1 L), which precipitated the lignin. The mixture was stirred at 500 RPM for 30 minutes to break the large agglomerations. The stir-bar was then removed. A filtration apparatus was assembled consisting of a 2 L filter flask, neoprene adapter, and membrane filtration apparatus with a 0.8 µm nylon membrane  
25 filter. The precipitated lignin solution was then filtered washing with deionized water (100 mL) through the nylon membrane filter to collect the lignin.

The filtrate was transferred to a 29/32 2 L round bottom flask and sulfuric acid (1.7 mL, 31 mmol, 0.16 equiv., 98 wt%) was added. The reaction solution was then concentrated *in vacuo* on a rotavap (90 °C, 200 mbar to 50 mbar) for three hours until  
30 all the water was evaporated from the reaction solution. To the reaction mixture was added methanol (400 mL) and an oval-type PTFE-coated stir bar. The reaction was

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then stirred for 12 hours at room temperature then neutralized with 10 N NaOH (3.1 mL). A filtration apparatus was assembled consisting of a 1 L filter flask, neoprene adapter, and a Buchner funnel (ground glass frit, porosity grade 3). The resultant salts and stir bars in the neutralized reaction solution were filtered off and the filtrate was

5 dried on a rotary evaporator at 45°C and 100 mbar. The residue was then dissolved in DCM (250 mL) and transferred to a 1 L separatory funnel. The solution as diluted with 250 mL of water and the funnel was sealed and shaken. The organic and aqueous phases were separated, and the aqueous phase was returned to the separatory funnel. It was extracted once more with DCM (250 mL). The layers were separated again, and

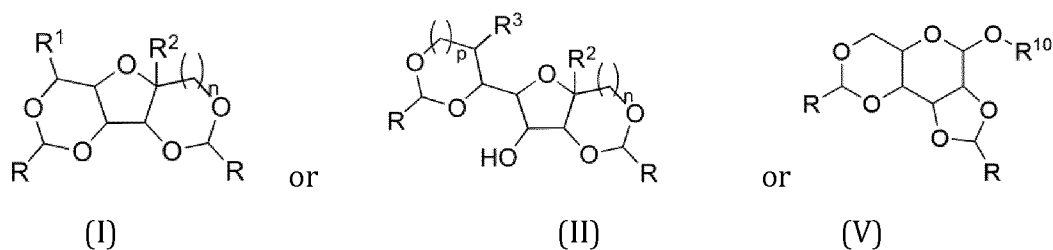
10 the organic phases were combined and dried with magnesium sulfate (1-2 g). A filtration apparatus was assembled consisting of a 1 L filter flask, neoprene adapter, and a Buchner funnel (ground glass frit, porosity grade 3). The organic phase was then filtered to remove the magnesium sulfate and then transferred into a 29/32 1 L round bottom flask. The dichloromethane was removed by using a rotary evaporator at 45 °C

15 and 500 mbar. The resulting oil was transferred to a 50 mL pear shaped round bottom flask and a PTFE coated stirbar was added. The flask was then fitted with a distillation train, two-neck round bottom flask, and a gas adapter and connected to a Schlenk line. Using an oil bath, the reaction solution was slowly heated to 180 °C. Residual methyl glyoxylate was distilled off at 90 – 180 °C and 0.1 mbar. The collection flask was then

20 swapped, and the desired product was pulled off as a distillate at 180 °C and 0.01 mbar. The distilled product was used for polymerization.

### Claims

1. Compound having the structure (I) or (II) or (V)



5 wherein

R<sup>1</sup> is -H, -CH<sub>2</sub>OH or -CH(OH)CH<sub>2</sub>OH;

R<sup>2</sup> is -H, -OH, or -CH<sub>2</sub>OH;

R<sup>3</sup> is -H, -OH, or -CH<sub>2</sub>OH;

10 R<sup>10</sup> is hydrogen or a hydrocarbon moiety with 1 to 20 carbon atoms, wherein each hydrogen atom of the hydrocarbon moiety may optionally be substituted with a C<sub>1</sub>-C<sub>4</sub>-alkyl group or a halogen atom;

n is 0 or 1;

p is 0 or 1;

R is either -Z-F or Y, and

15 wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>, -NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>, and

20 Y is hydrogen or a linear, branched or cyclic organic residue having 1 to 20 carbon atoms

wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group,

with the proviso that



if R is Y and n is 0 at least one of R<sup>1</sup> or R<sup>2</sup> is not hydrogen.

2. Compound according to claim 1,

wherein R is -Z-F, wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms,  
5 optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and  
F is -COOH, -CH(COOH)<sub>2</sub>, -COOR<sup>4</sup>, -CHO, -CH(CHO)<sub>2</sub>, -C<sub>2</sub>H<sub>3</sub>, -C<sub>2</sub>H, -N<sub>3</sub>,  
-NH<sub>2</sub>, -NHR<sup>7</sup>, -OH, -CH(CH<sub>2</sub>OH)<sub>2</sub>.

in particular wherein R is -(CH<sub>2</sub>)<sub>m</sub>COOH; -C<sub>6</sub>H<sub>4</sub>COOH, wherein the aromatic ring  
is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -  
10 C<sub>6</sub>H<sub>10</sub>COOH, wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-  
alkyl groups; -(CH<sub>2</sub>)<sub>m</sub>CH(COOH)<sub>2</sub>;

-(CH<sub>2</sub>)<sub>m</sub>COOR<sup>4</sup>; -C<sub>6</sub>H<sub>4</sub>COOR<sup>4</sup>, wherein the aromatic ring is optionally substituted  
with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>COOR<sup>4</sup>, wherein the  
aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -

15 (CH<sub>2</sub>)<sub>m</sub>CH(COOR<sup>4</sup>)<sub>2</sub>;

-(CH<sub>2</sub>)<sub>m</sub>CHO; -C<sub>6</sub>H<sub>4</sub>CHO, wherein the aromatic ring is optionally substituted with  
1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>CHO, wherein the  
aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -  
20 (CH<sub>2</sub>)<sub>m</sub>CH(CHO)<sub>2</sub>;

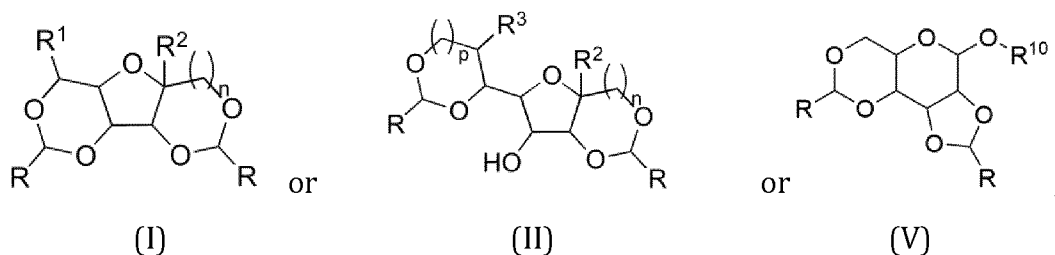
-(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H<sub>3</sub>; -C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H<sub>3</sub>, wherein the aromatic ring is optionally substituted with  
1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>C<sub>2</sub>H<sub>3</sub>, wherein the  
aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; -  
25 (CH<sub>2</sub>)<sub>m</sub>CH(C<sub>2</sub>H<sub>3</sub>)<sub>2</sub>;

-(CH<sub>2</sub>)<sub>m</sub>C<sub>2</sub>H; -C<sub>6</sub>H<sub>4</sub>C<sub>2</sub>H, wherein the aromatic ring is optionally substituted with 1  
to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>C<sub>2</sub>H, wherein the aliphatic  
ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;

-(CH<sub>2</sub>)<sub>m</sub>N<sub>3</sub>; -C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>, wherein the aromatic ring is optionally substituted with 1 to  
4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>N<sub>3</sub>, wherein the aliphatic ring  
is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;

