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(54) Title: PROCESS FOR THE PREPARATION OF POLYESTERS USING TEREPHTHALIC ACID

(57) Abstract: A special process for preparing polyesters from at least terephthalic acid, one or more alkylene glycols and one or more substances resulting in terminal groups is described. The process e.g. possesses the advantage that low levels of side products are generated. The polyesters may be used as soil release polymers, in particular in laundry detergent compositions.

WO 2025/132402 A1

PROCESS FOR THE PREPARATION OF POLYESTERS USING TEREPHTHALIC ACID

The invention relates to a process for preparing polyesters, products or polyesters obtainable by the process, the use of the products or polyesters as soil release polymers and laundry detergent compositions comprising the products or polyesters.

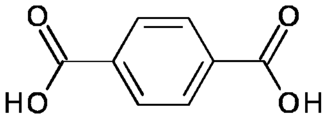
Polyesters based on dimethyl terephthalate and their use as soil release polymers especially in laundry detergent compositions are already known. GB 1,466,639, US 4,132,680, US 4,702,857, EP 0 199 403, US 4,711,730, US 4,713,194, and US 4,759,876 describe polyesters based on dimethyl terephthalate and their use as soil release polymers and disclose aqueous detergent compositions containing soil release polymers.

However, processes of the prior art for preparing soil release polymers often result in the formation of significant amounts of side products, e.g., dioxane, sublimated dimethyl terephthalate, and/or methanol.

Therefore, it was an object of the present invention to provide a process for the preparation of polyesters which might be used as soil release polymers during which a low amount of side products is generated.

It has been found that this object can be solved by a process for preparing a polyester by reacting at least

- terephthalic acid (formula (I))



(I)

and

- one or more alkylene glycols of the formula (II)

$$HO\text{-}(C_nH_{2n})\text{-}OH \qquad (II)$$

or mixtures thereof wherein (C_nH_{2n}) is a linear or branched alkylene group with n being an integer of from 2 to 10 or mixtures thereof, preferably with n being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof,

and

- one or more substances of the formula (III)

$$R^1\text{-}(OR^2)_a\text{-}OH \qquad \text{(III)}$$

or mixtures thereof wherein

R^1 is a linear or branched, preferably a linear, alkyl group comprising from 1 to 30 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 30 carbon atoms or mixtures thereof,
preferably is a linear or branched, preferably a linear, alkyl group comprising from 1 to 20 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 20 carbon atoms or mixtures thereof,

a is, based on a molar average, a number of from 1 to 200, preferably of from 2 to 200, more preferably of from 3 to 150, and

R^2 is a linear or branched alkylene group (C_mH_{2m}) with m being an integer of from 2 to 10 or mixtures thereof, preferably with m being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof, particularly preferably is (C_2H_4) or a mixture of (C_2H_4) and (C_3H_6), and extraordinarily preferably is (C_2H_4),

characterized in that the preparation of the polyester comprises the steps of:

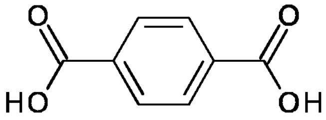
a) heating a mixture comprising terephthalic acid and one or more alkylene glycols of the formula (II) or mixtures thereof and removing water until the acid value of the system is reduced to 50 mg KOH/g or lower, preferably to 30 mg KOH/g or lower, more preferably to 15 mg KOH/g or lower, even more preferably to 10 mg KOH/g or lower, particularly preferably to 6 mg KOH/g or lower, and extraordinarily preferably to 4 mg KOH/g or lower;

b) combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a), preferably adding one or more substances of the formula (III) or mixtures thereof to the mixture obtained in step a)
and

c) polycondensing the mixture obtained in step b) under ambient pressure or reduced pressure, preferably under reduced pressure, while removing alkylene glycols of the formula (II) and preferably also side products.

Therefore, a subject matter of the invention is a process for preparing a polyester by reacting at least

- terephthalic acid (formula (I))



(I)

and

- one or more alkylene glycols of the formula (II)

$$HO\text{-}(C_nH_{2n})\text{-}OH \qquad (II)$$

or mixtures thereof wherein (C_nH_{2n}) is a linear or branched alkylene group with n being an integer of from 2 to 10 or mixtures thereof, preferably with n being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof,

and

- one or more substances of the formula (III)

$$R^1\text{-}(OR^2)_a\text{-}OH \qquad (III)$$

or mixtures thereof wherein

R^1 is a linear or branched, preferably a linear, alkyl group comprising from 1 to 30 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 30 carbon atoms or mixtures thereof,
preferably is a linear or branched, preferably a linear, alkyl group comprising from 1 to 20 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 20 carbon atoms or mixtures thereof,

a is, based on a molar average, a number of from 1 to 200, preferably of from 2 to 200, more preferably of from 3 to 150, and

R^2 is a linear or branched alkylene group (C_mH_{2m}) with m being an integer of from 2 to 10 or mixtures thereof, preferably with m being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof, particularly preferably is (C_2H_4) or a mixture of (C_2H_4) and (C_3H_6), and extraordinarily preferably is (C_2H_4),

characterized in that the preparation of the polyester comprises the steps of:

a) heating a mixture comprising terephthalic acid and one or more alkylene glycols of the formula (II) or mixtures thereof and removing water until the acid value of the system is reduced to 50 mg KOH/g or lower, preferably to 30 mg KOH/g or lower, more preferably to 15 mg KOH/g or lower, even more preferably to 10 mg KOH/g or lower, particularly preferably to 6 mg KOH/g or lower, and extraordinarily preferably to 4 mg KOH/g or lower;

b) combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a), preferably adding one or more substances of the formula (III) or mixtures thereof to the mixture obtained in step a)
and

c) polycondensing the mixture obtained in step b) under ambient pressure or reduced pressure, preferably under reduced pressure, while removing alkylene glycols of the formula (II) and preferably also side products.

WO 2016/146429 A1 describes polyesters obtainable from the dicarboxylic acid terephthalic acid and, where appropriate, isophthalic acid, and from ethylene glycol and polyethylene glycol, with average molecular weights ranging between 2000 g/mol and 8000 g/mol.

DE 44 17 686 A1 describes a process for preparing polyesters, wherein a dicarboxylic acid HOOC-Ph-COOH or its reactive derivative is reacted with a monomeric diol under esterification conditions, subsequently is reacted with a polymeric diol under transesterification conditions and is reacted with a monocarboxylic acid, hydroxymonocarboxylic acid, and/or dicarboxylic acid monoester under esterification conditions.

EP 1 734 171 A1 describes a fiber-treating agent, e.g., comprising a polyester compound produced by carrying out a condensation polymerization of a polyoxyalkylene monol, an alkylene glycol, and at least one member selected from the group consisting of aromatic dicarboxylic acids and their ester-forming derivatives.

WO 2021/233987 A1 describes a process for the preparation of a polyester comprising the steps of: heating one or more substances of the formula Q1-OOC-C_6H_4-COO-Q2, wherein Q1 and Q2, independently of one another, are selected from the group consisting of H and (C_1-C_4)-alkyl and preferably are CH_3, and

1,2-propyleneglycol, and one or more specific (poly)alkylene glycol mono C_7-C_{30} alkyl or alkenyl ethers or mixtures thereof, with the addition of a catalyst, to temperatures of from 160 to 220 °C, preferably beginning at atmospheric pressure, and then continuing the reaction under reduced pressure at temperatures of from 160 to 240 °C.

The inventive process possesses the advantage that low levels of side products such as dioxane, sublimated dimethyl terephthalate, and/or methanol are generated. The process is more sustainable compared to processes from the prior art based on dimethyl terephthalate as the yield per ton of monomers is higher and the mass of side products is lower. The process leads to products which possess good soil release properties.

Different grades of terephthalic acid can be used in the inventive process.

In one preferred embodiment of the invention, combinations of purified and non-purified terephthalic acid can be used, more preferably comprising at least 50 wt.-%, even more preferably comprising at least 80 wt.-%, and particularly preferably comprising 100 wt.-% purified terephthalic acid, in each case based on the total weight of terephthalic acid used in the inventive process.

In another preferred embodiment of the invention, combinations of recycled and non-recycled terephthalic acid can be used, more preferably comprising at least 50 wt.-%, even more preferably comprising at least 80 wt.-%, and particularly preferably comprising 100 wt.-% recycled terephthalic acid, in each case based on the total weight of terephthalic acid used in the inventive process.

The process of obtaining recycled terephthalic acid by hydrolysis of polyethylene terephthalate is known to the person skilled in the art. For example, it is available via the process described in V. Tournier et al., Nature, Vol. 580, 9. April 2020, p.216-219.

In another preferred embodiment of the invention, combinations of renewable and non-renewable terephthalic acid can be used, more preferably comprising at least 50 wt.-%, even more preferably comprising at least 80 wt.-%, and particularly preferably comprising 100 wt.-% renewable terephthalic acid, in each case based on the total weight of terephthalic acid used in the inventive process.

The process of obtaining renewable terephthalic acid is known to the person skilled in the art. US 2023/0125062 describes systems and methods for producing aromatic compounds such as para-xylene in high yield from oxygenated hydrocarbons such as carbohydrates, sugars, sugar alcohols, sugar degradation products, and the like. Renewable terephthalic acid can be obtained by oxidation of para-xylene.

Examples for the one or more alkylene glycols of the formula (II) or mixtures thereof are ethylene glycol, 1,2-propyleneglycol, 1,3-propyleneglycol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol, 2,2-dimethyl-1,3-propanediol, 1,2-pentanediol, 1,5-pentanediol, 1,2-hexanediol, 1,6-hexanediol or mixtures thereof.

In the case that more than one alkylene glycol of the formula (II) is used in the inventive process, the definition of "n" may vary between those alkylene glycols.

In a preferred embodiment of the invention, the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a) are selected from the group consisting of ethylene glycol, propylene glycol, and mixtures of ethylene glycol and propylene glycol, more preferably are selected from the group consisting of propylene glycol and mixtures of ethylene glycol and propylene glycol and even more preferably the alkylene glycol of the formula (II) used in step a) is propylene glycol.

In another preferred embodiment of the inventive process, combinations of recycled and non-recycled alkylene glycols of the formula (II) or mixtures thereof can be used, more preferably comprising at least 50 wt.-%, even more preferably comprising at least 80 wt.-%, and particularly preferably comprising 100 wt.-% recycled alkylene glycols of the formula (II) or mixtures thereof, in each case based on the total weight of alkylene glycols of the formula (II) or mixtures thereof used in the inventive process.

In another preferred embodiment of the inventive process, combinations of renewable and non-renewable alkylene glycols of the formula (II) or mixtures thereof can be used, more preferably comprising at least 50 wt.-%, even more preferably comprising at least 80 wt.-%, and particularly preferably comprising 100 wt.-% renewable alkylene glycols of the formula (II) or mixtures thereof, in each case based on the total weight of alkylene glycols of the formula (II) or mixtures thereof used in the inventive process.

Examples of the alkyl and alkenyl groups R^1 in the one or more substances of the formula (III) or mixtures thereof are, for example, methyl, ethyl, linear or branched propyl, butyl, pentyl, hexyl, heptyl, octyl (e.g., capryl), nonyl, decyl, undecyl, dodecyl, tridecyl (e.g. isotridecyl), tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, icosyl, henicosyl, docosyl, tricosyl, tetraicosyl, vinyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, octadecadienyl, octadecatrienyl, nonadecenyl, eicosenyl, eicosadienyl, eicosatetraenyl, docosenyl, docosahexaenyl, tetracosenyl, or mixtures thereof.

The groups R^1 in the one or more substances of the formula (III) or mixtures thereof may also be mixtures which have been derived or obtained from natural sources and comprise one or more alkyl and/or one or more alkenyl groups and in case these mixtures comprise one or more alkenyl groups, they may also be partially or totally hydrogenated. Examples of such mixtures are cocoyl, partially or totally hydrogenated variants of cocoyl, talloyl or partially or totally hydrogenated variants of talloyl.

