MIXED CATALYST COMPOSITION

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ABSTRACT

The present invention relates to catalytic compositions for esterification, transesterification and polycondensation reactions, a process for the catalysis of said reactions employing such catalytic compositions and polyesters or resins obtainable by this process.
MIXED CATALYST COMPOSITION

[0001] The present invention relates to catalytic compositions for esterification, transesterification and polycondensation reactions, a process for the catalysis of said reactions employing such catalytic compositions and polyesters or resins obtainable by this process.

[0002] Catalytic systems containing organotin compounds are widely known. JP-A 06-248060, JP-A 03-284414 and JP-A 03-218511 describe catalyst systems based on organotin compounds and trivalent and pentavalent heteroatom compounds especially phosphorus ligands, used in the ring opening polymerization of lactides. These systems are used to optimize the mechanical and thermal resistance of the polymer.

[0003] The application of such catalytic compositions for carrying out or accelerating other reactions has not been reported so far.

[0004] In contrast, DE-A-101 21 542 reports further that e.g. stabilizers containing heteroatoms are used for quenching the catalyst within the esterification, transesterification or pre-condensation step as these compounds form inactive products together with the catalyst.

[0005] Furthermore, special processes are known in which defined catalyst and stabilizer concentrations and defined locations for their addition are used. Herein the stabilizer is added after the catalyst. According to DE-A-19 50 997 it is common to deactivate the transesterification catalyst with a suited amount of a trivalent or pentavalent heteroatom containing compound by coordination or covalent bonding. This is done to avoid a detrimental influence of the transesterification catalyst within the polycondensation reaction. The polycondensation catalyst is added after this deactivation, a further polycondensation stabilizer might be added later.

[0006] Furthermore is known that during the production of polyesters for some applications for example wrappings and technical yarns, a crystallization and polycondensation in the solid state is carried out (U.S. Pat. No. 4,064,112, U.S. Pat. No. 4,263,425, U.S. Pat. No. 5,362,844). In other applications, fibers or filaments are spun directly and direct preforms are produced in a process wherein an intermediate transfer into the solid state and a repeated remelting is not applied.

[0007] Conventional polyester compositions are connected with a series of disadvantages (general summary in: Handbook of polyester thermoplastics, 1st edition, Wiley-VCH, Weinheim, 2002). Among these disadvantages are in particular:

[0008] Necessity of high temperatures for the synthesis

[0009] High catalyst concentration (100-500 ppm [as metal])

[0010] Degradation processes under processing and polycondensation conditions; for example formation of vinyl esters and due to the formation of acetic aldehyde in polyethylene terephthalate (PET), formation of acrolein in polypropylene terephthalate (PPT) and tetrahydrofuran formation in polybutylene terephthalate (PBT).

[0011] Limited use of the catalyst systems, dependent on the technology of the process and the chemical structure of the substrate; classic titanium based catalysts cannot be added for example during the esterification- and/or precondensation step, as these are readily hydrolyzed to inactive titanium oxides.

[0012] Application of the catalyst system only in selected process stages for example only during the esterification- or only during the transesterification- or only during the polycondensation stage.

[0013] Optical turbidity of the produced polyester for example by deposits of elementary metal impurities as this can occur by the use of antimony based catalyst systems.

[0014] Discoloration of the polyester by the catalyst itself, for example titanium based catalyst systems cause a yellow coloring of the polymer or formation of chromophor by-products, respectively.

[0015] Problematic metering and addition of catalysts and catalyst formulations.

[0016] Object of the present invention is to provide a catalytic composition, suitable for catalyzing esterification, transesterification and polycondensation reactions, an improved process of esterification, transesterification and polycondensation reactions and the production of improved polyesters for bottles, films, foils, yarn, molded padding, resins for powder coatings and technical synthetic materials, which avoid the disadvantages of the prior art.

[0017] The problem is solved according to the invention by a catalytic composition according to claim 1, a process according to claim 6 and polyesters or resins according to claims 18 and 19.