30 -(CH<sub>2</sub>)<sub>m</sub>NH<sub>2</sub>; -C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, wherein the aromatic ring is optionally substituted with  
1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; -C<sub>6</sub>H<sub>10</sub>NH<sub>2</sub>, wherein the

- aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; –  
(CH<sub>2</sub>)<sub>m</sub>CH(NH<sub>2</sub>)<sub>2</sub>;  
–(CH<sub>2</sub>)<sub>m</sub>NHR<sup>7</sup>; –C<sub>6</sub>H<sub>4</sub>NHR<sup>7</sup>, wherein the aromatic ring is optionally substituted  
with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; –C<sub>6</sub>H<sub>10</sub>NHR<sup>7</sup>, wherein the  
5 aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; –  
(CH<sub>2</sub>)<sub>m</sub>CH(NHR<sup>7</sup>)<sub>2</sub>;  
–(CH<sub>2</sub>)<sub>m</sub>OH; –C<sub>6</sub>H<sub>4</sub>OH, wherein the aromatic ring is optionally substituted with 1  
to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms; –C<sub>6</sub>H<sub>10</sub>OH, wherein the aliphatic  
ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or  
10 –(CH<sub>2</sub>)<sub>m</sub>CH(CH<sub>2</sub>OH)<sub>2</sub>;  
wherein R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl group;  
m is an integer from 0 to 10, in particular from 0 to 4; and R<sup>7</sup> is a C<sub>1</sub>-C<sub>4</sub>-alkyl  
group.
3. Compound according to claim 2, wherein n is 0 and R<sup>2</sup> is –H.
- 15 4. Compound according to claim 2 or claim 3, wherein R is –(CH<sub>2</sub>)<sub>m</sub>COOR<sup>4</sup>; –  
C<sub>6</sub>H<sub>4</sub>COOR<sup>4</sup>, wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-  
alkyl groups; –C<sub>6</sub>H<sub>10</sub>COOR<sup>4</sup>, wherein the aliphatic ring is optionally substituted  
with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or –(CH<sub>2</sub>)<sub>m</sub>CH(COOR<sup>4</sup>)<sub>2</sub>, wherein m is 0 to 4, and R<sup>4</sup>  
is a C<sub>1</sub>-C<sub>4</sub>-alkyl group, in particular wherein R<sup>4</sup> is –CH<sub>3</sub> and m is 0.
- 20 5. Compound according to any one of claims 1 to 4, wherein the compound has the  
structure (I), and wherein m is 0.
6. Compound according to claim 1, wherein Y a linear or branched organic residue  
with 1 to 10 carbon atoms, preferably 1 to 7 carbon atoms, most preferably 1 to 3  
carbon atoms.
- 25 7. Method for the preparation of a compound according to any one of claims 1 to 6  
or a composition comprising at least two different compounds according to any  
one of claims 1 to 6, having one of the structures (I) or (II)



wherein

R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined in any one of claims 1 to 6, comprising the

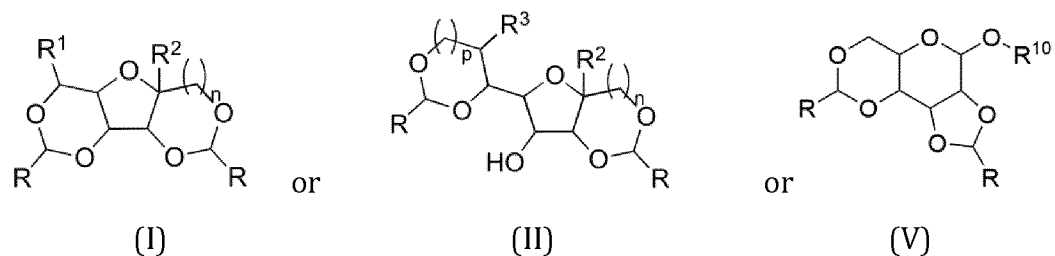
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- a. providing a carbohydrate or a lignocellulose-containing composition;
- b. adding an aldehyde optionally comprising at least one functional group selected from the group consisting of carboxylic acid, carboxylic amide, ether, alkyne, alkene, aldehyde, chloride, hydroxyl, azide, carboxylic acid ester, aldehyde, vinyl, and amine to the carbohydrate or to the lignocellulose-

10

- c. heating the mixture under acidic conditions; and
- d. separating, in particular isolating, the compound according to any one of claims 1 to 6 or the composition comprising at least two different compounds

15



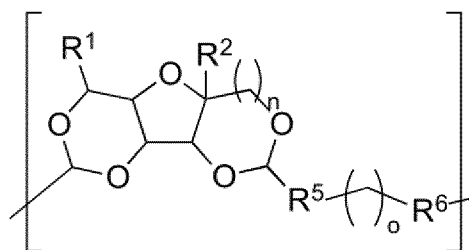
wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined in any one of claims 1 to 6.

8. Method according to claim 7, wherein the aldehyde of step b) is selected from a

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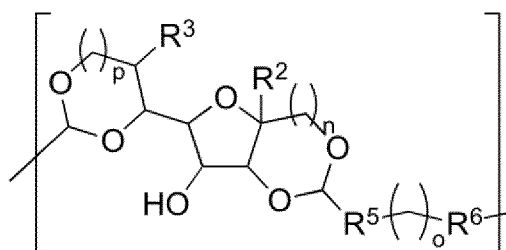
group consisting of acetaldehyde, propionaldehyde, isobutyraldehyde, glyoxylic acid, dialdehyde, cyclopropanecarboxaldehyde, isobutyraldehyde, pivaldehyde, tolualdehyde, and benzaldehyde.

9. Method according to any one of claims 7 or 8, wherein the carbohydrate is an aldopentose, an aldohexose, an aldoheptose, a ketohexose, a ketoheptose or a mixture thereof, preferably wherein the carbohydrate is selected from the group consisting of ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, glucoheptose, mannoheptose, psicose, fructose, sorbose, tagatose, sedoheptulose, mannoheptulose, taloheptulose, alloheptulose, and mixtures thereof, more preferably, wherein the carbohydrate is xylose or glucose, or a mixture thereof; or wherein the lignocellulose-containing composition has a lignin content of 20 to 40 wt.%, based on the total weight of the lignocellulose-containing composition and/or wherein the aldehyde has the formula R-CHO, wherein R is as defined in claim 1.
10. Method according to any one of claims 7 to 9, wherein the aldehyde has the formula  $\text{CHO}-(\text{CH}_2)_m\text{COOH}$ ;  $\text{CHO}-\text{C}_6\text{H}_4\text{COOH}$ , wherein the aromatic ring is optionally substituted with 1 to 4  $\text{C}_1\text{-C}_4$ -alkyl groups;  $\text{CHO}-\text{C}_6\text{H}_{10}\text{COOH}$ , wherein the aliphatic ring is optionally substituted with 1 to 4  $\text{C}_1\text{-C}_4$ -alkyl groups; or  $\text{CHO}-(\text{CH}_2)_m\text{CH}(\text{COOH})_2$ , and wherein the method comprises the additional step of adding a  $\text{C}_1\text{-C}_4$ -alkylalcohol, preferably methanol, after step c. and before step d.
11. Method according to any one of claims 7 to 10, wherein the mixture is heated at 50 to 120 °C, preferably at 60 to 110 °C, more preferably at 60 to 110 °C, most preferably at 60 to 85 °C and/or wherein the heating is conducted at a pressure of 70 to 130 mbar, preferably at 80 to 120 mbar, more preferably at 90 to 110 mbar.
12. Method according to any one of claims 7 to 11, wherein the lignocellulose-containing composition is biomass, in particular lignocellulosic biomass.
13. Polymer comprising as repeat unit



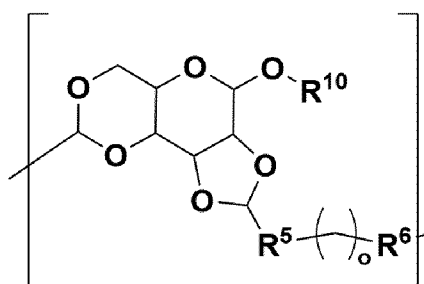
(III)

and/or



(IV)

and/or



(VI)

wherein

10

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>10</sup>, n, and p are as defined in claim 1; and