In a preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 1 to 18 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 18 carbon atoms or mixtures thereof.

In a more preferred embodiment of the invention, R^1 in the one or substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 10 to 18 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 10 to 18 carbon atoms or mixtures thereof.

In an even more preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 10 to 16 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 10 to 16 carbon atoms or mixtures thereof.

In another preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 1 to 20 and preferably from 1 to18 carbon atoms, or mixtures thereof.

In another more preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is methyl.

In another more preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 10 to 20 carbon atoms or mixtures thereof.

In another even more preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 10 to 18 carbon atoms or mixtures thereof.

In a particularly preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is a linear or branched, preferably a linear, alkyl group comprising from 10 to 16 carbon atoms or mixtures thereof.

In another preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is selected from the group consisting of linear or branched alkyl groups comprising from 10 to 16 carbon atoms (such as lauryl, myristyl or isotridecyl), cocoyl, partially or totally hydrogenated variants of cocoyl, talloyl, partially or totally hydrogenated variants of talloyl and mixtures thereof, more preferably is selected from the group consisting of linear or branched, preferably linear, alkyl groups comprising from 10 to 16 carbon atoms, talloyl, partially or totally hydrogenated variants of talloyl and mixtures thereof, even more preferably is selected from the group consisting of linear or branched, preferably linear, alkyl groups comprising from 10 to 16 carbon atoms, partially or totally hydrogenated variants of talloyl and mixtures thereof and particularly preferably is selected from the group consisting of lauryl, myristyl, partially or totally hydrogenated variants of talloyl and mixtures thereof.

In an extraordinarily preferred embodiment of the invention, R^1 in the one or more substances of the formula (III) or mixtures thereof is selected from the group consisting of lauryl, myristyl and mixtures thereof.

In a preferred embodiment of the invention, in the one or more substances of the formula (III) or mixtures thereof, at least a part of the groups R^2 are (CH_2CH_2) groups. More preferably, in the one or more substances of the formula (III) or mixtures thereof, at least 50 mol-%, even more preferably at least 60 mol-% and particularly preferably at least 70 mol-% of the groups R^2, in each case based on the total amount of the groups R^2, are (CH_2CH_2) groups.

In the one or more substances of the formula (III) or mixtures thereof, the groups R^2 extraordinarily preferably are (CH_2CH_2) groups or a mixture of (CH_2CH_2) groups and (C_3H_6) groups, wherein preferably at least 50 mol-%, more preferably at least 60 mol % and even more preferably at least 70 mol-% of the groups R^2, in each case based on the total amount of the groups R^2, are (CH_2CH_2) groups and especially preferably, the groups R^2 are (CH_2CH_2) groups.

In another preferred embodiment of the invention, in the one or more substances of the formula (III) or mixtures thereof, at least a part of the groups R^2 are (CH_2CH_2) groups made from renewable ethylene oxide. More preferably, in the one or more substances of the formula (III) or mixtures thereof, at least 50 mol-%, even more preferably at least 60 mol-% and particularly preferably at least 70 mol-% of the groups R^2, in each case based on the total amount of the groups R^2, are (CH_2CH_2) groups made from renewable ethylene oxide.

In the one or more substances of the formula (III) or mixtures thereof, the groups R^2 extraordinarily preferably are (CH_2CH_2) groups made from renewable ethylene oxide or a mixture of (CH_2CH_2) groups made from renewable ethylene oxide and (C_3H_6) groups, wherein preferably at least 50 mol-%, more preferably at least 60 mol % and even more preferably at least 70 mol-% of the groups R^2, in each case based on the total amount of the groups R^2, are (CH_2CH_2) groups made from renewable ethylene oxide and especially preferably, the groups R^2 are (CH_2CH_2) groups made from renewable ethylene oxide.

In the case that at least two different types of $[O(C_mH_{2m})]$ groups, for example $[O(C_2H_4)]$, $[O(C_3H_6)]$, and $[O(C_4H_8)]$ groups, exist in the one or more substances of the formula (III) or mixtures thereof, they may be arranged blockwise, alternating, periodically and/or statistically, preferably blockwise and/or statistically. This means that in a substance of the formula (III), the $[O(C_mH_{2m})]$ groups, and, e.g., the groups $[O(C_2H_4)]$, $[O(C_3H_6)]$ and $[O(C_4H_8)]$, may be arranged, for example, in a purely statistically or blockwise form but may also be arranged in a form which could be considered as both statistical and blockwise, e.g., small blocks of $[(OC_2H_4)]$ and $[O(C_3H_6)]$ arranged in a statistical manner, or in a form wherein adjacent instances of statistical and blockwise arrangements of the groups $[O(C_2H_4)]$, $[O(C_3H_6)]$, and $[O(C_4H_8)]$ exist.

Any of the groups $[O(C_mH_{2m})]$, e.g., any of the groups $[O(C_2H_4)]$, $[O(C_3H_6)]$, and $[O(C_4H_8)]$, can be linked to R^1- and -OH in a substance of the formula (III). This means, for example, that both, R^1- and -OH in a substance of the formula (III), may be connected to a $[O(C_2H_4)]$ group, they may both be connected to a $[O(C_3H_6)]$ group, they may both be connected to a $[O(C_4H_8)]$ group, or they may be connected to different groups $[O(C_mH_{2m})]$, e.g., selected from $[O(C_2H_4)]$, $[O(C_3H_6)]$ and $[O(C_4H_8)]$.

In a preferred embodiment of the invention, the one or more substances of the formula (III) or mixtures thereof are of the formula (III-1)

$$R^1\text{-}(OC_2H_4)_b\text{-}(OC_3H_6)_c\text{-}OH \qquad \text{(III-1)}$$

or mixtures thereof, wherein

R^1 has the meaning as described above for formula (III), the -(OC_2H_4) groups and the -(OC_3H_6) groups are arranged blockwise, alternating, periodically and/or statistically, preferably blockwise, wherein the block consisting of the -(OC_3H_6) groups is bound to -OH,

b is, based on a molar average, a number of from 1 to 199, preferably of from 2 to 199, more preferably of from 3 to 149, even more preferably of from 12 to 120 and particularly preferably of from 40 to 50,

c is, based on a molar average, a number of from 1 to 199, preferably of from 1 to 10 and more preferably of from 1 to 7, and

the sum b + c is, based on a molar average, a number less than or equal to 200 and preferably a number less than or equal to 150.

In the one or more substances of the formula (III-1) or mixtures thereof, preferably at least 50 mol-%, more preferably at least 60 mol-% and even more preferably at least 70 mol-% of the groups (OC_2H_4) and (OC_3H_6), in each case based on the total amount of the groups (OC_2H_4) and (OC_3H_6), are (OCH_2CH_2) groups.

In the one or more substances of the formula (III-1) or mixtures thereof, particularly preferably at least 50 mol-%, more preferably at least 60 mol-% and even more preferably at least 70 mol-% of the groups (OC_2H_4) and (OC_3H_6), in each case based on the total amount of the groups (OC_2H_4) and (OC_3H_6), are (OCH_2CH_2) groups made from renewable ethylene oxide.

Renewable ethylene oxide can be obtained from bio-ethanol, which can be obtained from natural sources like corn, sugarcane, or cellulosic biomass through fermentation. Bio-ethanol can be dehydrated to produce bio-ethylene which can be oxidized with oxygen over a silver catalyst to produce renewable ethylene oxide.

In the case that more than one substance of the formula (III) is used in the inventive process, the definition of R^1, R^2 and “a” may vary between those substances.

In the case that more than one substance of the formula (III-1) is used in the inventive process for preparing a polyester, the definition of R^1, “b” and “c” may vary between those substances.

In the inventive process, step b) is performed after step a) has been performed and step c) is performed after step b) has been performed.

When heating a mixture comprising terephthalic acid and one or more alkylene glycols of the formula (II) or mixtures thereof and removing water until the acid value of the system is reduced to 50 mg KOH/g or lower, preferably to 30 mg KOH/g or lower, more preferably to 15 mg KOH/g or lower, even more preferably to 10 mg KOH/g or lower, particularly preferably to 6 mg KOH/g or lower, and extraordinarily preferably to 4 mg KOH/g or lower in step a), e.g. monoalkyleneglycol terephthalate, dialkyleneglycol terephthalate, oligomers, polymers, and mixtures thereof are formed.

Preferably, the mixture in step a) is heated to temperatures of more than 90 °C, more preferably to temperatures of from 100 °C to 300 °C, even more preferably to temperatures of from 120 °C to 280 °C, particularly preferably to temperatures of from 140 °C to 260 °C and extraordinarily preferably to temperatures of from 160 °C to 250 °C.

In one preferred embodiment of the inventive process, heating in step a) is executed under ambient pressure or reduced pressure, more preferably under ambient pressure, to temperatures of more than 90 °C, more preferably to temperatures of from 100 °C to 300 °C, even more preferably to temperatures of from 120 °C to 280 °C, particularly preferably to temperatures of from 140 °C to 260 °C and extraordinarily preferably to temperatures of from 160 °C to 240 °C.

In another preferred embodiment of the inventive process, heating in step a) is executed partly under ambient pressure and partly under elevated pressure or completely under elevated pressure and more preferably partly under ambient pressure and partly under elevated pressure to temperatures of more than 90 °C, more preferably to temperatures of from 100 °C to 300 °C, even more preferably to temperatures of from 120 °C to 280 °C, particularly preferably to temperatures of from 140 °C to 260 °C and extraordinarily preferably to temperatures of from 160 °C to 250 °C.

The acid value of a sample taken during step a) may be determined by volumetric titration with phenolphthalein as indicator, preferably as detailed in the following: 0.5 g of a homogeneous sample, which may e.g. be a homogeneous dispersion, melt or solution, is dissolved in 60 mL isopropanol. Up to 60 mL, preferably up to 10 mL, xylene may be added to obtain a clear solution. In case no clear solution is reached, the acid value is considered not measurable, and heating in step a) is continued. Three drops of a solution of phenolphthalein in isopropanol (1.0 wt.-%) are added. The obtained solution is slowly titrated with a fresh solution of potassium hydroxide (KOH) in isopropanol (0.01 mol/L) until a color change from colorless to pink is observed. The acid value in mg KOH/g is calculated from the amount of used KOH, and from the mass of the sample according to

$$AV = \frac{V_{KOH}[mL] \cdot c_{KOH}[mol/L] \cdot M_{KOH}[g/mol]}{m_{sample}[g]}$$

wherein AV is the acid value in mg KOH/g, $V_{KOH}[mL]$ is the added volume of the fresh solution of potassium hydroxide until a color change from colorless to pink is observed in mL, $c_{KOH}[mol/L]$ is the concentration of the fresh solution of potassium hydroxide (KOH) in isopropanol (0.01 mol/L), $M_{KOH}[g/mol]$ is 56.11 g/mol, and $m_{sample}[g]$ is the mass of the sample in g.

In step b) of the inventive process, combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a) can be performed by adding one or more substances of the formula (III) or mixtures thereof and the mixture obtained in step a) in any order.

In a preferred embodiment of the inventive process, in step b), combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a) is achieved by adding one or more substances of the formula (III) or mixtures thereof to the mixture obtained in step a).

In another preferred embodiment of the inventive process, in step b), combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a) is achieved by adding the mixture obtained in step a) to one or more substances of the formula (III) or mixtures thereof.

In another preferred embodiment of the inventive process, in step b), combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a) is achieved by simultaneously adding the mixture obtained in step a) and one or more substances of the formula (III) or mixtures thereof to a vessel.