[0018] The catalytic composition for esterification, transesterification and polycondensation reactions according to the invention contains a mixture of at least one organotin compound (compound I) of the general formula (I):

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_4 \\
\text{R}_1 & \quad \text{R}_2 \quad \text{R}_3 \quad \text{R}_4
\end{align*}
\]

(formula I)

[0019] wherein

[0020] \( \text{R}_1 \) is selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, or substituents selected from the group: —X-R², wherein \( \text{R}² \) is —CN, —COOH, —COO-methyl, —COO-ethyl, —COO-n-propyl, —COO-isopropyl, —COO-n-buty1, —COO-2-buty1, —COO-isobuty1, —COO-tert-butyl, —COO-n-pentyl, —COO-isopentyl, —COO-n-pentyl, —COO-tetra-pentyl, —COO-hexyl, —COO-heptyl, —COO-n-octyl, —COO-iso-octyl, —COO-2-ethyl-1-hexyl, —COO-2,2,4-trimethylpentyl, —COO-nonyl, —COO-dodecyl, —COO-dodecyl, —COO-cyclopentyl, —COO-cyclohexyl, —COO-cycloheptyl, —COO-methylcyclohexyl, —COO-vinyl,
—COO-1-propenyl, —COO-2-propenyl, —COO-naphthyl, —COO-anthranil, —COO-phenanthryl, —COO-o-tolyl, —COO-p-tolyl, —COO-m-tolyl, —COO-tolyl, —COO-ethylphenyl, —COO-mesityl, —COO-naphthyl, —COO-phenyl, —COOC₆H₄OH, —COOC₆H₅OH, —COOC₆H₄(CH₃)₂CH₂OH; and —X—is —CH₃, —CH₃, —C₆H₅—C₆H₄—, —C₆H₄OH, or —CH₃H₂⁺.

[0021] R₂ is selected from the groups of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms and anionlic ligands with O-coordination of the group selected from —O—OH, linear, branched or cyclic alkyl or arylcarboxy groups having 1 to 40 carbon atoms, linear, branched or cyclic alkyl- and aryl alcoholate groups having 1 to 40 carbon atoms;

[0022] R₃ and R₄ independently each are selected from the groups of anionic ligands with O-coordination of the group selected from —O—OH, linear, branched or cyclic alkyl groups or arylcarboxy groups having 1 to 40 carbon atoms, linear, branched or cyclic alkyl- and aryl alcoholate groups having 1 to 40 carbon atoms and anions of a mineral acid selected from the group of sulphate, sulphite, phosphate, halogen- or pseudohalogens anion and at least one compound (compound II) according to one of the formulae (II), (III) and/or (IV),

\[
X_{\text{m}}(R')_{\text{n}} \quad \text{(Formula II)}
\]

\[
O_{\text{o}}=X_{\text{m}}(R')_{\text{n}} \quad \text{(Formula III)}
\]

\[
O_{\text{o}}=X_{\text{m}}(R')_{\text{n}} \quad \text{(Formula IV)}
\]

wherein X is a heteroatom selected from the group consisting of N, P, Si, Cl, Br, I or S,

[0023] m is an integer from 1 to 5,

[0024] n is an integer from 1 to 5,

[0025] o is an integer from 1 to 5,

[0026] p is an integer from 0 to 5,

[0027] q is an integer from 0 to 5,

[0028] r is an integer from 0 to 3, wherein

[0029] R' in formula (II) denotes n different or identical groups, each being independent from each other selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, anionic ligands with O-coordination selected from the group of —O—OH, linear, branched or cyclic alkyl- and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₃⁺ or a metal ion,

[0030] R' in formula (III) denotes o different or identical groups, each being independent from each other selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40, anionic ligands with O-coordination selected from the group of —O—OH, linear, branched or cyclic alkyl- and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₃⁺ or a metal ion,

R' in formula (IV) denotes q different or identical groups, each being independent from each other selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40, anionic ligands with O-coordination selected from the group of —O—OH, linear, branched or cyclic alkyl- and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₃⁺ or a metal ion.

[0031] Said catalytic compositions proved highly effective in the catalysis of esterification, transesterification, polycondensation, polyesterification and polytransesterification reactions.

[0032] It has to be pointed out that according to the invention compound I and compound II form a physical mixture and do not chemically react with each other. That means compound I and compound II are neither connected by a complex nor a covalent bond. For example, in the case that compound II is a phosphorous compound this is confirmed by the 31P NMR data of the physical mixture of compound I and compound II.

[0033] Preferred metal ions according to the invention include NH₄⁺, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Zn, B, Al, Sc, Y.