R<sup>5</sup> is -Z-F<sup>1</sup>- or Y<sup>1</sup> and R<sup>6</sup> is -F<sup>2</sup>-Z- or Y<sup>1</sup>, wherein Z is a hydrocarbon moiety with 0 to 10 carbon atoms, optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms, and wherein F<sup>1</sup> is -C(=O)O-, -OC(=O)-, -

C(=O)NR<sup>8</sup>-, -R<sup>8</sup>NC(=O)-, or a covalent bond, and F<sup>2</sup> is -OC(=O)-, -C(=O)O-, -

15

R<sup>8</sup>NC(=O)-, -C(=O)NR<sup>8</sup>-, or a covalent bond, and

Y<sup>1</sup> is a linear, branched or cyclic organic residue having 1 to 20 carbon atoms, in particular wherein

R<sup>5</sup> is  $-(\text{CH}_2)_m\text{C}(=\text{O})\text{O}-$  and R<sup>6</sup> is  $-\text{OC}(=\text{O})(\text{CH}_2)_m-$ ; or

R<sup>5</sup> is  $-\text{C}_6\text{H}_4\text{C}(=\text{O})\text{O}-$  and R<sup>6</sup> is  $-\text{OC}(=\text{O})\text{C}_6\text{H}_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms;

or

5 R<sup>5</sup> is  $-\text{C}_6\text{H}_{10}\text{C}(=\text{O})\text{O}-$  and R<sup>6</sup> is  $-\text{OC}(=\text{O})\text{C}_6\text{H}_{10}-$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is  $-(\text{CH}_2)_m\text{OC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{O}(\text{CH}_2)_m-$ ; or

R<sup>5</sup> is  $-\text{C}_6\text{H}_4\text{OC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{OC}_6\text{H}_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms;

10 or

R<sup>5</sup> is  $-\text{C}_6\text{H}_{10}\text{OC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{OC}_6\text{H}_{10}-$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is  $-(\text{CH}_2)_m\text{C}(=\text{O})\text{NR}^8-$  and R<sup>6</sup> is  $-\text{R}^8\text{NC}(=\text{O})(\text{CH}_2)_m-$ ; or

R<sup>5</sup> is  $-\text{C}_6\text{H}_4\text{C}(=\text{O})\text{NR}^8-$  and R<sup>6</sup> is  $-\text{R}^8\text{NC}(=\text{O})\text{C}_6\text{H}_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms;

15 or

R<sup>5</sup> is  $-\text{C}_6\text{H}_{10}\text{C}(=\text{O})\text{NR}^8-$  and R<sup>6</sup> is  $-\text{R}^8\text{NC}(=\text{O})\text{C}_6\text{H}_{10}-$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups; or

R<sup>5</sup> is  $-(\text{CH}_2)_m\text{R}^8\text{NC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{NR}^8(\text{CH}_2)_m-$ ; or

20 R<sup>5</sup> is  $-\text{C}_6\text{H}_4\text{R}^8\text{NC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{NR}^8\text{C}_6\text{H}_4-$ , wherein the aromatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups or 1 to 4 halogen atoms;

or

R<sup>5</sup> is  $-\text{C}_6\text{H}_{10}\text{R}^8\text{NC}(=\text{O})-$  and R<sup>6</sup> is  $-\text{C}(=\text{O})\text{NR}^8\text{C}_6\text{H}_{10}-$ , wherein the aliphatic ring is optionally substituted with 1 to 4 C<sub>1</sub>-C<sub>4</sub>-alkyl groups;

25 wherein R<sup>8</sup> is H or a C<sub>1</sub>-C<sub>4</sub>-alkyl group;

m is an integer from 0 to 10, in particular from 0 to 4; and

o is an integer from 2 to 10, in particular from 2 to 4.

with the proviso that

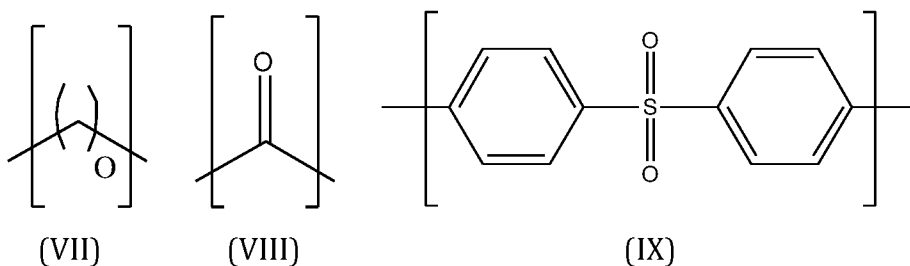
if R<sup>5</sup> and R<sup>6</sup> are Y<sup>1</sup> and n is 0 at least one of R<sup>1</sup> or R<sup>2</sup> is not hydrogen.

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14. Polymer according to claim 13, wherein the polymer comprises the repeat unit with the structure (III), wherein  $n$  and  $R^2$  are as defined in claim 3 and  $R^1$  is H or  $\text{CH}_2\text{OH}$ , in particular  $R^1$  is H, and  $m$  are as defined in claim 5.

15. Polymer according to claim 13 or 14, wherein  $R^5$  is  $-\text{C}(=\text{O})\text{O}-$  and  $R^6$  is  $-\text{OC}(=\text{O})-$  and  $o$  is 2.

16. Method for the preparation of a polymer according to any one of claims 13 to 15, wherein at least one compound according to any one of claims 1 to 6 is subjected to a reaction, optionally with a compound with the formula  $R^9\text{-L-R}^{9A}$ , wherein L is selected from the group consisting of  $(\text{CH}_2)_o$  (VII), CO (VIII) and diphenyl sulfone (IX)



$R^9$  and  $R^{9A}$  are independently selected from the group consisting of  $-\text{OR}^{11}$ ,  $-\text{OH}$ ,  $-\text{NR}^8$ ,  $-\text{COOH}$ ,  $-\text{COOR}^4$  and a halogen atom;

wherein  $R^{11}$  is selected from the group consisting of aryl and alkyl or  $R^{11}$  of residue  $R^9$  and  $R^{11}$  of residue  $R^{9A}$  form together a ring system;

wherein the halogen atom is selected from the group consisting of fluorine, chlorine, bromine and iodine;

wherein  $R^8$  is as defined in claim 13;

wherein  $R^4$  is as defined in claim 2 or 4; and

$o$  is as defined in claim 13 or 15.

17. Method for the preparation of a polymer according to claim 16, wherein  $R^9$  and  $R^{9A}$  are identical.

18. Method according to any of claims 16 or 17, wherein L is  $(\text{CH}_2)_o$  (VII).

19. Method for the preparation of a polymer according to any of claims 16 or 17, R<sup>9</sup>-L-R<sup>9A</sup> is a bis-(4-halogenphenyl) sulfone, in particular bis-(4-chlorophenyl) sulfone or a bis-(4-fluorophenyl) sulfone.
20. Method for the preparation of a polymer according any of claims 16 or 17,  
5 wherein  
R<sup>9</sup>-L-R<sup>9A</sup> is an organic carbonate, preferably  
a dialkyl carbonate, preferably dimethyl carbonate, diethyl carbonate or methyl  
ethylcarbonate;  
a diaryl carbonate, preferably diphenyl carbonate or dimethylphenyl carbonate;  
10 or  
a cyclic carbonate, preferably ethylene carbonate or trimethylene carbonate.
21. Method according to any of claims 16 to 20, wherein the reaction is conducted in the presence of a catalyst and/or an initiator and/or at a temperature of 30 to 250 °C.
- 15 22. Use of a polymer according to any one of claims 13 to 15 for the manufacture of sheets, fibers or molded objects, in particular as a replacement for poly(ethylene terephthalate).