In step b), combining the one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a), preferably adding of the one or more substances of the formula (III) or mixtures thereof to the mixture obtained in step a) is preferably executed at temperatures of from 10 °C to 300 °C, more preferably at temperatures of from 20 °C to 280 °C, even more preferably at temperatures of from of 30 °C to 260 °C, particularly preferably at temperatures of from 40 °C to 240 °C, and extraordinarily preferably at temperatures of from 50 °C to 220 °C. In order to reach the temperature, the mixture obtained in step a) may be heated or cooled before combining it with the one or more substances of the formula (III) or mixtures thereof in step b), preferably before adding the one or more substances of the formula (III) or mixtures thereof in step b).

Polycondensing in step c) is preferably executed under a pressure of from 0.1 to 900 mbar, more preferably under a pressure of from 0.5 to 500 mbar, and preferably at temperatures of more than 90 °C, more preferably at temperatures of from 100 °C to 300 °C, even more preferably at temperatures of from 150 °C to 280 °C, particularly preferably at temperatures of from 160 °C to 270 °C and extraordinarily preferably at temperatures of from 180 °C to 260 °C.

Preferably, removal of water in step a) and/or removal of alkylene glycols of the formula (II) in step c) is achieved in part or completely by distillation.

In case removal of water in step a) is achieved partly or completely by distillation, distillation of water in the presence of one or more alkylene glycols of the formula (II) or mixtures thereof may preferably be achieved by using a fractionating column.

In step c), removing alkylene glycols of the formula (II) may include but is not limited to (i) removing alkylene glycols which have reacted, e.g., in step a) and/or step c) and are released during polycondensation, and (ii) removing alkylene glycols which have been present as a solvent and have not taken part in a reaction.

Preferably, step a) and/or step b) and/or step c), more preferably step a) and step b) and step c), are performed under protective atmosphere. Preferably, the protective atmosphere is achieved by replacing parts of the oxygen of the atmosphere by nitrogen, e.g., by alternatingly applying reduced pressure and flooding with nitrogen or by alternatingly increasing the pressure by the addition of nitrogen and releasing the pressure.

In a preferred embodiment of the invention, the molar ratio of the one or more alkylene glycols of the formula (II) or mixtures thereof to terephthalic acid (formula (I)), in step a) is at least 1.2:1.0, more preferably is at least 1.5:1.0, even more preferably is at least 1.8:1.0, particularly preferably is at least 2.0:1.0, and extraordinarily preferably is at least 2.2:1.0. Furthermore, the molar ratio of the one or more alkylene glycols of the formula (II) or mixtures thereof to terephthalic acid (formula (I)), in step a) preferably is lower than 10.0:1.0, more preferably is lower than 7.0:1.0 and even more preferably is lower than 3.0:1.0.

In another preferred embodiment of the invention, the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 1:1 to 30:1, more preferably is from 1:1 to 20:1, even more preferably is from 1:1 to 15:1, particularly preferably is from 1:1 to 10:1 and extraordinarily preferably is from 1:1 to 8:1.

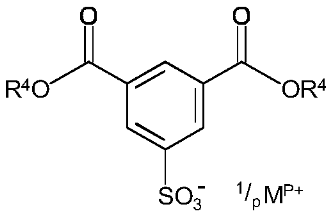
In a more preferred embodiment of the invention, the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 1:1 to 8:1, R^1 is methyl, and “a” is, based on a molar average, a number of from 1 to 150, preferably of from 10 to 100, and more preferably of from 15 to 60.

In another more preferred embodiment of the invention, the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 2:1 to 8:1, R^1 is a linear or branched alkyl group comprising from 10 to 20 carbon atoms or mixtures thereof, preferably is a linear alkyl group comprising from 10 to 16 carbon atoms or mixtures thereof, and more preferably is selected from the group consisting of lauryl, myristyl and mixtures thereof, and “a” is, based on a molar average, a number of from 60 to 150, and preferably is a number of from 70 to 140.

In a preferred embodiment of the invention, one or more alkylene glycols of the formula (II) or mixtures thereof are additionally combined in step b) with the mixture obtained in step a) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and are preferably additionally added in step b).

In case one or more alkylene glycols of the formula (II) or mixtures thereof are contained in the mixture used in step a) and one or more alkylene glycols of the formula (II) or mixtures thereof are combined in step b) with the mixture obtained in step a) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof, and preferably are added in step b), the definition of “n” may vary between the alkylene glycols of the formula (II) used in step a) and the alkylene glycols of the formula (II) combined in step b) with the mixture obtained in step a) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof, preferably added in step b).

In another preferred embodiment of the invention, one or more substances of the formula (IV) or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably are added in step b)



(IV)

wherein

$^{1}/_{p}$ M^{p+} is a cation, preferably selected from the group consisting of monovalent cations M^+ (p = 1), divalent cations ½ M^{2+} (p = 2) and trivalent cations ⅓ M^{3+} (p = 3) and more preferably selected from the group consisting of H^+, Li^+, Na^+, K^+, ½ Mg^{2+}, ½ Ca^{2+}, ⅓ Al^{3+}, NH_4^+ and $R_aR_bR_cR_dN^+$, wherein R_a, R_b, R_c and R_d, independently of one another, are H, linear or branched, preferably linear, alkyl groups comprising from 1 to 22 carbon atoms or linear or branched, preferably linear, hydroxyalkyl groups comprising from 2 to 10 carbon atoms, and wherein in the cations $R_aR_bR_cR_dN^+$ at least one of R_a, R_b, R_c and R_d is not H,

R^4 is H or an alkyl group comprising from 1 to 4 carbon atoms, preferably is H or methyl, and more preferably is methyl.

Typically, such further substances of the formula (IV) or mixtures thereof would be used in a molar ratio of the one or more substances of the formula (IV) or mixtures thereof to the terephthalic acid (formula (I)) of less than 1:2, and preferably of less than 1:3.

In another preferred embodiment of the invention, one or more polyalkyleneglycols of the formula (V) or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably are added in step b)

$$H\text{-}(OR^3)_d\text{-}OH \qquad (V)$$

wherein

R^3 is a linear or branched alkylene group (C_pH_{2p}), with p being an integer of from 2 to 10 or mixtures thereof, preferably with p being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof, and particularly preferably is (C_2H_4), and

d is, based on a molar average, a number of from 2 to 200, preferably of from 4 to 150, more preferably of from 10 to 120 and even more preferably of from 35 to 120.

In a preferred embodiment of the invention, in the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, at least a part of the groups R^3 are (CH_2CH_2) groups. More preferably, in the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, at least 50 mol-%, even more preferably at least 60 mol-% and particularly preferably at least 70 mol-% of the groups R^3, in each case based on the total amount of the groups R^3, are (CH_2CH_2) groups.

In the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, the groups R^3 extraordinarily preferably are (CH_2CH_2) groups or a mixture of (CH_2CH_2) groups and (C_3H_6) groups, wherein preferably at least 50 mol-%, more preferably at least 60 mol % and even more preferably at least 70 mol-% of the groups R^3, in each case based on the total amount of the groups R^3, are (CH_2CH_2) groups and especially preferably, the groups R^3 are (CH_2CH_2) groups.

In another preferred embodiment of the invention, in the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, at least a part of the groups R^3 are (CH_2CH_2) groups made from renewable ethylene oxide. More preferably, in the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, at least 50 mol-%, even more preferably at least 60 mol-% and particularly preferably at least 70 mol-% of the groups R^3, in each case based on the total amount of the groups R^3, are (CH_2CH_2) groups made from renewable ethylene oxide.

In the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, the groups R^3 extraordinarily preferably are (CH_2CH_2) groups made from renewable ethylene oxide or a mixture of (CH_2CH_2) groups made from renewable ethylene oxide and (C_3H_6) groups, wherein preferably at least 50 mol-%, more preferably at least

60 mol % and even more preferably at least 70 mol-% of the groups R^3, in each case based on the total amount of the groups R^3, are (CH_2CH_2) groups made from renewable ethylene oxide and especially preferably, the groups R^3 are (CH_2CH_2) groups made from renewable ethylene oxide.

In the case that at least two different types of [$O(C_pH_{2p})$] groups, for example [$O(C_2H_4)$], [$O(C_3H_6)$], and [$O(C_4H_8)$] groups, exist in the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, they may be arranged blockwise, alternating, periodically and/or statistically, preferably blockwise and/or statistically. This means that in a polyalkyleneglycol of the formula (V), the [$O(C_pH_{2p})$] groups, and, e.g., the groups [$O(C_2H_4)$], [$O(C_3H_6)$], and [$O(C_4H_8)$], may be arranged, for example, in a purely statistically or blockwise form but may also be arranged in a form which could be considered as both statistical and blockwise, e.g., small blocks of [$O(C_2H_4)$] and [$O(C_3H_6)$] arranged in a statistical manner, or in a form wherein adjacent instances of statistical and blockwise arrangements of different [$O(C_pH_{2p})$] groups, e.g., the groups [$O(C_2H_4)$], [$O(C_3H_6)$], and [$O(C_4H_8)$], exist.

Within the structure element $-(OR^3)_d-$ in a polyalkyleneglycol of the formula (V), any of the groups [$O(C_pH_{2p})$], e.g., any of the groups [$O(C_2H_4)$], [$O(C_3H_6)$] and [$O(C_4H_8)$], can form an end group of the structure element $-(OR^3)_d-$. This means, for example, that the two end groups of the structure element $-(OR^3)_d-$ in a polyalkyleneglycol of the formula (V) may be formed by [$O(C_2H_4)$] groups, may be formed by [$O(C_3H_6)$] groups, may be formed by [$O(C_4H_8)$] groups or may be formed by different [$O(C_pH_{2p})$] groups, e.g., different groups selected from [$O(C_2H_4)$], [$O(C_3H_6)$] and [$O(C_4H_8)$].

In the case that more than one polyalkyleneglycol of the formula (V) is used in the inventive process, the definition of R^3 and “d” may vary between those polyalkyleneglycols.

Typically, such further substances of the formula (V) or mixtures thereof would be used in a molar ratio of the one or more polyalkyleneglycols of the formula (V) or mixtures thereof to the one or more alkylene glycols of the formula (II) or mixtures thereof of less than 1:2, preferably of less than 1:3 and more preferably of less than 1:4.

In another preferred embodiment of the invention, one or more crosslinking compounds, preferably having 3 to 6 functions capable of polycondensation, or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b).

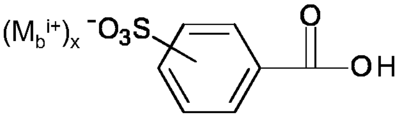
For example, compounds with multiple hydroxyl functions such as triols (e.g., glycerol or 1,2,3-hexanetriol), tetraols (e.g, pentaerythritol), or hexaols (e.g., sorbitol or mannitol), compounds with multiple carboxylic acid functions or their salts, their alkylesters, or their anhydrides such as trimellitic acid, trimellitic anhydride, or trimesic acid, or compounds with both hydroxyl functions and carboxylic acid functions or their salts, their alkylesters, or their anhydrides such as citric acid, malic acid, tartaric acid, or gallic acid may be additionally reacted and preferably may be contained in the mixture used in step a) and/or added in step b).

More preferably, the one or more crosslinking compounds or mixtures thereof are selected from the group consisting of citric acid, malic acid, tartaric acid, gallic acid, pentaerythritol, glycerol, sorbitol, mannitol, 1,2,3-hexanetriol, trimellitic acid, trimellitic anhydride, trimesic acid, and mixtures thereof.

Typically, such crosslinking compounds or mixtures thereof would be used in a molar ratio of the one or more crosslinking compounds or mixtures thereof to the one or more alkylene glycols of the formula (II) or mixtures thereof of less than 1:10, preferably of less than 1:15 and more preferably of less than 1:20.