[0035] Especially preferred substituents according to the invention are: methyl, n-butyl, n-octyl and n-dodecyl.

[0036] According to the invention —X—is preferably —C₄H₆—, and preferred moieties R₄ are —CN, —COOH, —COO-methyl, —COO-ethyl.

[0037] Preferred examples for R₂ are according to the invention:

[0038] a) methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2-ethyl-1-hexyl, 2,2,4-trimethylpentyl, nonyl, decyl,
dodecyl, n-dodecyl, cyclopentyl, cyclohexyl, cycloheptyl, methylcyclohexyl, vinyl, 1-propanol, 2-propanol, naphthyl, anthranil, phenanthral, o-tolyl, p-tolyl, m-tolyl, xylol, ethylphenyl, mesityl, phenyl, benzyl. Preferred substituents for the invention are: Methyl, butyl, octyl and dodecyl, or,

b) 0, OH, methanol, ethanol, n-propanol, iso-propanol, n-butanol, 2-butanol, iso-butanol, tert-butanol, n-pentanol, iso-pentanol, neo-pentanol, tert-pentanol, 2-methyl-1-butanol, hexanol, heptanol, n-octanol, iso-octanol, 2,2,4-trimethylpentanol, nonanol, decanol, dodecanol, n-dodecanol, cyclopentanol, cyclohexanol, cycloheptanolate, methylcyclohexanolate, glycolate, glycinate, pinacolone neopentylglycolate, vinylalcoholate, propargylalcoholate, 2-ethyl-1-hexanolate, formate, acetate, propionate, butyrate, valerate, caprate, caprylate, laurate, 2-ethyl-1-hexanoate, neodecanoate, palmitate, stearate, benzoate, terephthalate, phthalate, isophthalate, acrylate, methacrylate, crotonate, isocrotonate, vinylacacetate, oleate, sorbte, linolate, linolenate, trilurocacetate, p-toluenesulfonate, oxalate, malonate, succinate, glutarate, adipate, fumarate, maleinate, trimethylphosphite, n-propylmaleic acid monoester, methylmaleic acid monoester, ethylmaleic acid monoester, butylmaleic acid monoester, iso-propylmaleic acid monoester, n-butylmaleic acid monoester, 2-butylmaleic acid monoester, iso-butylmaleic acid monoester, tert-butylmaleic acid monoester, n-pentylmaleic acid monoester, iso-pentylmaleic acid monoester, neo-pentylmaleic acid monoester, tert-pentylmaleic acid monoester, 2-methyl-1-butylmaleic acid monoester, hexylmaleic acid monoester, heptylmalic acid monoester, octylmalic acid monoester, nonylmalic acid monoester, decylmalic acid monoester, dodecylmalic acid monoester, cyclohexylmalic acid monoester, cyclohexylmaleic acid monoester, cyclohexylmaleic acid monoester, glycolmaleic acid monoester, glycerolmaleic acid monoester, pinakolmaleic acid monoester, neopentylglycolic acid monoester, vinylmaleic acid monoester, propargylmaleic acid monoester and 2-ethyl-1-hexylmaleic acid monoester, citrate, lactate, tartrate, naphthalene-2,6-dicarboxylate, naphthalene-1,6-dicarboxylate, F, Cl, CIO, CIO₂, CIOn, Br, J, CN, SCN, OCN, sulphate, hydrogensulfate, sulphite, hydrogensulfite, sulfide, phosphate, hydrophosphate, dihydrophosphate, bis(2-ethyl-1-hexyl)phosphate, butylphosphate, dibutylphosphate, 3-phosphonpropionate, phenylphosphonic acid, benzolphosphonic acid, p-aminophosphonic acid, n-octylphosphonic acid favored substituents are: O, OH, Br, 2-ethyl-1-hexanoate, neodecanoate, oxalate, 2-ethyl-1-hexylmaleic acid monoester and acetate.