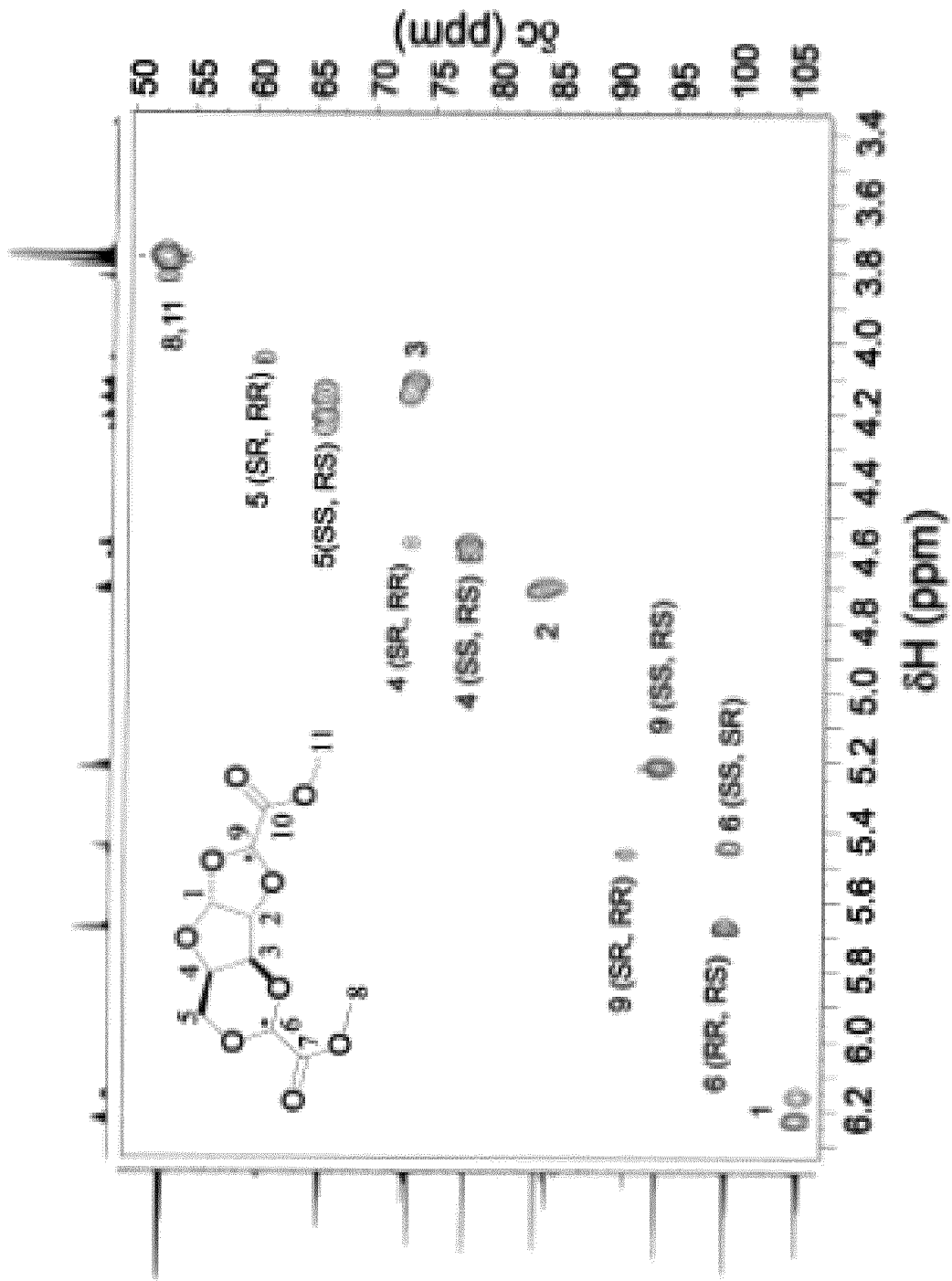


Figure 1

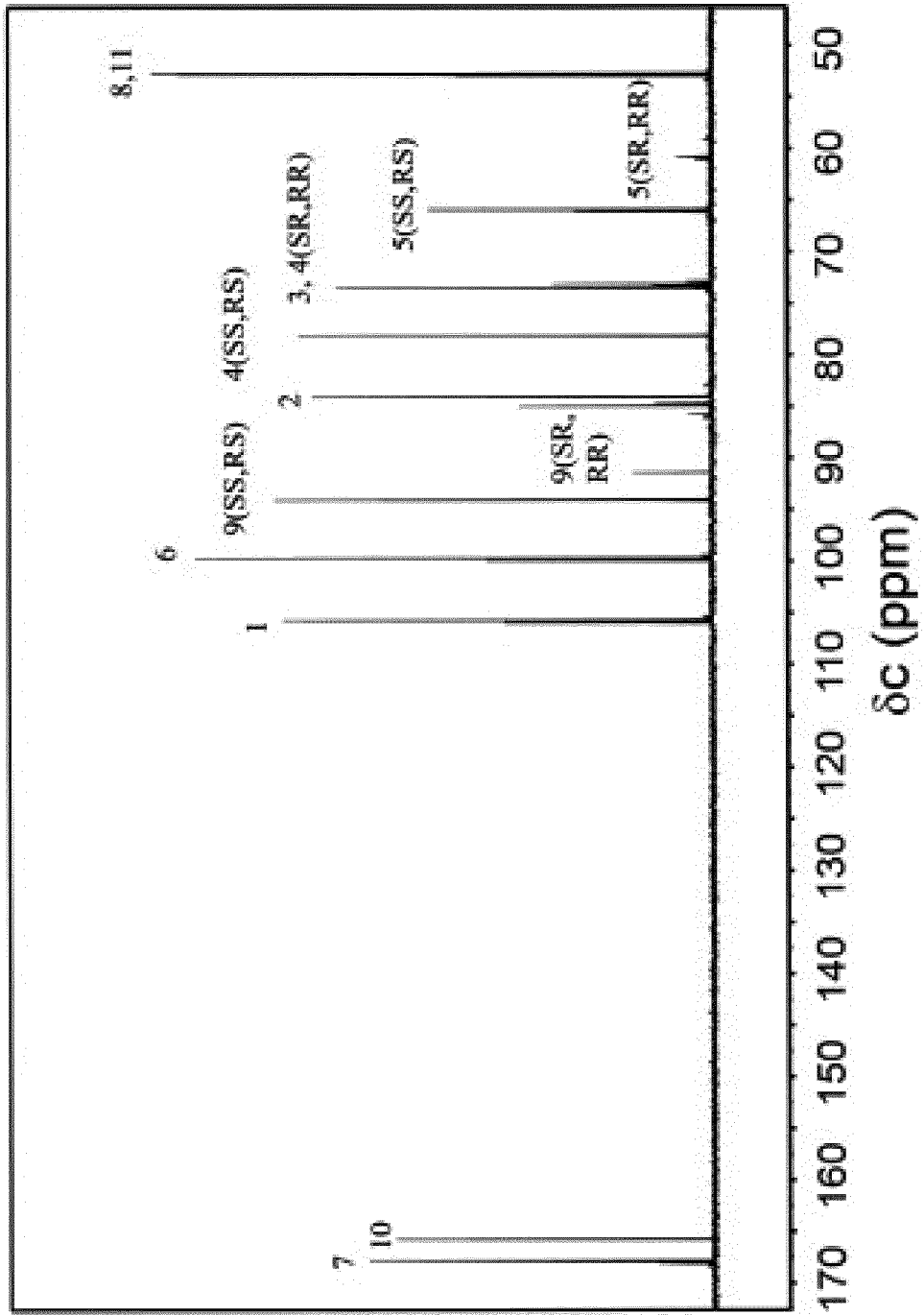


Figure 2

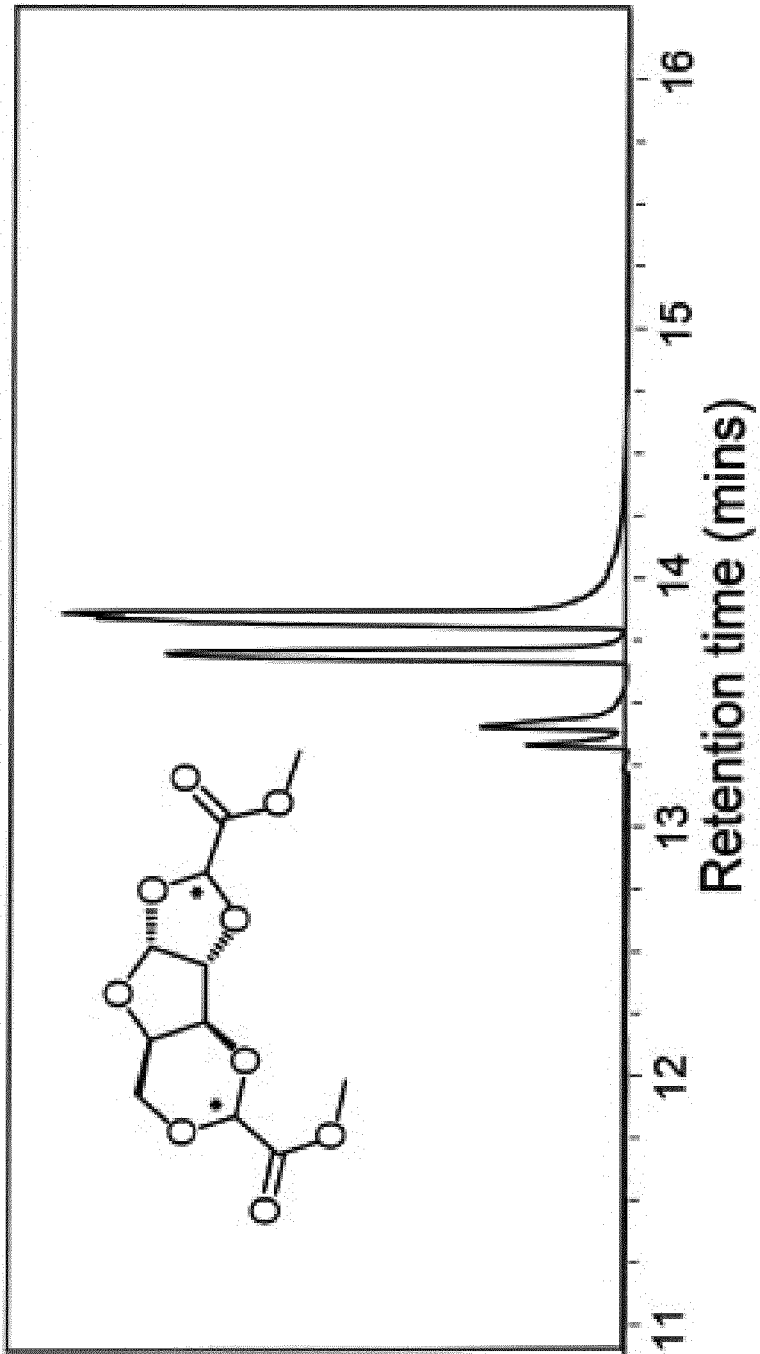


Figure 3

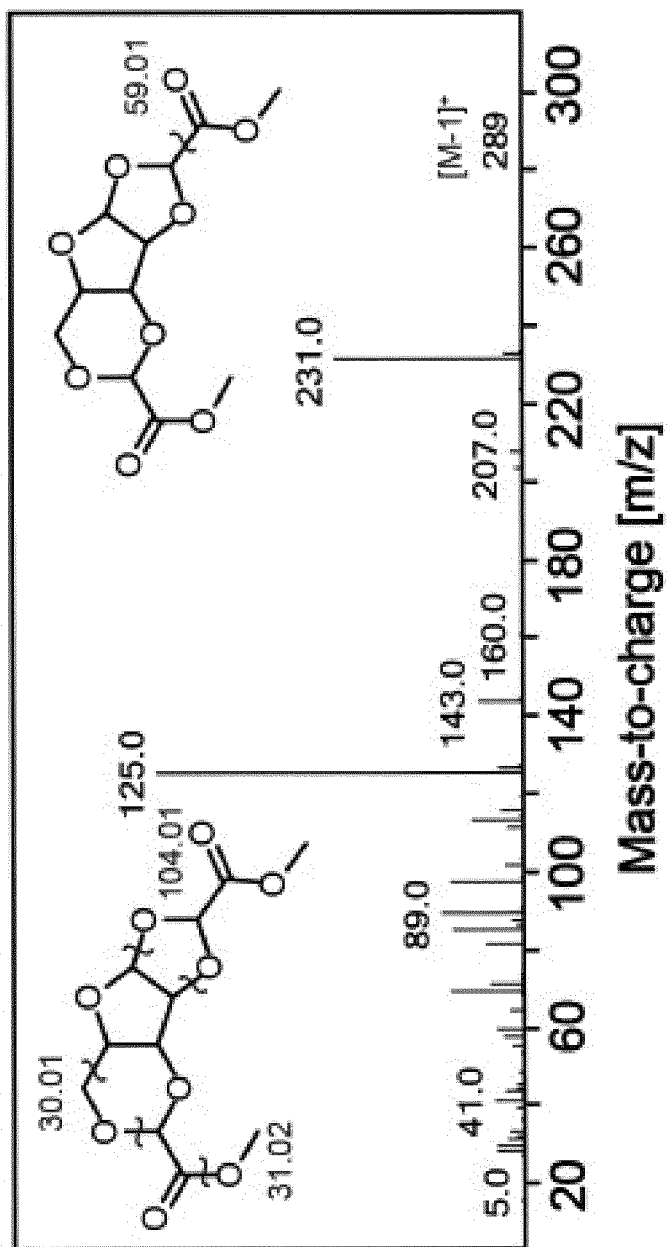


Figure 4

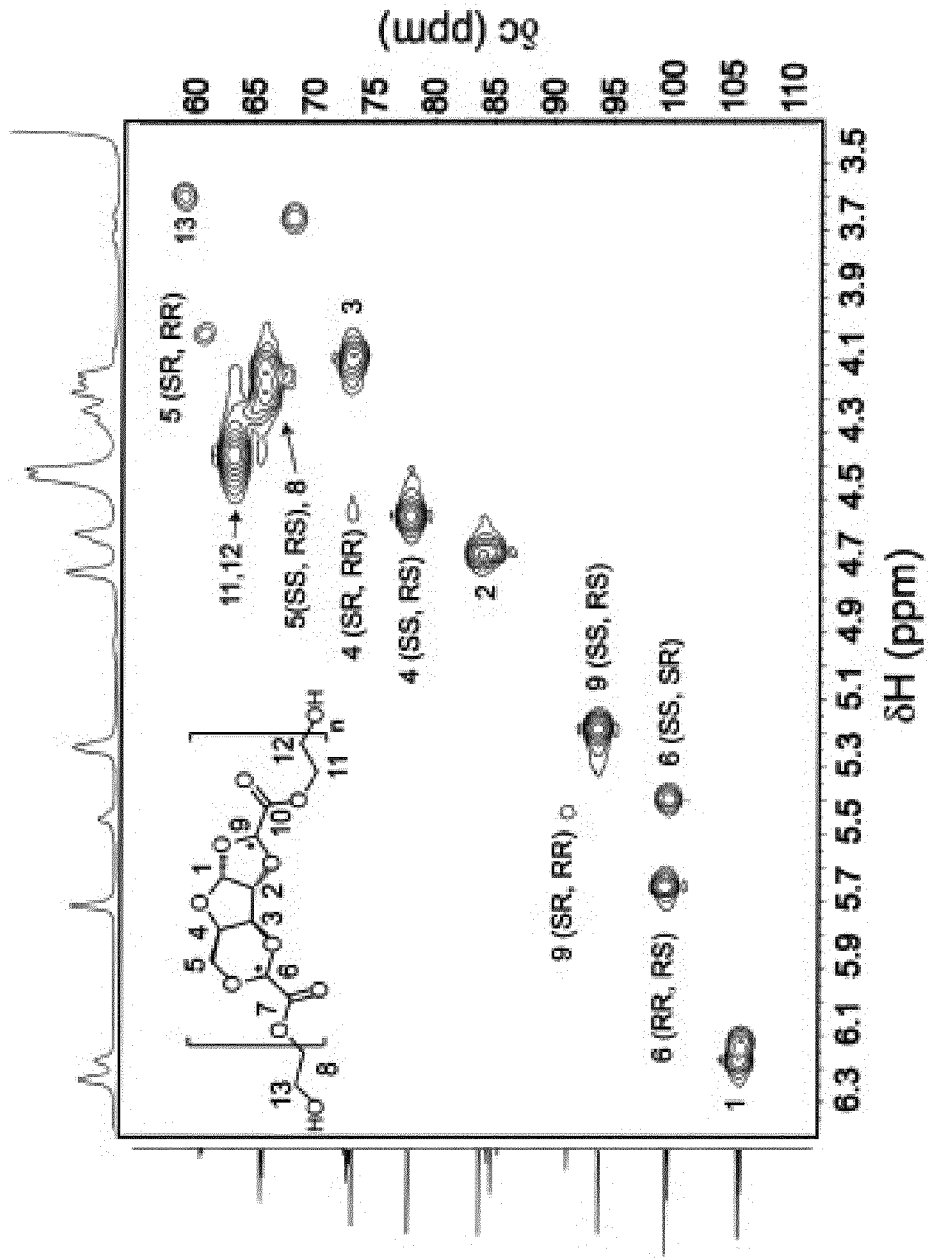


Figure 5

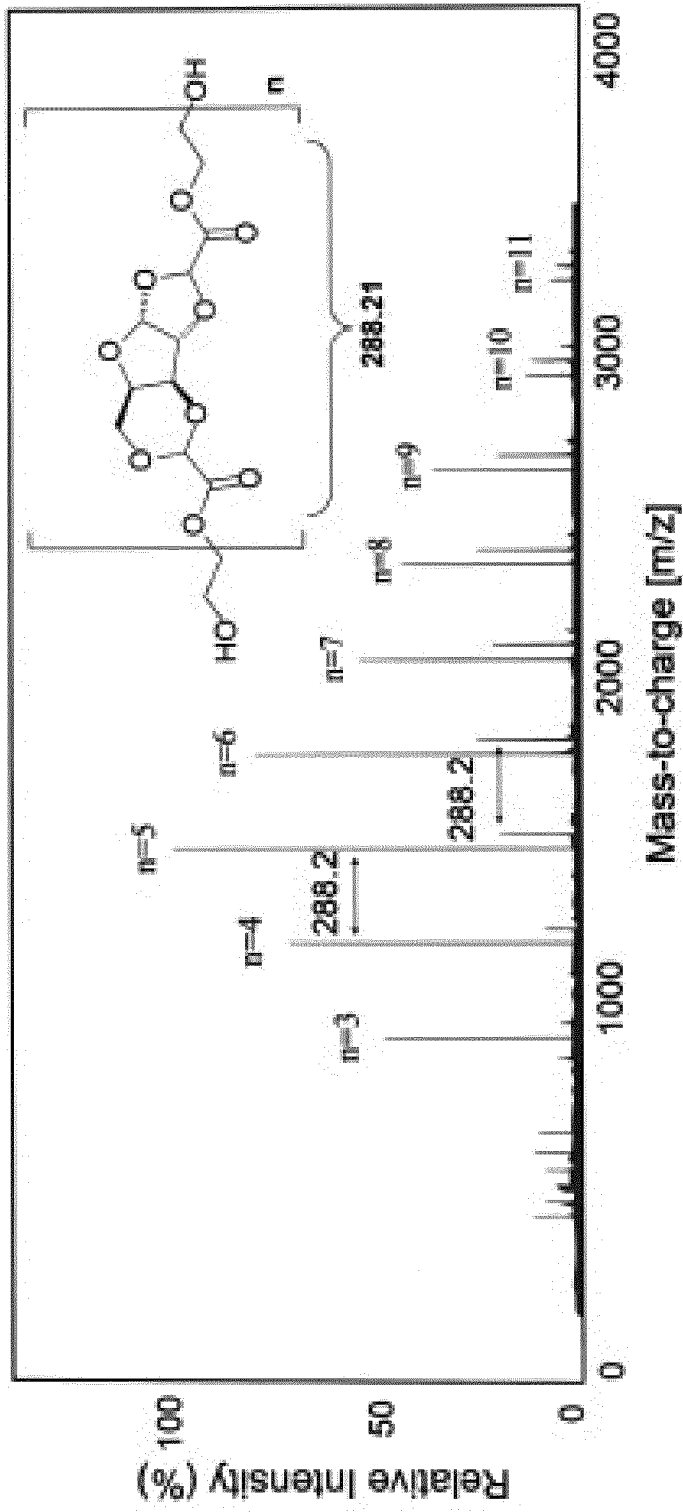


Figure 6