In another preferred embodiment of the invention, one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably are added in step b)

$$(M_b^{i+})_x\ {}^{-}O_3S{-}(C_2H_4O)_y{-}H \qquad \text{(VI-1)}$$


(VI-2)

wherein

M_b is hydrogen or a monovalent cation or bivalent cation, preferably an ammonium cation, a substituted ammonium cation, or an alkali metal cation,

i is 1 or 2,

x is 0.5 or 1, and the product $i \cdot x = 1$, and

y is, based on a molar average, a number from 1 to 15, preferably from 1 to 3 and more preferably is 1.

Typically, such substances of the formula (VI-1) or (VI-2) or mixtures thereof would be used in a molar ratio of the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof to the one or more substances of the formula (III) or mixtures thereof of less than 1:2, preferably of less than 1:3 and more preferably of less than 1:4.

In addition to the terephthalic acid (formula (I)) and the one or more alkylene glycols of the formula (II) or mixtures thereof and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, optionally, the one or more substances of the formula (IV) or mixtures thereof and, optionally, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, optionally, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, optionally, one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof, one or more further substances which can take part in polycondensation reactions can additionally be reacted and be added separately or be contained in the mixture used in step a) and/or added in step b). Examples for such further substances which can take part in polycondensation reactions are phthalic acid, isophthalic acid, 3-sulfophthalic acid, 4-sulfophthalic acid, naphthalene-1,4-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, tetrahydrophthalic acid, diphenoxyethane-4,4'-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, 2,5-furandicarboxylic acid, adipic acid, sebacic acid, decan-1,10-dicarboxylic acid, fumaric acid, succinic acid, 1,4-cyclohexanedicarboxylic acid, cyclohexanediacetic acid, glutaric acid, azelaic acid, or their salts or their (di)alkyl esters, preferably their (C_1-C_4)-(di)alkyl esters and more preferably their (di)methyl esters, or mixtures thereof. Typically, such further substances would be used to a minor extent, for example in a molar amount smaller than 5 mol%, based on the total amount of terephthalic acid (formula (I)) used in the inventive process.

In addition to reactants, e.g., terephthalic acid (formula (I)) and one or more alkylene glycols of the formula (II) or mixtures thereof and, optionally, one or more substances of the formula (IV) or mixtures thereof and, optionally, one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, optionally, one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, optionally, one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof, the mixture used in step a) of the inventive process may comprise further substances such as catalyst systems or substances which do not take part in polycondensation reactions, e.g., one or more solvents or one or more additives.

In addition to reactants, e.g., one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, optionally, one or more substances of the formula (IV) or mixtures thereof and, optionally, one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, optionally, one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, optionally, one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof, further substances such as catalyst systems or substances which do not take part in polycondensation reactions, e.g., one or more solvents or one or more additives, may be added in step b) of the inventive process.

Furthermore, further substances such as catalyst systems or substances which do not take part in polycondensation reactions, e.g., one or more solvents or one or more additives, do not have to be contained in the mixture used in step a) or added in step b) of the inventive process but may be added separately to the reaction vessel.

Preferably, one or more catalyst systems, and more preferably one or more metal catalyst systems, are used in step a) and/or in step c) and are contained in the mixture used in step a) and/or are added in step b) or are added to the reaction vessel at any other time before or during the reaction, e.g., are added during heating in step a) and/or are added to the mixture obtained in step b) and/or are added during step c) separately.

More preferably, one or more catalyst systems, and even more preferably one or more metal catalyst systems, are used in step a) and/or in step c).

Examples for the one or more catalyst systems comprise carboxylic acids, phenols, metal alkoxides, and/or other typical condensation catalyst systems known in the art such as antimony, titanium, germanium, cobalt, zinc, magnesium, manganese, and/or calcium-based catalyst systems. The one or more catalyst systems may further comprise, e.g., additives, stabilizers, and bluing agents.

More preferably, one or more metal catalyst systems are used in the inventive process, and even more preferably, the one or more metal catalyst systems comprise at least one titanium-based catalyst, and particularly preferably comprise titanium tetraisopropylate and/or titanium tetrabutylate.

In the inventive process, the amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof, or, in case one or more polyalkyleneglycols of the formula (V) or mixtures thereof are additionally reacted, the combined amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and the one or more polyalkyleneglycols of the formula (V) or mixtures thereof, preferably is at least 10 wt.-%, more preferably is at least 20 wt.-%, even more preferably is at least 40 wt.-%, particularly preferably is from 40 to 90 wt.-% and extraordinarily preferably is from 50 to 90 wt.-%, in each case based on the combined weight of the terephthalic acid (formula (I)) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (IV) or mixtures thereof and, if used in the inventive process, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if used in the inventive process, the one or more crosslinking compounds having

3 to 6 functions capable of polycondensation or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof.

In a preferred embodiment of the invention, the amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof in the inventive process is at least 40 wt.-%, more preferably is from 40 to 90 wt.-% and even more preferably is from 50 to 90 wt.-%, in each case based on the combined weight of the terephthalic acid (formula (I)) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, if used in the inventive process, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if used in the inventive process, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof. In such an inventive process, preferably no substances of the formula (IV) or mixtures thereof are additionally reacted.

In another preferred embodiment of the invention, the amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof in the inventive process is at least 10 wt.-%, more preferably is from 12 to 90 wt.-%, even more preferably is from 15 to 85 wt.-% and particularly preferably is from 50 to 80 wt.-%, in each case based on the combined weight of the terephthalic acid (formula (I)) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (IV) or mixtures thereof and, if used in the inventive process, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if used in the inventive process, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof. In such an inventive process, preferably substances of the formula (IV) or mixtures thereof are additionally reacted.

In an inventive process which comprises one or more polyalkyleneglycols of the formula (V) or mixtures thereof as reactant, the combined amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and the one or more polyalkyleneglycols of the formula (V) or mixtures thereof preferably is at least 35 wt.-%, more preferably is from 40 to 90 wt.-%, even more preferably is from 50 to 90 wt.-%, particularly preferably is from 60 to 90 wt.-% and extraordinarily preferably is from 70 to 90 wt.-%, in each case based on the combined weight of the terephthalic acid (formula (I)) and the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (IV) or mixtures thereof and, if used in the inventive process, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, if used in the inventive process, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof.

In step a) of the inventive process, the combined amount of the terephthalic acid (formula (I)) and the one or more alkylene glycols of the formula (II) or mixtures thereof which are used as reactants (and not as solvent) and, if present, the one or more substances of the formula (IV) or mixtures thereof and, if present, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if present, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, if present, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof, preferably is at least 50 wt.-%, more preferably is at least 60 wt.-% and even more preferably is at least 70 wt.-%, in each case based on the total weight of all reactants contained in the mixture used in step a).

In a preferred embodiment of the invention, in addition to the reactants 1) and 2) contained in the mixture used in step a)

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof

further reactants contained in the mixture used in step a) are selected from the group consisting of 3), 4), 5) and 6)

3) one or more substances of the formula (IV) or mixtures thereof,
4) one or more polyalkyleneglycols of the formula (V) or mixtures thereof,
5) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof, and

6) one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof.

The mixture may further comprise, e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents.

In a more preferred embodiment of the invention, in addition to the reactants 1) and 2) contained in the mixture used in step a)

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof

further reactants contained in the mixture used in step a) are selected from the group consisting of 3) and 4)

3) one or more polyalkyleneglycols of the formula (V) or mixtures thereof, and
4) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof.

The mixture may further comprise, e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents.

In another more preferred embodiment of the invention, the reactants contained in the mixture used in step a) are

1) terephthalic acid (formula (I)), and
2) one or more alkylene glycols of the formula (II) or mixtures thereof, and
3) one or more substances of the formula (IV) or mixtures thereof.

The mixture may further comprise, e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents.

In an even more preferred embodiment of the invention, the reactants contained in the mixture used in step a) are

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof and
3) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof.

The mixture may further comprise, e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents.

In another even more preferred embodiment of the invention, the reactants contained in the mixture used in step a) are

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof.

The mixture may further comprise, e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents.

In a particularly preferred embodiment of the invention, the mixture used in step a) consists of

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof and
3) a catalyst system, preferably a metal catalyst system.

In another particularly preferred embodiment of the invention, the mixture used in step a) consists of

1) terephthalic acid (formula (I)) and
2) one or more alkylene glycols of the formula (II) or mixtures thereof.

In step b) of the inventive process, the combined amount of the one or more substances of the formula (III) (or (III-1)) or mixtures thereof and, if present, the one or more alkylene glycols of the formula (II) or mixtures thereof which are used as reactants (but not as solvent) and, if present, the one or more substances of the formula (IV) or mixtures thereof and, if present, the one or more polyalkyleneglycols of the formula (V) or mixtures thereof and, if present, the one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof and, if present, the one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof, preferably is at least 50 wt.-%, more preferably is at least 60 wt.-% and even more preferably is at least 70 wt.-%, in each case based on the total weight of all reactants combined in step b) with the mixture obtained in step a), preferably based on the total weight of all reactants added in step b).

In a preferred embodiment of the invention, in addition to the reactants 1) combined in step b) with the mixture obtained in step a), preferably added in step b),

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof

further reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are selected from the group consisting of 2), 3), 4), 5), and 6)

2) one or more alkylene glycols of the formula (II) or mixtures thereof,
3) one or more substances of the formula (IV) or mixtures thereof,
4) one or more polyalkyleneglycols of the formula (V) or mixtures thereof,
5) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof, and
6) one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In a more preferred embodiment of the invention, in addition to the reactants 1) combined in step b) with the mixture obtained in step a), preferably added in step b),

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof

further reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are selected from the group consisting of 2) and 3)

2) one or more alkylene glycols of the formula (II) or mixtures thereof, and
3) one or more substances of the formula (IV) or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In another more preferred embodiment of the invention, in addition to the reactants 1) combined in step b) with the mixture obtained in step a), preferably added in step b),

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof

further reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are selected from the group consisting of 2), 3) and 4)

2) one or more alkylene glycols of the formula (II) or mixtures thereof,
3) one or more polyalkyleneglycols of the formula (V) or mixtures thereof, and
4) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In another more preferred embodiment of the invention, in addition to the reactants 1) combined in step b) with the mixture obtained in step a), preferably added in step b),

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof

further reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are selected from the group consisting of 2), 3), 4), and 5)

2) one or more substances of the formula (IV) or mixtures thereof,
3) one or more polyalkyleneglycols of the formula (V) or mixtures thereof,
4) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof, and
5) one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In an even more preferred embodiment of the invention, in addition to the reactants 1) combined in step b) with the mixture obtained in step a), preferably added in step b),

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof

further reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are selected from the group consisting of 2), 3), and 4)

2) one or more substances of the formula (IV) or mixtures thereof,
3) one or more polyalkyleneglycols of the formula (V) or mixtures thereof, and
4) one or more crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In a particularly preferred embodiment of the invention, the reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are

1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof and
2) one or more substances of the formula (IV) or mixtures thereof.

Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In another particularly preferred embodiment of the invention, the reactants combined in step b) with the mixture obtained in step a), preferably added in step b), are
1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof and
2) one or more polyalkyleneglycols of the formula (V) or mixtures thereof.
Furthermore, in step b), e.g., a catalyst system, preferably a metal catalyst system, further additives, and/or one or more solvents may be added.

In an extraordinarily preferred embodiment of the invention,
1) one or more substances of the formula (III) (or (III-1)) or mixtures thereof and
2) a catalyst system, preferably a metal catalyst system
are combined in step b) with the mixture obtained in step a), preferably are added in step b).

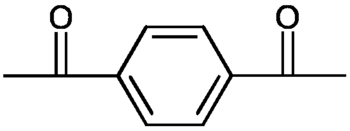
Preferably, at least 20 wt.-%, more preferably at least 30 wt.-%, even more preferably at least 50 wt.-% and particularly preferably 100 wt.-% of the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a), in each case based on the total weight of the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a), are alkylene glycols of the formula (II) or mixtures thereof which have been obtained from step c) of a previous polycondensation reaction.

A further subject matter of the invention is a product or polyester obtainable by the inventive process.