Prefered examples for R3 and R4 are according to the invention: 0, OH, methanol, ethanol, n-propanol, iso-propanol, n-butanol, 2-butanol, iso-butanol, tert-butanol, n-pentanol, iso-pentanol, neo-pentanol, tert-pentanol, 2-methyl-1-butanol, hexanol, heptanol, n-octanol, iso-octanol, 2,2,4-trimethylpentanol, nonanol, decanol, dodecanol, n-dodecanol, cyclopentanol, cyclohexanolate, cyclo-

behanolate, methylecyclohexanolate, glycolate, glycinate, pinacolone neopentylglycolate, vinylalcoholate, propargylo-
kolate, 2-ethyl-1-hexanolate, formiate, acetate, pro-
pienate, butyrate, valerate, caprate, caprylate, caprine, la-
urate, 2-ethyl-1-hexanoate, neodecanoate, palmitate, stearate, benzoate, terephhalate, phthalate, isophthalate, acrylate, methacrylate, crotonate, isocrotonate, vinylacetate, oleate, sorbate, linolate, linolenate, triluroacetate, p-toluenesulfonate, oxalate, malonate, succinate, glutarate, adipate, fumarate, maleinate, trimethylphosphite, n-propylmaleic acid monoester, methylmaleic acid monoester, ethylmaleic acid monoester, butylmaleic acid monoester, iso-propylmaleic acid monoester, n-butylmaleic acid monoester, 2-butylmaleic acid monoester, iso-butylmaleic acid monoester, tert-butylmaleic acid monoester, n-pentylmaleic acid monoester, iso-pentylmaleic acid monoester, neo-pentylmaleic acid monoester, tert-pen-
ylmaleic acid monoester, 2-methyl-1-butylmaleic acid monoester, hexylmaleic acid monoester, heptylmalic acid monoester, octylmalic acid monoester, iso-octylmaleic acid monoester, 2,2,4-trimethylpentylmaleic acid monoester, nonylmalic acid monoester, decylmaleic acid monoester, dodecylmalic acid monoester, cyclohexylmalic acid monoester, cyclohexylmaleic acid monoester, cyclohexylmaleic acid monoester, glycolmaleic acid monoester, glycerolmaleic acid monoester, pinakolmaleic acid monoester, neopentylglycolic acid monoester, vinylmaleic acid monoester, propargylmaleic acid monoester and 2-ethyl-1-hexylmaleic acid monoester, citrate, lactate, tartrate, naphthalene-2,6-dicarboxylate, naphthalene-1,6-dicarboxylate, F, Cl, CIO, CIO₂, CIOn, Br, J, CN, SCN, OCN, sulphate, hydrogensulfate, sulphite, hydrogensulfite, sulfide, phosphate, hydrophosphate, dihydrophosphate, bis(2-ethyl-1-hexyl)phosphate, butylphosphate, dibutylphosphate, 3-phosphonpropionate, phenylphosphonic acid, benzolphosphonic acid, p-aminophosphonic acid, n-octylphosphonic acid. Most preferred substituents are: O, OH, Cl, laurate, 2-ethyl-1-hexanoate, neodecanoate, oxalate, 2-ethyl-1-hexylmaleic acid monoester and acetate.

Prefered examples for compound II of the invention are phosphites, phosphines, phosphonic acid esters, pyrophosphates, alkaline halogenides, earth alkaline halogenides, aluminum halogenides.

According to the invention combinations with the following examples of compound II are particularly preferred: Formula II (X=P): triocyl-, trisococyl-, trilauryl-, triecyl-, tridodecyl-, trisododecyl-, tritridecyl-, tritryptadecyl-, trileoyl-, tristearyl-, triphenyl-, triresyl-, trisononylph-

ol, tris(2,4,4-t-butyl-phenyl)- or tricyclohexylphosphite.

Further preferred phosphites of several ary1 dialkyl or alkyl-diarylphosphate may be advantageously applied, such as phenylidy-aryl-, phenylididecy1-, phenylididodecy1-, phenyliditridecy1-, phenyliditradecyl-, octyldiphenyl-, decyldiphenyl-, undecyldiphenyl-, dodce-
cyldiphenyl-, tridecyldiphenyl-, tetrade cyldiphenyl-, penta
decyldiphenyl-, ocyldiphenyl-, stearyldiphenyl-und dode
cyl-bis-2,4-di-t-butylphenylphosphate, tris(2,4,4-di-t-butylphenyl)phosphate, diphenyl-isodecylphosphate.