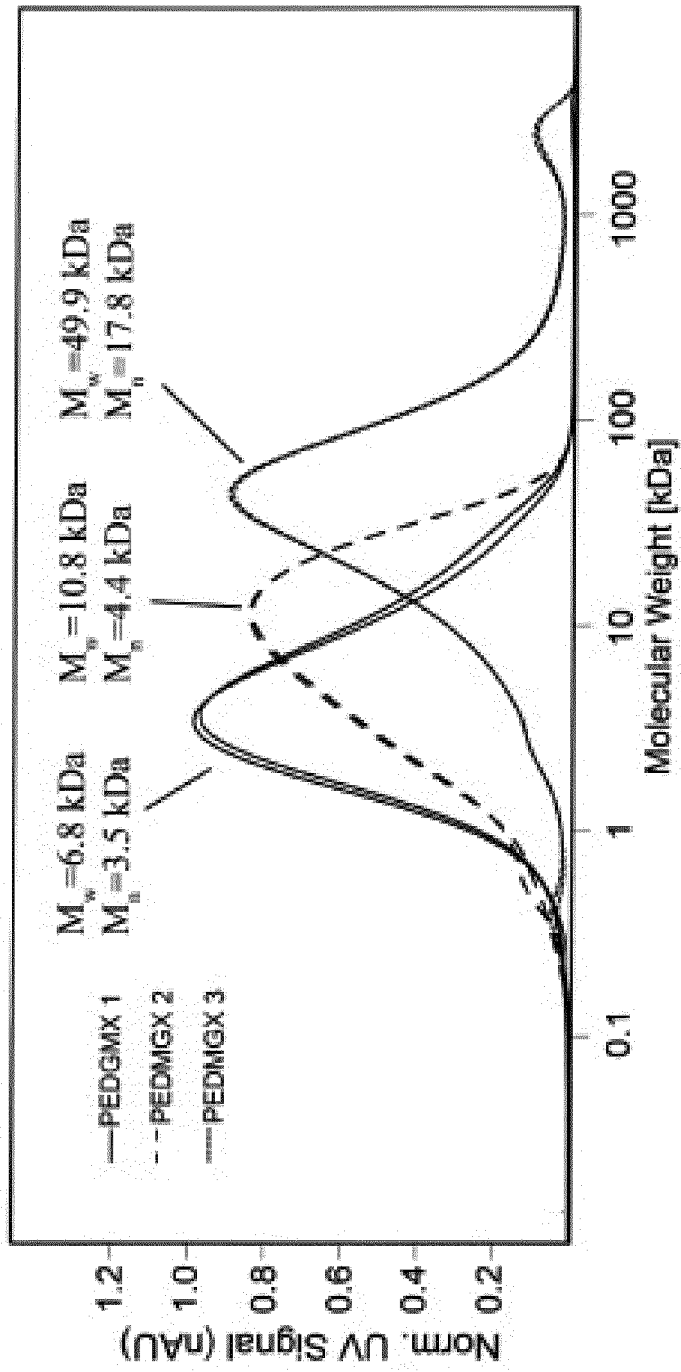


Figure 7

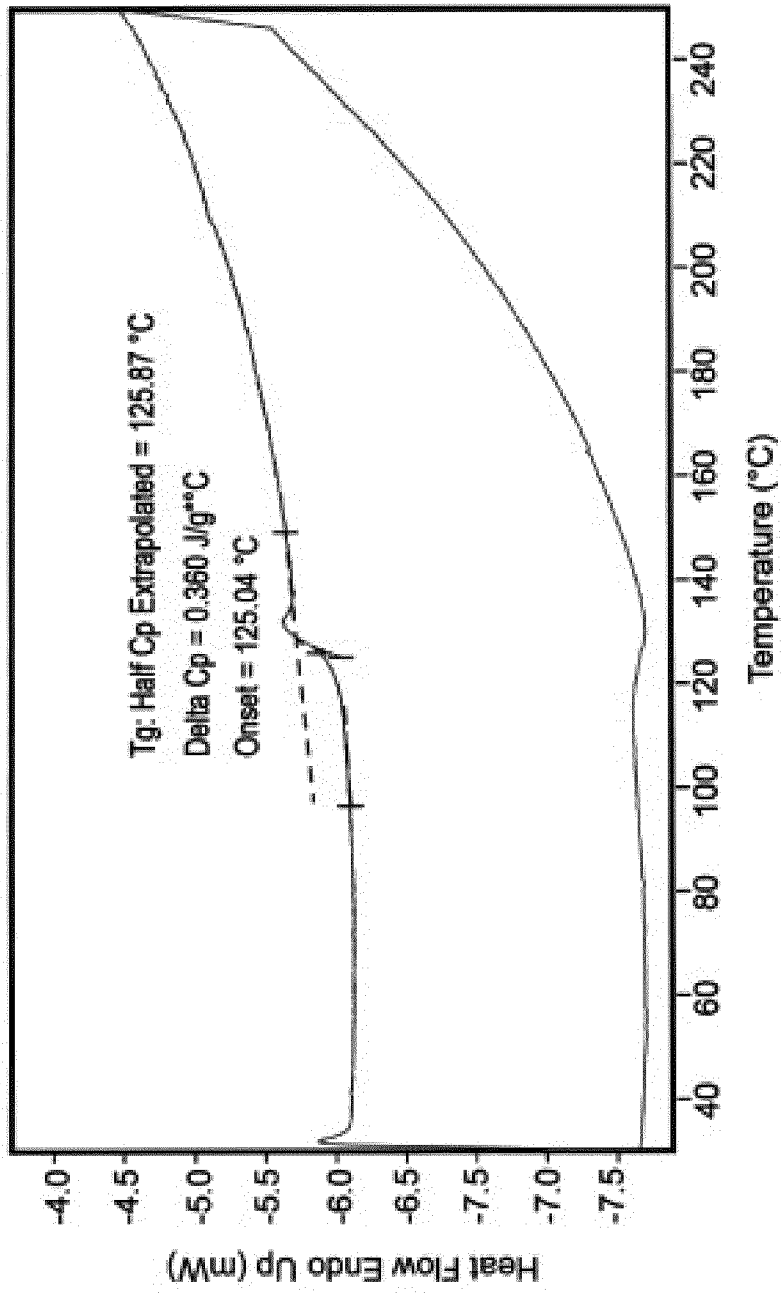


Figure 8



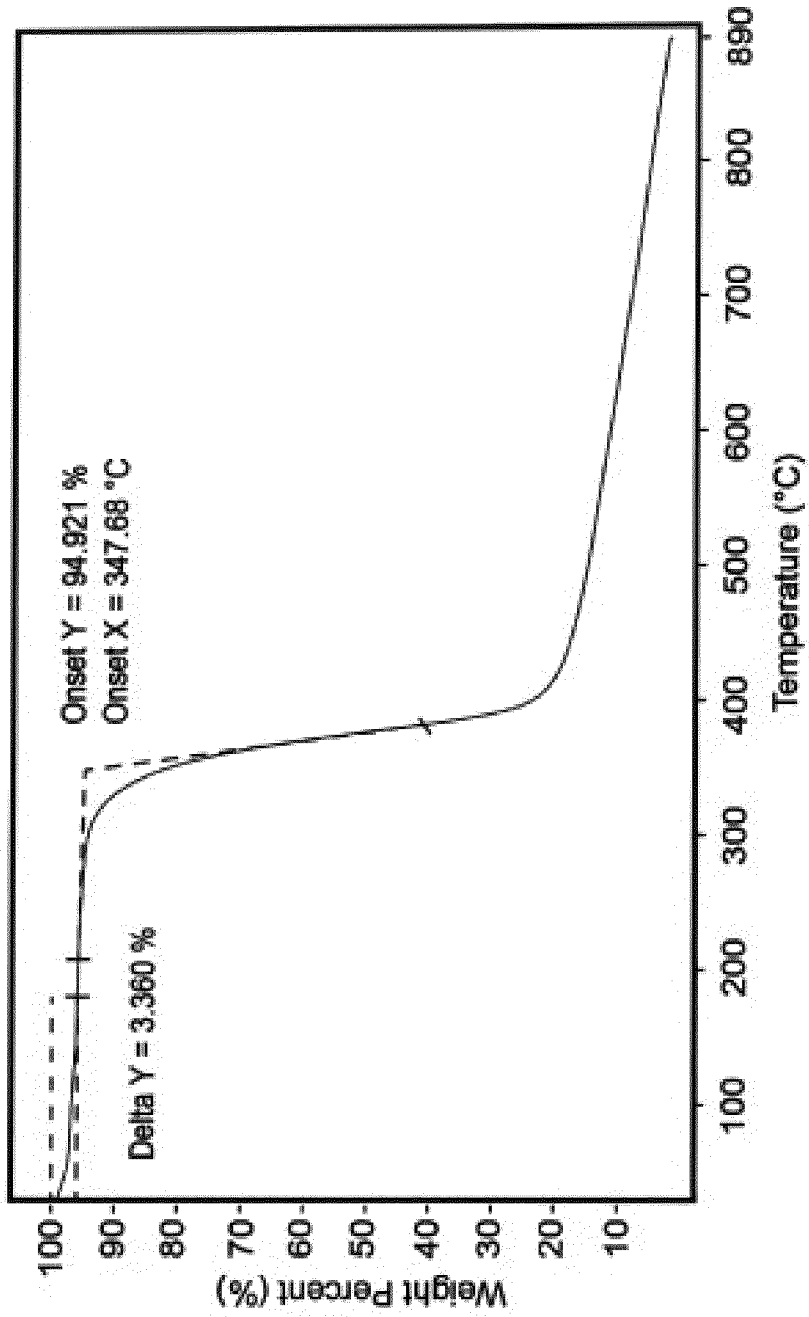


Figure 9

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2020/078874

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07H9/04 C07D493/14 C08G63/42  
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)  
C07H C07D 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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP WO20 1102 1398 A1 (UENOYAMA YOSHITAKA ET AL.) 17 January 2013 (2013-01-17) cited in the application Abstract; examples.	1-22
A	-& Yoshitaka Uenoyama ET AL: "JP 2011/021398 A1. English machine translation.",  17 January 2013 (2013-01-17), pages 1-62, XP055680661, Retrieved from the Internet: URL:https://aipn.j-platpat.inpit.go.jp/p0200 [retrieved on 2020-03-30] DESC pages 3-4: claim 1; DESC pages 10-11: claims 13-22, and paragraph [0001]. ----- -/--	1-22