Preferred embodiments for the inventive process apply analogously to the product or polyester obtainable by the inventive process.

Products obtainable by the inventive process comprise the polyesters and additionally may comprise unreacted reactants, side products, catalysts, decomposition products, additives, and/or solvents.

Polyesters obtainable by the inventive process comprise one or more structural units of the formula (Ia)



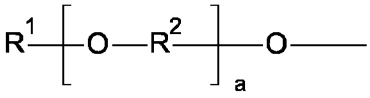
(Ia)

and one or more structural units of the formula (IIa)

$$-O-(C_nH_{2n})-O- \qquad \text{(IIa)}$$

or mixtures thereof wherein (C_nH_{2n}) has the meaning as described above for formula (II),

and one or more terminal groups of the formula (IIIa)



$$R^1\left[-O-R^2-\right]_a-O- \qquad \text{(IIIa)}$$

or mixtures thereof wherein R^1, a, and R^2 have the meaning as described above for formula (III).

Polyesters obtainable by the inventive process in which the one or more substances of the formula (III) or mixtures thereof are of the formula (III-1) comprise one or more structural units of the formula (III-1a)

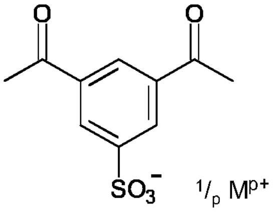
$$R^1-(OC_2H_4)_b-(OC_3H_6)_c-O- \qquad \text{(III-1a)}$$

wherein

R^1 has the meaning as described above for formula (III), the $-(OC_2H_4)$ groups and the $-(OC_3H_6)$ groups are arranged blockwise, alternating, periodically and/or statistically, preferably blockwise, wherein the block consisting of the $-(OC_3H_6)$ groups is bound, in the polyester, to a COO group, and

b and c have the meaning as described above for formula (III-1).

Polyesters obtainable by the inventive process in which one or more substances of the formula (IV) or mixtures thereof are additionally reacted additionally comprise one or more structural units of the formula (IVa)



(IVa)

or mixtures thereof wherein $^1/_p M^{p+}$ has the meaning as described above for formula (IV).

Polyesters obtainable by the inventive process in which one or more polyalkyleneglycols of the formula (V) or mixtures thereof are additionally reacted additionally comprise one or more structural units of the formula (Va)

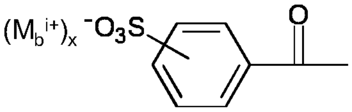
$$-(OR^3)_d-O- \qquad (Va)$$

or mixtures thereof, wherein R^3 and "d" have the meaning as described above for formula (V).

Polyesters obtainable by the inventive process in which one or more crosslinking compounds or mixtures thereof are additionally reacted additionally comprise one or more crosslinking structural units or mixtures thereof, preferably derived from crosslinking compounds having 3 to 6 functions capable of polycondensation or mixtures thereof.

Polyesters obtainable by the inventive process in which one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof are additionally reacted additionally comprise one or more further terminal groups of the formula (VI-1a) or (VI-2a)

$$(M_b^{i+})_x\ {}^-O_3S—(C_2H_4O)_y— \qquad (VI\text{-}1a)$$



(VI-2a)

or mixtures thereof wherein M_b, i, x, and y have the meaning as described above for formulas (VI-1) and (VI-2).

Polyesters obtainable by the inventive process in which one or more further substances which can take part in polycondensation reactions are additionally reacted additionally comprise the respective one or more structural units derived from the one or more further substances which can take part in polycondensation reactions.

The weight average molecular weight (Mw) of the polyesters obtainable by the inventive process preferably is from 1500 to 20000 g/mol, more preferably from 4000 to 20000 g/mol and even more preferably from 5000 to 20000 g/mol.

The weight average molecular weight (Mw) of the polyesters obtainable by the inventive process may be determined by GPC analysis, preferably as detailed in the following: 10 µl of sample is injected onto a PSS Suprema column of dimensions 300 x 8 mm with porosity 30 Å and particle size 10 µm. The detection is monitored at 235 nm on a multiple wavelength detector. The employed eluent is 1.25 g/l of disodium hydrogen phosphate in a 45 / 55 % (v/v) water / acetonitrile mixture. Separations are conducted at a flow rate of 0.8 ml/minute. Quantification is performed by externally calibrating standard samples of different molecular weight polyethylene glycols.

Preferably, the number of structural units of the formula (Ia) in the polyesters obtainable by the inventive process is, based on a molar average, from 2 to 60, more preferably from 2 to 40, even more preferably from 2 to 30, particularly preferably from 2 to 20 and extraordinarily preferably from 5 to 20.

The polyesters obtainable by the inventive process comprise one or more terminal groups of the formula (IIIa) or mixtures thereof. In addition to these one or more terminal groups or mixtures thereof, the polyesters obtainable by the inventive process may comprise further terminal groups, preferably selected from the group consisting of -OH, -O-(C_nH_{2n})-OH, wherein “n” has the meaning given above for formula (II), and mixtures thereof. Polyesters obtainable by the inventive process may also comprise terminal groups of the formula -(OR^3)$_d$-O-H wherein R^3 and “d” have the meaning given above for formula (V) in case one or more polyalkyleneglycols of the formula (V) or mixtures thereof are additionally reacted. Polyesters obtainable by the inventive process may also comprise terminal groups derived from crosslinking structural units in case one or more crosslinking compounds, preferably having 3 to 6 functions capable of polycondensation or mixtures thereof, are additionally reacted. Furthermore, and as already stated above, the polyesters obtainable by the inventive process may also comprise one or more terminal groups of the formula (VI-1a) or (VI-2a) or mixtures thereof in case one or more substances of the formula (VI-1) or (VI-2) or mixtures thereof are additionally reacted.

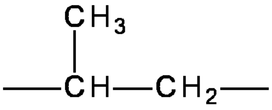
Preferably, the polyester molecules of the polyesters obtainable by the inventive process comprise two or more terminal groups of the formula (IIIa) or mixtures thereof. Even more preferably, all terminal groups of the polyester molecules of the polyesters obtainable by the inventive process are terminal groups of the formula (IIIa) or mixtures thereof.

The polyesters obtainable by the inventive process preferably are anionic or nonionic and more preferably are nonionic.

The groups (C_2H_4) in the alkylene glycols of the formula (II) or in the structural units of the formula (IIa), in the substances of the formula (III) (or (III-1)) or in the terminal groups of the formula (IIIa) (or (III-1a)), in the polyalkyleneglycols of the formula (V) or in the structural units of the formula (Va), or in the substances of the formula (VI-1) or in the terminal groups of the formula (VI-1a) preferably are of the formula -CH_2-CH_2-.

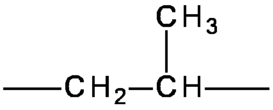
The groups (C_3H_6) in the alkylene glycols of the formula (II) or in the structural units of the formula (IIa), in the substances of the formula (III) (or (III-1)) or in the terminal groups of the formula (IIIa) (or (III-1a)), or in the polyalkyleneglycols of the formula

(V) or in the structural units of the formula (Va) preferably are of the formula -CH(CH$_3$)-CH$_2$- or –CH$_2$-CH(CH$_3$)-, i.e., of the formula:



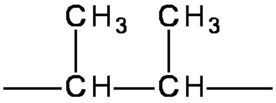
$$-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-$$

or



$$-CH_2-\overset{\overset{\large CH_3}{|}}{C}H-$$

The groups (C$_4$H$_8$) in the alkylene glycols of the formula (II) or in the structural units of the formula (IIa), in the substances of the formula (III) or in the terminal groups of the formula (IIIa), or in the polyalkyleneglycols of the formula (V) or in the structural units of the formula (Va) preferably are of the formula -CH(CH$_3$)-CH(CH$_3$)-, i.e., of the formula:



$$-\overset{\overset{\large CH_3}{|}}{C}H-\overset{\overset{\large CH_3}{|}}{C}H-$$

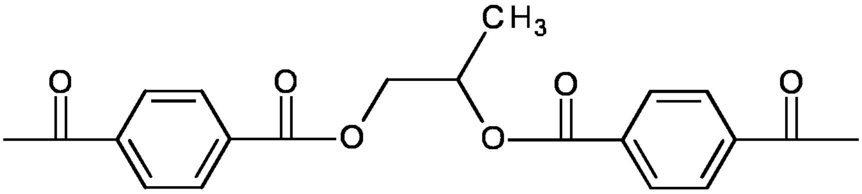
In the polyesters obtainable by the inventive process, the terminal groups or structural units of the formulae (IIa), (IIIa), (III-1a), (Va), or (VI-1a) may, e.g., be linked directly to structural units of the formula (Ia) or, if present, to structural units of the formula (IVa) resulting in ester groups.

In the polyesters obtainable by the inventive process, the terminal groups of the formula (VI-2a) may, e.g., be linked directly to structural units of the formulae (IIa) or (Va) resulting in ester groups.

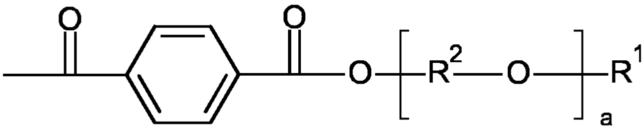
The inventive process describes a polycondensation process. Such a process leads to statistically determined mixtures of polyesters in which a mixture of molecular species with a distribution around a molar average is obtained.

The following paragraphs will show illustrative, but by no means limiting, structural entities that can be found in the polyesters obtainable by the inventive process.

The structural units of the formula (Ia) and optional additional di- or polycarboxylic acid-derived structural units are linked indirectly, preferably via the structural units of the formula (IIa), which – in the case of structural units of the formulae (Ia) and (IIa), wherein the structural units of the formula (IIa) are derived from 1,2-propylene glycol – results in the following structural entity:



Preferably, the terminal group of the formula (IIIa) is linked to an acyl group derived from a dicarboxylic acid, preferably to the structural unit of the formula (Ia) derived from terephthalic acid, which – in the case of structural unit of the formula (Ia) and terminal group of the formula (IIIa) – results in the following structural entity:



The products or polyesters obtainable by the inventive process may be used as soil release polymer.

Therefore, a further subject matter of the invention is the use of a product or polyester obtainable by the inventive process as soil release polymer.

"Soil release polymer” as used herein means a product or polymer that enhances soil removal during laundering by modifying the surface of the fabric that is laundered, preferably by increasing surface polarity.

In the use according to the invention as soil release polymer, the product or polyester preferably is present in a laundry detergent composition.

A further subject matter of the present invention is laundry detergent compositions comprising

Z1) one or more products or polyesters obtainable by the inventive process.

The laundry detergent compositions of the invention comprise the one or more products or polyesters of component Z1) preferably in an amount of at least 0.1 wt.-%, more preferably in an amount from 0.1 to 10 wt.-%, even more preferably in an amount from 0.2 to 5 wt.-% and particularly preferably in an amount from 0.2 to 3 wt.-%, in each case based on the total weight of the laundry detergent composition.

The laundry detergent compositions of the invention preferably comprise

Z2) one or more surfactants.

Surfactants assist in removing soil from textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor.

Preferably, the one or more surfactants of component Z2) of the laundry detergent compositions of the invention are selected from the group consisting of anionic, nonionic, cationic and zwitterionic surfactants, and more preferably from the group consisting of anionic, nonionic and zwitterionic surfactants.

Anionic Surfactants

Suitable anionic surfactants that may be used are any of the conventional anionic surfactant types typically used in laundry detergent compositions. These include alkyl sulfonates, alkyl ether sulfates, alkyl sulfates, alkyl ester sulfonates and soaps. Preferred anionic surfactants are alkylbenzene sulfonates, alkyl ether sulfates, alkyl sulfates and soaps.

Preferred alkyl sulfonates are alkylbenzene sulfonates, particularly linear alkylbenzene sulfonates (LAS) having an alkyl chain length of C_8-C_{15}. Possible counter ions for concentrated alkaline liquids are ammonium ions, e.g., those generated by the neutralization of alkylbenzene sulfonic acid with one or more ethanolamines, for example monoethanolamine (MEA) and triethanolamine (TEA), or alternatively, alkali metals, e.g., those arising from the neutralization of alkylbenzene sulfonic acid with alkali hydroxides. The linear alkyl benzene sulfonate surfactants may be LAS with an alkyl chain length of preferably from 8 to 15 and more preferably from 12 to 14. The neutralization of the acid may be performed before addition to the laundry detergent compositions of the invention or during the process of formulating the laundry detergent compositions of the invention through excess addition of neutralizing agent.

Preferred alkyl ether sulfates (AES) are alkyl polyethoxylate sulfate anionic surfactants of the formula

$$R^5O(C_2H_4O)_zSO_3^-M_c^+$$

wherein

R^5 is a saturated or unsaturated alkyl chain having preferably from 10 to 22 carbon atoms, and more preferably from 12 to 16 carbon atoms,

M_c^+ is a cation which makes the compound water-soluble, preferably an ammonium cation, a substituted ammonium cation, an alkali metal cation, or other material chosen from the list of buffers, and

z averages preferably from 1 to 15, more preferably from 1 to 3 and even more preferably is 3.

Preferred alkyl sulfates (AS) are surfactants of the formula

$$R^6OSO_3^-M_d^+$$

wherein

R^6 is a linear or branched alkyl chain having preferably from 8 to 24 carbon atoms, and more preferably from 12 to 18 carbon atoms, and

M_d^+ is a cation which makes the compound water-soluble, preferably an ammonium cation, a substituted ammonium cation, an alkali metal cation, or other material chosen from the list of buffers.

Soaps are preferably fatty acids and more preferably linear saturated or unsaturated fatty acids having from 10 to 18 carbon atoms.

Nonionic Surfactants

Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C_8-C_{20} aliphatic alcohol ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamides) such as N-methyl glucamides. Mixtures of nonionic surfactant may be used.

If included therein, the laundry detergent compositions of the invention contain preferably from 0.2 to 40 wt.-% and more preferably from 1 to 20 wt.-% of a nonionic surfactant, such as alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides"), in each case based on the total weight of the laundry detergent composition.

Zwitterionic Surfactants

The laundry detergent compositions of the invention may comprise up to 10 wt.-% of a zwitterionic surfactant, e.g., amine oxide or betaine, based on the total weight of the laundry detergent composition.

Typical amine oxides used are of the formula

$$R^7N(O)(CH_2R^8)_2$$

wherein

R^7 is a long chain moiety, and each CH_2R^8 are short chain moieties, and
R^8 is preferably selected from the group consisting of H, CH_3 and $-CH_2OH$.

In general, R^7 is a primary or branched hydrocarbyl moiety with a chain length of from 8 to 18, which can be saturated or unsaturated. Preferably, R^7 is a primary alkyl moiety with a chain length of 8 to 18 carbon atoms.

Preferred amine oxides have compositions wherein R^7 is a C_8-C_{18} alkyl and R^8 is H. These amine oxides are illustrated by C_{12-14} alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

A preferred amine oxide material is lauryl dimethylamine oxide, also known as dodecyldimethylamine oxide or DDAO.

Betaines may be alkyldimethyl betaines or alkylamido betaines, wherein the alkyl groups have C_{12-18} chains.

In a preferred embodiment of the invention, the one or more surfactants of component Z2) of the laundry detergent compositions of the invention are selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates, alkyl sulfates, soaps, nonionic surfactants, amine oxides and betaines, and preferably the one or more surfactants of component Z2) of the laundry detergent compositions of the invention are selected from the group consisting of linear alkyl benzene sulfonates, alkyl ether sulfates, alkyl sulfates, soaps and nonionic surfactants.

Additional Surfactants

Other surfactants than the preferred LAS, AES, AS, soaps and nonionic surfactants may be added to the mixture of surfactants.

The laundry detergent compositions of the invention comprise the one or more surfactants of component Z2) preferably in an amount of at least 3 wt.-%, more preferably in an amount from 3 to 65 wt.-%, even more preferably in an amount from 4 to 60 wt.-% and particularly preferably in an amount from 5 to 55 wt.-%, in each case based on the total weight of the laundry detergent composition.

Further Optional Ingredients

In addition to the one or more products or polyesters of component Z1) and optionally the one or more surfactants of component Z2), the laundry detergent compositions of the invention may comprise one or more further optional ingredients, e.g., they may comprise conventional ingredients commonly used in laundry detergent compositions. Examples of optional ingredients include, but are not limited to builders, bleaching agents, bleach active compounds, bleach activators, bleach catalysts, photobleaches, dye transfer inhibitors, colour protection agents, anti-redeposition agents, dispersing agents, fabric softening and antistatic agents, fluorescent whitening agents, enzymes, enzyme stabilizing agents, foam regulators, defoamers, malodor reducers, preservatives, disinfecting agents, hydrotropes, fibre lubricants, anti-shrinkage agents, buffers, fragrances, processing aids, colorants, dyes, pigments, anti-corrosion agents, fillers, stabilizers and other conventional ingredients for laundry detergent compositions.

Polyalkoxylated polyethyleneimine

For detergency boosting, it is advantageous to use a second polymer alongside the one or more polyesters of component Z1) in the laundry detergent compositions of the invention. This second polymer is preferably a polyalkoxylated polyethyleneimine (EPEI). Polyethylene imines are materials composed of ethylene imine units $-CH_2CH_2NH-$ and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like.

Other Polymers

In addition to the one or more products or polyesters of component Z1) and the optional EPEI, the laundry detergent compositions of the invention may comprise other polymeric materials, for example: dye transfer inhibition polymers, anti-redeposition polymers, and cotton soil release polymers, especially those based on modified cellulosic materials. Especially, if EPEI is not present, the laundry detergent compositions of the invention may further comprise a polymer of polyethylene glycol and vinyl acetate, for example the lightly grafted copolymers described in WO 2007/138054. Such amphiphilic graft polymers based on water-soluble polyalkylene oxides as graft base and side chains formed by polymerisation of a vinyl ester component have the ability to enable reduction of surfactant levels whilst maintaining high levels of oily soil removal.

Hydrotropes

In the context of this invention a hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components, especially polymer and sequestrant, in the liquid to render it isotropic. Among suitable hydrotropes there may be mentioned as preferred: monopropylene glycol (MPG), glycerol, sodium cumene sulfonate, ethanol, other glycols, e.g., dipropylene glycol, diethers, and urea. MPG and glycerol are preferred hydrotropes.

Enzymes

It is preferable that one or more enzymes selected from protease, mannanase, pectate lyase, cutinase, lipase, amylase, and cellulase may be present in the laundry detergent compositions of the invention. Less preferred additional enzymes may be selected from esterase, peroxidase and oxidase. The enzymes are preferably present with corresponding enzyme stabilizers. The total enzyme content in the laundry detergent compositions of the invention is preferably from 0 to 5 wt.-%, more preferably from 0.2 to 4 wt.-% and even more preferably from 0.4 to 2 wt.-%, in each case based on the total weight of the laundry detergent composition.

Sequestrants

Sequestrants are preferably included. Preferred sequestrants include organic phosphonates, alkanehydroxy phosphonates, and carboxylates available under the DEQUEST trademark from Thermphos. The preferred sequestrant level is less than 10 wt.-% and preferably less than 5 wt.-%, in each case based on the total weight of the laundry detergent composition of the invention. A particularly preferred sequestrant is HEDP (1-Hydroxyethylidene-1,1-diphosphonic acid). Also suitable but less preferred as it gives inferior cleaning results is diethylenetriamine penta(methylene phosphonic acid) (DTPMP) or Heptasodium DTPMP.

Buffers

In addition to agents optionally included for the generation of anionic surfactants, e.g., from LAS or fatty acids, the presence of buffer is preferred for pH control.

Possible buffers are one or more ethanolamines, e.g., monoethanolamine (MEA) or triethanolamine (TEA). They are preferably used in the laundry detergent compositions of the invention at levels of from 1 to 15 wt.-%, based on the total weight of the laundry detergent composition. Other suitable amino alcohol buffer materials may be selected from the group consisting of compounds having a molecular weight above 61 g/mol, which includes MEA. Suitable materials also include, in addition to the already mentioned materials: monoisopropanolamine, diisopropanolamine, triisopropanolamine, monoamino hexanol, 2-[(2-methoxyethyl) methylamino]-ethanol, propanolamine, N-methylethanolamine, diethanolamine, monobutanolamine, isobutanolamine, monopentanolamine, 1-amino-3-(2-methoxyethoxy)-2-propanol, 2-methyl-4-(methylamino)-2-butanol and mixtures thereof.

Potential alternatives to amino ethanol buffers are alkali hydroxides such as sodium hydroxide or potassium hydroxide.

Builders

Further washing and cleaning ingredients which may be present in the laundry detergent compositions of the invention include inorganic and/or organic builders in order to reduce the degree of hardness of the water. These builders may be present in the laundry detergent compositions of the invention in amounts of from about 5 to about 80 wt.-%, based on the total weight of the laundry detergent compositions. Inorganic builders include, for example, alkali metal, ammonium and alkanolammonium salts of polyphosphates, silicates, carbonates, sulfates and aluminosilicates.

Suitable organic builders include polycarboxyl compounds, such as, for example, ether polycarboxylates, ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxybenzene-2,4,6-trisulfonic acid and carboxymethyloxysuccinic acid, the alkali metal, ammonium and substituted ammonium salts of polyacetic acids, such as, for example, ethylenediaminetetraacetic acid and nitrilotriacetic acid, and also polycarboxylic acids, such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene-1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof. Builders based on citrates, for example citric acid and its soluble salts, in particular the sodium salt, are preferred polycarboxylic acid builders, which can also be used in granulated compositions, in particular together with zeolites and/or sheet silicates.

It may be advantageous to include fluorescer and/or bleach catalyst in the laundry detergent compositions of the invention as further high efficiency performance additives. Perfume and colorants will also desirably be included. The laundry detergent compositions of the invention may additionally contain viscosity modifiers, foam boosting agents, preservatives (e.g., bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, and ironing aids. The laundry detergent compositions of the invention may further comprise pearlisers and/or opacifiers or other visual cues and shading dye.

Form, packaging and dosing

The laundry detergent compositions of the invention may be in solid or in liquid form, including a gel form. The laundry detergent compositions of the invention may be packaged as unit doses in a polymeric film soluble in the wash water. Alternatively, the laundry detergent compositions of the invention may be supplied in multidose plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system.

In one embodiment of the invention the laundry detergent composition is solid.

In a further embodiment of the invention the laundry detergent composition is liquid.

A further subject matter of the invention is a method of washing a textile comprising the step of contacting the textile with an aqueous solution comprising a laundry detergent composition according to the invention, preferably at a temperature between 10°C and 90°C, furthermore preferably for a time between 5 minutes and 4 hours, and more preferably in a washing machine.

The concentration of the one or more products or polyesters obtainable by the inventive process in the aqueous solution is typically in the range of from 0.001 g/l to

0.5 g/l, from 0.002 g/l to 0.5 g/l, from 0.01 g/l to 0.5 g/l, from 0.02 g/l to 0.5 g/l, from 0.1 g/l to 0.5 g/l, or from 0.2 g/l to 0.4 g/l, or from 0.001 g/l to 0.2 g/l, from 0.002 g/l to 0.2 g/l, from 0.01 g/l to 0.2 g/l, from 0.02 g/l to 0.2 g/l, or from 0.1 g/l to 0.2 g/l.

Further preferred embodiments of the invention may arise from the combination of above-described preferred embodiments.