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  10 December 2020	Date of mailing of the international search report  23/12/2020
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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  Weisbrod, Thomas
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2020/078874

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017/178513 A1 (ECOLE POLYTECHNIQUE FEDERALE LAUSANNE) 19 October 2017 (2017-10-19) Abstract; claims 1-2; page 30, line 30 to page 9, line 37; page 13, lines 14-21. -----	1-22
X	WOOD ET AL.: "1,2:3,5-Di-O-benzylidene-[alpha]-D-glucose", J. AM. CHEM. SOC., vol. 79, no. 14, 1 July 1957 (1957-07-01), pages 3862-3864, XP055758369, US ISSN: 0002-7863, DOI: 10.1021/ja01571a064 Page 3863, compound (I). -----	1,5
X	KLEMER ET AL.: "Reaktionen von Acetalen der L-Sorbose mit n-Butyllithium", CHEM. BER., vol. 113, no. 5, 1 January 1980 (1980-01-01), pages 1761-1767, XP055758386, DE ISSN: 0009-2940, DOI: 10.1002/cber.19801130511 Page 1762, compound 4. -----	1,5
X	FRANZKOWIAK ET AL.: "Synthese phosphat-verbrückter d-glucose-einheiten als teilstrukturen phosphorylierter stärken", CARBOHYDRATE RESEARCH, vol. 158, 1 December 1986 (1986-12-01), pages 13-35, XP055758376, GB ISSN: 0008-6215, DOI: 10.1016/0008-6215(86)84003-4 Page 16, compound 12. -----	1,5
X	WINN; GOODMAN: "Studies on the formation of a tricyclic C <sup>2</sup> -symmetric sulfide", TETRAHEDRON LETT., vol. 42, no. 40, 1 October 2001 (2001-10-01), pages 7091-7093, XP004317899, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(01)01455-1 Page 7092, scheme 1: compound 8. -----	1,5
	-/--	

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/078874

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>CHAKRABORTY ET AL.: "Synthesis and conformational studies of peptidomimetics containing furanoid sugar amino acids and a sugar diacid",            J. ORG. CHEM.,            vol. 65, no. 20,            6 October 2000 (2000-10-06), pages            6441-6457, XP002223135,            ISSN: 0022-3263, DOI: 10.1021/J0000408E            Page 6444, scheme 3: compound 28.</p> <p style="text-align: center;">-----</p>	1,5
X	<p>FERRIER; HATTON: "The acid-catalysed condensation of d-xylose with benzaldehyde in the presence of alcohols. Two diastereoisomeric 1,2:3,5-di-O-benzylidene-[alpha]-d-xylofuranoses",            CARBOHYDRATE RESEARCH,            vol. 5, no. 2, 1 January 1967 (1967-01-01),            pages 132-139, XP055680773,            GB            ISSN: 0008-6215, DOI:            10.1016/S0008-6215(00)86035-8            Page 134, compound 6, 7.</p> <p style="text-align: center;">-----</p>	1,5
X	<p>YÜCEER: "Formation of the butylidene acetates of [alpha]-chloralose",            CARBOHYDRATE RESEARCH,            vol. 56, no. 1, 1 June 1977 (1977-06-01),            pages 87-91, XP055758630,            GB            ISSN: 0008-6215, DOI:            10.1016/S0008-6215(00)84239-1            Page 88, compounds 2, 3, 11.</p> <p style="text-align: center;">-----</p>	1,5,6
X	<p>FORSEN ET AL.: "Trichloroethylidene Derivatives of D-Glucose",            ACTA CHEMICA SCANDINAVICA,            vol. 19, 1 January 1965 (1965-01-01),            pages 359-369, XP055758653,            The whole document: dichloralglucose A, C, D, E.</p> <p style="text-align: center;">-----</p>	1,6
X	<p>GENG ET AL.: "Organocatalysis for the Acid-Free O -Arylidenation of Carbohydrates",            EUR. J. ORG. CHEM.,            vol. 2013, no. 31,            2 November 2013 (2013-11-02), pages            7035-7040, XP055199127,            ISSN: 1434-193X, DOI:            10.1002/ejoc.201301116            Page 7037, compounds 6e, 6h; page 7038,            compound 9e.</p> <p style="text-align: center;">-----</p>	1
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2020/078874

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MUKHERJEE ET AL.: "Tandem Acetalation-Acetylation of Sugars and Related Derivatives with Enolacetates under Solvent-Free Conditions", J. ORG. CHEM., vol. 72, no. 23, 1 November 2007 (2007-11-01), pages 8965-8968, XP055758670, Japan ISSN: 0022-3263, DOI: 10.1021/jo070363i Page 8966, scheme 1: compound 4. -----	1,6
X	GUIZO ET AL.: "Methylene acetals as protecting groups - an improved preparation method", TETRAHEDRON LETT., vol. 38, no. 24, 16 June 1997 (1997-06-16), pages 4291-4294, XP004074814, ISSN: 0040-4039, DOI: 10.1016/S0040-4039(97)00882-4 Page 4293, compound 2g. -----	1
X	HONEYMAN; MORGAN: "Reactions of methyl [alpha]-D-mannoside with aldehydes", J. CHEM. SOC., 1954, pages 744-746, XP055758693, ISSN: 0368-1769, DOI: 10.1039/JR9540000744 Page 745, line 14; methyl 2:3-4:6-di-0-ethylidene-alpha-D-mannoside; page 746, lines 23, 38: methyl 2:3-4:6-di-0-propylidene-alpha-D-mannoside, methyl 2:3-4:6-di-0-benzylidene-alpha-D-mannoside . -----	1,6
X	JEDLINSKI ET AL.: "Synthesis and configuration of some dialkenylidene derivatives of methyl [alpha]-d-mannopyranoside", CARBOHYDRATE RESEARCH, vol. 42, no. 2, 1 July 1975 (1975-07-01), pages 227-231, XP055758707, GB ISSN: 0008-6215, DOI: 10.1016/S0008-6215(00)84264-0 Page 228, table 1: all compounds, and compounds 3-7, 9. ----- -/--	1,2,6

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2020/078874

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MASLINSKA-SOLICH ET AL.: "The formation of a cyclic diacetal of methyl [alpha]-D-mannopyranoside with a 16-membered macrocyclic loop", CHEM. COMMUN., no. 9, 19 April 2002 (2002-04-19), pages 984-985, XP055758729, ISSN: 1359-7345, DOI: 10.1039/b202273g Page 984, scheme 2: compound 4. -----	1
X	DATABASE REGISTRY [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; 27 May 2011 (2011-05-27), XP002801433, Database accession no. 1301732-70-6 abstract -----	1,2,6

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP2020/078874

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: **1, 5-9, 11, 12, 16-21(all partially)**  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
**see FURTHER INFORMATION sheet PCT/ISA/210**
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box II.2

Claims Nos.: 1, 5-9, 11, 12, 16-21(all partially)

The application relates to renewable monomers and polymers thereof. However, the claims 1, 3, 5-9, 11-12, and 16-21 relate also to compounds (I), (II), and (V) which do not comprise a polymerizable group, i.e. when R is Y. Contrary to Article 6 PCT, it is not evident which relevant technical problem might be solved by subject-matter referring to compounds wherein Y is R. In addition, the initial phase of the search revealed a very large number of documents relevant to the issue of novelty of claim 1 and dependent claims when R is Y. So many documents were retrieved that it is impossible to determine which Y values may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, the search with regard to compounds (I), (II), and (V) has been limited to embodiments wherein R is -Z-F.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) PCT declaration be overcome.



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/EP2020/078874

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP W02011021398 A1	17-01-2013	JP W02011021398 A1	17-01-2013
		TW 201120063 A	16-06-2011
		WO 2011021398 A1	24-02-2011
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WO 2017178513 A1	19-10-2017	BR 112018071060 A2	07-05-2019
		CA 3029301 A1	19-10-2017
		CN 109328185 A	12-02-2019
		EP 3442938 A1	20-02-2019
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