EXAMPLES

The examples below are intended to illustrate the invention in detail without, however, limiting it thereto. Unless explicitly stated otherwise, all percentages given are percentages by weight (% by wt. or wt.-%).

Key to abbreviations used:

TPA	terephthalic acid
EG	ethylene glycol
PG	1,2-propylene glycol
5-SIM	dimethyl 5-sulfoisophthalate Na salt
TTB	titanium tetrabutanolate
IPT	tetraisopropyl orthotitanate
mPEG200	mono hydroxyl-functional polyethylene glycol monomethyl ether, average molecular weight 0.2 kDa
mPEG750	mono hydroxyl-functional polyethylene glycol monomethyl ether, average molecular weight 0.75 kDa
mPEG2000	mono hydroxyl-functional polyethylene glycol monomethyl ether, average molecular weight 2 kDa
mPEG5000	mono hydroxyl-functional polyethylene glycol monomethyl ether, average molecular weight 5 kDa
mPEG45PPG3	H_3C-$(OC_2H_4)_{45}$-$(OC_3H_6)_3$-OH wherein the –(OC_2H_4) groups and the –(OC_3H_6) groups are arranged blockwise and the block consisting of the –(OC_3H_6) groups is bound to the OH group
lPEG4000	lauryl alcohol ($C_{12/14}$, C_{12} rich) ethoxylate, average molecular weight 4 kDa made from ethylene oxide from renewable source (sugarcane)

General procedure:

The synthesis was carried out in three steps. In step a), terephthalic acid was esterified with one or more alkylene glycols. In step b), a terminal capped polyalkylene glycol and optionally comonomers were combined with the mixture obtained in step a), preferably were added to the product or mixture of step a). In step c), the resulting mixture was polycondensed. One or more catalyst systems were used in the examples.

Examples I to III

Products of step a) were prepared. Terephthalic acid and propylene glycol were introduced into reaction vessels at room temperature under a nitrogen atmosphere and stirred. The reaction mixtures were heated up to 100 °C. At this temperature, catalysts were added, and the mixtures were further slowly heated up to 190 °C. Water was distilled out of the systems using heated distillation columns. In each example, the temperature was slowly increased up to 220 °C to keep distillation going on, subsequently held at this temperature, and further stirred. One or more samples were taken during the heating period, and their acid value was determined. Once the desired acid value was reached, approximately 5 to 15 hours after distillation commenced, the reaction mixtures were cooled and stored for further reaction steps.

Table I – Examples I to III

	Example		
	I	II	III
Reactant or catalyst			
TPA [g]	116.87	116.87	210.00
PG [g]	133.83	120.45	202.00
TTB [g]	1.80	1.80	3.22
Acid value of the product [mg KOH/g]	1.6	1.6	0.5
Formed dioxane [mg]	Not detected (<0.027)	Not detected (<0.027)	Not detected (<0.050)

Examples IV to VII

Polyesters were prepared. A product as obtained in Examples I or II and a terminal capped polyalkylene glycol were introduced into reaction vessels at room temperature under a nitrogen atmosphere and stirred. The reaction mixtures were heated up to 100 °C. At this temperature, optionally catalysts were added, and the mixtures were further slowly heated up to 230 °C. Subsequently, in each example, the pressure was slowly reduced to 1 mbar. Propylene glycol and impurities were distilled out of the systems. The mixtures were stirred for 4 hours at 230 °C and a pressure of 1 mbar. After the end of this time period, the inner pressure of the reaction vessels was increased to 1 bar using nitrogen, and the molten products were subsequently removed from the reactors and allowed to solidify.

Example VIII

A polyester was prepared. A product as obtained in Example III, mPEG200, 5-SIM, and EG were introduced into a reaction vessel at room temperature under a nitrogen atmosphere and stirred. The reaction mixture was heated up to 100 °C. At this temperature, TTB was added, and the mixture was further slowly heated up to 210 °C and stirred for 3 hours at 210 °C. Subsequently, the temperature was reduced to 195 °C, and the pressure was slowly reduced to 1 mbar. Alkylene glycols and impurities were distilled out of the system. The mixture was stirred for 4 hours at 195 °C and a pressure of 1 mbar. After the end of this time period, the inner pressure of the reaction vessel was increased to 1 bar using nitrogen, and the molten product was subsequently removed from the reactor and allowed to solidify.

Table II – Examples IV to VIII (composition and properties)

	Example				
	IV	V	VI	VII	VIII
Reactant or catalyst					
Product of Example I [g]	65.00	--	--	85.00	--
Product of Example II [g]	--	90.00	85.00	--	--
Product of Example III [g]	--	--	--	--	65.00
mPEG200 [g]	--	--	--	--	11.07
mPEG2000 [g]	--	119.46	--	--	--
mPEG5000 [g]	--	--	156.71	--	--
mPEG45PPG3 [g]	--	--	--	159.20	--
IPEG4000 [g]	180.35	--	--	--	--
EG [g]	--	--	--	--	18.40
5-SIM [g]	--	--	--	--	22.51
TTB [g]	--	0.20	--	--	0.0009
IPT [g]	--	--	0.21	--	--
Formed dioxane [mg]	0.63	0.58	0.76	0.046	5.52

Examples IX to XI

Polyesters were prepared. Terephthalic acid and propylene glycol were introduced into reaction vessels at room temperature under a nitrogen atmosphere and stirred. The reaction mixtures were heated up to 100 °C. At this temperature, catalysts were added, and the mixtures were further slowly heated up to 190 °C. Water was distilled out of the systems using heated distillation columns. In each example, the temperature was slowly increased up to 220 °C to keep distillation going on, subsequently held at this temperature, and further stirred. One or more samples were taken during the heating period, and their acid value was determined. Once the desired acid value was reached, approximately 5 to 7 hours after distillation commenced, the reaction mixtures were cooled to 100 °C under stirring. To each of them, mPEG750 was added. The mixtures were heated to 230 °C, and in each example, the pressure was slowly reduced to 1 mbar. Propylene glycol and impurities were distilled out of the system. The mixtures were stirred for 4 hours at 230 °C and a pressure of 1 mbar. After the end of this time period, the inner pressure of the reaction vessels was increased to 1 bar using nitrogen, and the molten products were subsequently removed from the reactors and allowed to solidify.

Table III – Examples IX to XI (composition and properties)

	Example		
	IX	X	XI
Reactant or catalyst			
TPA [g]	46.75	51.91	46.75
PG [g]	53.54	71.33	42.83
TTB [g]	0.72	0.80	0.72
mPEG750 [g]	183.54	183.54	183.54
Acid value after step a) [mg KOH/g]	2.7	2.2	2.3
Formed dioxane [mg]	3.72	1.51	3.74

Example XII

A polyester was prepared. 780.00 g terephthalic acid and 714.54 g propylene glycol were introduced into a reaction vessel at room temperature under a nitrogen atmosphere and stirred. The reaction mixture was heated up to 110 °C. At this temperature, 6.01 g TTB was added, and the mixture was further slowly heated until distillation started (approximately 183 °C). Water was distilled out of the system using a heated distillation column. The temperature slowly increased during distillation towards 220 °C. Samples were taken during the heating period, and their acid value was determined. At an acid value of 1.2, approximately 10 hours after distillation commenced, the reaction mixture was cooled to room temperature and stored for further reaction steps. 1307 g reaction mixture were obtained. 444 g of the stored reaction mixture was heated to 50 °C under stirring, and 1020 g mPEG750 were added. The mixture was heated to 230 °C, and the pressure was slowly reduced to 15 mbar. Propylene glycol and impurities were distilled out of the system. The mixture was stirred for 1 hour at 230 °C and a pressure of 15 mbar. After the end of this time period, the inner pressure of the reaction vessels was increased to 1 bar using nitrogen, and the molten product was subsequently removed from the reactor and allowed to solidify.

Table IV – Formed dioxane during preparation of polyester of Example XII

	Example XII
Formed dioxane [mg]	41.3

Comparative Example I

A polyester was prepared. 46.75 g terephthalic acid, 42.83 g propylene glycol, and 183.54 g mPEG750 were introduced into a reaction vessel at room temperature under a nitrogen atmosphere and stirred. The reaction mixture was heated up to 100 °C. At this temperature, 0.72 g TTB was added, and the mixture was further slowly heated up to 195 °C. Water was distilled out of the system using a heated distillation column. The temperature was slowly increased up to 235 °C to keep distillation going on, subsequently held at this temperature and further stirred. Samples were taken during the heating period, and their acid value was determined. Once an acid value of 0.96 mg KOH/g was reached, the temperature was set to 230 °C, and the pressure was slowly reduced to 1 mbar. Propylene glycol and impurities were distilled out of the system. The mixture was stirred for 4 hours at 230 °C and a pressure of 1 mbar. After the end of this time period, the inner pressure of the reaction vessel was increased to 1 bar using nitrogen and the molten product was subsequently removed from the reactor and allowed to solidify. 15.2 mg dioxane were formed in this process.

Comparative Example II

A polyester was prepared. 259.83 g terephthalic acid, 238.02 g propylene glycol, and 1020 g mPEG750 were introduced into a reaction vessel at room temperature under a nitrogen atmosphere and stirred. The reaction mixture was heated up to 110 °C. At this temperature, 2.02 g TTB was added, and the mixture was further slowly heated until distillation started (approximately 194 °C). Water was distilled out of the system using a heated distillation column. The temperature was slowly increased up to 230 °C to keep distillation going on, subsequently held at this temperature and further stirred. Samples were taken during the heating period, and their acid value was determined. Once an acid value of 3.9 mg KOH/g was reached, the mixture was heated to 230 °C, and the pressure was slowly reduced to 15 mbar. Propylene glycol and impurities were distilled out of the system. The mixture was stirred for 1 hour at 230 °C and a pressure of 15 mbar. After the end of this time period, the inner pressure of the reaction vessel was increased to 1 bar using nitrogen, and the molten product was subsequently removed from the reactor and allowed to solidify. 86.1 mg dioxane were formed in this process.

Laundry detergent formulations

Key to ingredients used in the formulations of Table VI

LAS	is C_{12-14} linear alkylbenzene sulfonate, sodium salt
SLES 2EO	is sodium lauryl ether sulfate with 2 moles EO
NI 7EO	is C_{12-15} alcohol ethoxylate 7EO nonionic
Fatty Acid	is a C_{12-18} stripped palm kernel fatty acid

A series of exemplary liquid laundry detergent formulations according to the invention (with a polyester obtained by the inventive process) were prepared. Pre-formulations of Examples IX to XII were prepared according to the compositions listed in Table V. Exemplary liquid laundry detergent formulations were subsequently prepared according to the compositions listed in Table VI.

Table V – Pre-formulations for preparing liquid laundry detergent formulations

	Pre-formulation			
	1	2	3	4
Ingredient				
Product of Example IX [wt.-%]	70.0	--	--	--
Product of Example X [wt.-%]	--	70.0	--	--
Product of Example XI [wt.-%]	--	--	70.0	--
Product of Example XII [wt.-%]	--	--	--	70.0
Propylene glycol [wt.-%]	10.0	10.0	10.0	10.0
Lactic acid [wt.-%]	0.2	0.2	0.2	0.2
Demineralized water [wt.-%]	ad 100	ad 100	ad 100	ad 100

Table VI – Liquid laundry detergent compositions for performance testing

	Formulation				
	1	2	3	4	5
Ingredient					
LAS [wt.-%]	5.2	5.2	5.2	5.2	5.2
SLES 2EO [wt.-%]	6.5	6.5	6.5	6.5	6.5
NI 7EO [wt.-%]	5.2	5.2	5.2	5.2	5.2
Fatty Acid [wt.-%]	2.8	2.8	2.8	2.8	2.8
Glycerol [wt.-%]	2.4	2.4	2.4	2.4	2.4
Ethanol [wt.-%]	1.2	1.2	1.2	1.2	1.2
Sodium citrate [wt.-%]	1.7	1.7	1.7	1.7	1.7
Pre-formulation 1 [wt.-%]	--	1.4	--	--	--
Pre-formulation 2 [wt.-%]	--	--	1.4	--	--
Pre-formulation 3 [wt.-%]	--	--	--	1.4	--
Pre-formulation 4 [wt.-%]	--	--	--	--	1.4
Demin water and NaOH to adjust pH [wt.-%]	ad 100	ad 100	ad 100	ad 100	ad 100
pH Value	8.4	8.4	8.4	8.4	8.4
Appearance at room temperature	clear	clear	clear	clear	clear

Soil release test

The detergent formulations 1 to 5 were tested for their soil release performance according to the “Dirty-Motor Oil” Test (DMO-Test) using a Lini Apparatus. The conditions for the test are listed in Table VII.

Table VII – Washing conditions – Soil Release Test

Equipment	Linitest Plus (SDL Atlas)
Water hardness	14°dH
Washing temperature	40 °C
Washing time	30 minutes
Detergent concentration	4.3 g/L
Soiled fabric : liquor ratio	1 : 40

As test fabric, white polyester standard swatches (WFK 30A from WFK Testgewebe GmbH) were used. The fabrics were prewashed three times with the laundry detergent formulations. The swatches were then rinsed, dried, and soiled with 25 µL of dirty motor oil. After 1 hour the soiled fabrics were washed again with the same stored laundry detergent compositions used in the pre-washing step. After rinsing and drying the washed swatches, a measurement of the remission of the stained fabric at 457 nm was made using a spectrophotometer (Datacolor 650).

The soil release performance is shown as an improvement in soil removal of the swatches washed with a formulation containing a polyester obtained by the inventive process (Soil Release Polymer, SRP), formulation 2 to formulation 5, compared with the same formulation containing no SRP, formulation 1:

$$\Delta R = R_{\text{with SRP}} - R_{\text{without SRP}}$$

The washing results obtained for the laundry detergent formulations comprising a polyester obtained by the inventive process are shown in Table VIII, expressed as ΔR along with the 95% confidence intervals (95 % CI).

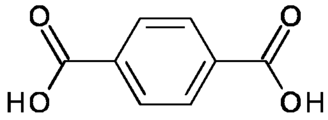
Table VIII – Washing results for liquid detergents

Formulation no.	ΔR	95 % CI
2 (containing product of Example IX)	7.24	0.70
3 (containing product of Example X)	7.64	0.80
4 (containing product of Example XI)	9.49	2.60
5 (containing product of Example XII)	5.75	0.30

Claims:

1. Process for preparing a polyester by reacting at least

- terephthalic acid (formula (I))



(I)

and

- one or more alkylene glycols of the formula (II)

$$HO\text{-}(C_nH_{2n})\text{-}OH \qquad (II)$$

or mixtures thereof wherein (C_nH_{2n}) is a linear or branched alkylene group with n being an integer of from 2 to 10 or mixtures thereof, preferably with n being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof,

and

- one or more substances of the formula (III)

$$R^1\text{-}(OR^2)_a\text{-}OH \qquad (III)$$

or mixtures thereof wherein

R^1 is a linear or branched, preferably a linear, alkyl group comprising from 1 to 30 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 30 carbon atoms or mixtures thereof,

preferably is a linear or branched, preferably a linear, alkyl group comprising from 1 to 20 carbon atoms or a linear or branched, preferably a linear, alkenyl group comprising one or more double bonds and from 2 to 20 carbon atoms or mixtures thereof,

a is, based on a molar average, a number of from 1 to 200, preferably of from 2 to 200, more preferably of from 3 to 150, and

R^2 is a linear or branched alkylene group (C_mH_{2m}) with m being an integer of from 2 to 10 or mixtures thereof, preferably with m being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof, particularly preferably is (C_2H_4) or a mixture of (C_2H_4) and (C_3H_6), and extraordinarily preferably is (C_2H_4),

characterized in that the preparation of the polyester comprises the steps of:

a) heating a mixture comprising terephthalic acid and one or more alkylene glycols of the formula (II) or mixtures thereof and removing water until the acid value of the system is reduced to 50 mg KOH/g or lower, preferably to 30 mg KOH/g or lower, more preferably to 15 mg KOH/g or lower, even more preferably to 10 mg KOH/g or lower, particularly preferably to 6 mg KOH/g or lower, and extraordinarily preferably to 4 mg KOH/g or lower;

b) combining one or more substances of the formula (III) or mixtures thereof with the mixture obtained in step a)
and

c) polycondensing the mixture obtained in step b) under ambient pressure or reduced pressure, preferably under reduced pressure, while removing alkylene glycols of the formula (II) and preferably also side products.

2. The process according to claim 1, characterized in that the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a) are selected from the group consisting of ethylene glycol, propylene glycol and mixtures of ethylene glycol and propylene glycol, preferably are selected from the group consisting of propylene glycol and mixtures of ethylene glycol and propylene glycol

and more preferably the alkylene glycol of the formula (II) used in step a) is propylene glycol.

3. The process according to claim 1 or 2, characterized in that the mixture in step a) is heated to temperatures of more than 90 °C, preferably to temperatures of from 100 °C to 300 °C, more preferably to temperatures of from 120 °C to 280 °C, even more preferably to temperatures of from 140 °C to 260 °C and particularly preferably to temperatures of from 160 °C to 250 °C.

4. The process according to one or more of claims 1 to 3, characterized in that polycondensing in step c) is executed under a pressure of from 0.1 to 900 mbar, preferably under a pressure of from 0.5 to 500 mbar, and preferably at temperatures of more than 90 °C, more preferably at temperatures of from 100 °C to 300 °C, even more preferably at temperatures of from 150 °C to 280 °C, particularly preferably at temperatures of from 160 °C to 270 °C and extraordinarily preferably at temperatures of from 180 °C to 260 °C.

5. The process according to one or more of claims 1 to 4, characterized in that removal of water in step a) and/or removal of alkylene glycols of the formula (II) in step c) is achieved in part or completely by distillation.

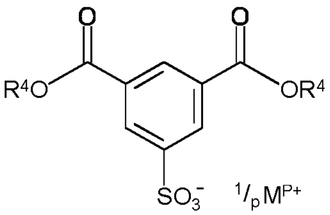
6. The process according to one or more of claims 1 to 5, characterized in that the molar ratio of the one or more alkylene glycols of the formula (II) or mixtures thereof to terephthalic acid (formula (I)), in step a) is at least 1.2:1.0, preferably is at least 1.5:1.0, more preferably is at least 1.8:1.0, even more preferably is at least 2.0:1.0, and particularly preferably is at least 2.2:1.0, and preferably is lower than 10.0:1.0, more preferably is lower than 7.0:1.0 and even more preferably is lower than 3.0:1.0.

7. The process according to one or more of claims 1 or 6, characterized in that the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 1:1 to 30:1, preferably is from 1:1 to 20:1, more preferably is from 1:1 to 15:1, even more preferably is from 1:1 to 10:1 and particularly preferably is from 1:1 to 8:1.

8. The process according to one or more of claims 1 to 7, characterized in that the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 1:1 to 8:1, R^1 is methyl, and a is, based on a molar average, a number of from 1 to 150, preferably of from 10 to 100, and more preferably of from 15 to 60.

9. The process according to one or more of claims 1 to 7, characterized in that the molar ratio of the terephthalic acid (formula (I)) to the one or more substances of the formula (III) or mixtures thereof is from 2:1 to 8:1, R^1 is a linear or branched alkyl group comprising from 10 to 20 carbon atoms or mixtures thereof, preferably is a linear alkyl group comprising from 10 to 16 carbon atoms or mixtures thereof, and more preferably is selected from the group consisting of lauryl, myristyl and mixtures thereof, and a is, based on a molar average, a number of from 60 to 150, and preferably is a number of from 70 to 140.

10. The process according to one or more of claims 1 to 9, characterized in that one or more substances of the formula (IV) or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably are added in step b)



(IV)

wherein

$^1/_p\,M^{p+}$ is a cation, preferably selected from the group consisting of monovalent cations M^+ (p = 1), divalent cations ½ M^{2+} (p = 2) and trivalent cations ⅓ M^{3+} (p = 3) and more preferably selected from the group consisting of H^+, Li^+, Na^+, K^+, ½ Mg^{2+}, ½ Ca^{2+}, ⅓ Al^{3+}, NH_4^+ and $R_aR_bR_cR_dN^+$, wherein R_a, R_b, R_c and R_d, independently of one another, are H, linear or branched, preferably linear, alkyl groups comprising from 1 to 22 carbon atoms or linear or branched, preferably linear, hydroxyalkyl groups comprising from 2 to 10 carbon atoms, and wherein in the cations $R_aR_bR_cR_dN^+$ at least one of R_a, R_b, R_c and R_d is not H,

R^4 is H or an alkyl group comprising from 1 to 4 carbon atoms, preferably is H or methyl, and more preferably is methyl.

11. The process according to one or more of claims 1 to 10, characterized in that one or more polyalkyleneglycols of the formula (V) or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably are added in step b)

$$H\text{-}(OR^3)_d\text{-}OH \qquad (V)$$

wherein

R^3 is a linear or branched alkylene group (C_pH_{2p}), with p being an integer of from 2 to 10 or mixtures thereof, preferably with p being an integer of from 2 to 6 or mixtures thereof, more preferably is selected from the group consisting of (C_2H_4), (C_3H_6), (C_4H_8) and mixtures thereof, even more preferably is selected from the group consisting of (C_2H_4), (C_3H_6) and mixtures thereof, and particularly preferably is (C_2H_4), and

d is, based on a molar average, a number of from 2 to 200, preferably of from 4 to 150, more preferably of from 10 to 120 and even more preferably of from 35 to 120.

12. The process according to one or more of claims 1 to 11, characterized in that one or more crosslinking compounds, preferably having 3 to 6 functions capable of polycondensation, or mixtures thereof are additionally reacted and are preferably contained in the mixture used in step a) and/or are added in step b), and more preferably, the one or more crosslinking compounds or mixtures thereof are selected from the group consisting of citric acid, malic acid, tartaric acid, gallic acid, pentaerythritol, glycerol, sorbitol, mannitol, 1,2,3-hexanetriol, trimellitic acid, trimellitic anhydride, trimesic acid, and mixtures thereof.

13. The process according to one or more of claims 1 to 12, characterized in that one or more catalyst systems, and preferably one or more metal catalyst systems, are used in step a) and/or in step c), which more preferably comprise at least one titanium-based catalyst, and even more preferably comprise titanium tetraisopropylate and/or titanium tetrabutylate.

14. The process according to one or more of claims 1 to 13, characterized in that at least 20 wt.-%, preferably at least 30 wt.-%, more preferably at least 50 wt.-% and even more preferably 100 wt.-% of the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a), in each case based on the total weight of the one or more alkylene glycols of the formula (II) or mixtures thereof used in step a), are alkylene glycols of the formula (II) or mixtures thereof which have been obtained from step c) of a previous polycondensation reaction.

15. A product or polyester obtainable by the process according to one or more of claims 1 to 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/086864

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G63/50 C08G63/672 C08G63/688 C08G63/78 C08G65/332
C11D3/37

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2023/183612 A1 (GILLISSEN MARTIJN [NL] ET AL) 15 June 2023 (2023-06-15)	1-15
Y	paragraphs [0001], [0126] - [0130]; claim 1 -----	1-15
X	US 2021/261728 A1 (ARNDT MATTHIAS [DE] ET AL) 26 August 2021 (2021-08-26)	1-15
Y	paragraphs [0001], [0151] - [0169]; table 1 -----	1-15
Y	US 2018/179474 A1 (JANSSEN FRANK [DE] ET AL) 28 June 2018 (2018-06-28) paragraph [0001]; examples 1,2 -----	1-15
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☐ Further documents are listed in the continuation of Box C.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/086864

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