Also phosphites of several di- or polyols are very well suited and therefore preferred, e.g. phenylisopent-

ylglycolphosphate, leptakis-(1,1-dipropyleneglycol)triphos-
phite, 2,4,6-tri-tert-butylphenyl-2-butyl-2-ethyl-1,3-propanodiphosphate, bis(2,4,6-tri-tert-butylphenyl)pentacyrthriophosphate, tetracyclpropylyleneolkiphosphatethione, polydi-propylene glycolphosphatethione, tetramethylcylohexanoldicystido-phosphate, tetramethylocyclohexanol-butoxyethyolphosphate, tetracyclohexanol-nonylphosphatethione, bis-nonylphosphin-dimethylpropanediphosphate, bis-2-butoxyethyl-dimethylpropanediphosphate, trisbromoxyethyloxycamuri-hexadecytriophosphate, tris(dipropyleneglycol)phosphate, poly-4,4'-isopropylidene-diphenol-cl-12-alkanolphosphate, bisdiocysceptetacythri-toldiphosphate, didicyclpentacyrthriophosphate, dicysteintetacyrthriophosphate, also mixtures of these phosphites and aryl/alkylphosphates-mixtures of the statistic composition (H3C6H4-CH2)12P[O(CH2)3H2]3 or [C6H5-CH2-C6H5-O-P(O-CH2-H2)]3, or [C6H5-CH2-CH2-P(O-CH2-H2)]3 are suitable as well as phosphines with R1, R2, R3=methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, isobutyl, tert-buty, n-pentyl, isopentyl, n-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclohexyl, cycloheptyl, methycyclohexyl, 1-toly, p-toly, m-toly, xylyl, ethylhexylyl, mesityl, phenyl, benzyl and also DIOB, Chiroros and Norphos.

According to the invention especially favored are heterocoupling compounds II including heterocouples such as according to formula II wherein R1, R2, R3 are each independently selected from C6H5, OC6H4 and OC6H4.

Moreover, according to the invention mixtures of compound I with a compound II according to formula III are particularly preferred, such as e.g. (X=Z): R1, R2, R3==Methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, iso-butyl, tert-butyl, n-pentyl, isopentyl, n-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclohexyl, cycloheptyl, methycyclohexyl, vinyl, 1-propenyl, 2-prope-nyl naphthyl, anhryl, phenanthyryl, o-toly, p-toly, m-toly, xylyl, ethylhexylyl, mesityl, phenyl, benzyl, xantholane, n-propanolate, iso-propanolate, n-butanolate, 2-butanolate, iso-butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, n-hexanolate, heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate, nonanolate, decanolate, dodecanolate, n-dodecanolate, tetracyclo-hexanolate, tetracycloheptanolate, methylcyclohexanolate, glycolate, glycerate, pinacolate, neopentylglycolate, vinylalkanolate, propargylalkolate, 2-ethyl-1-hexanolate, ethylhexylglycol, diethylenehexylglycol, triethylenehexylglycol and benzylalkolate, R3=H such as e.g. diphenylphosphate. Triphenylphosphinoxide, triethylphosphate, tributylphosphate, triphenylphosphate, and diphenylphosphate are especially preferred.

Further, according to the invention mixtures of compound I with one or more of the following examples of compound II are particularly preferred (formula II, X==Z): Triisocyl-, trimisocyl-, triaranyl, tridecyl-, tridecyldic-, tri-soxidocyl-, tritriflucyl-, trimepentaclyl-, trioleyl, tristearinyl-, triphenyl-, tricyclosyl-, tris-nonylphenoxy, tris-2,4,4-t-butylphenyl-, tricyclohexylamine, also amine with a composition R1, R2, R3==independent, the same or different: methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, tert-buty, n-pentyl, isopentyl, n-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclohexyl, cycloheptyl, methycyclohexyl, 1-toly, p-toly, m-toly, xylyl, ethylhexylyl, mesityl, phenyl, benzyl are suitable, as well as R1, R2, R3, R4==H, R5==Cl, or R1, R2, R3, R4==H, R5==Br.

Mixtures of compound I with one or more of the following examples of compound II of formula II are according to the invention preferred (X==S): R1, R2, R3==independent, the same or different: methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl, tert-buty, n-pentyl, isopentyl, iso-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclohexyl, cycloheptyl, methycyclohexyl, O-toly, p-toly, m-toly, xylyl, ethylhexylyl, mesityl, phenyl, benzyl, R4==O, OH, xantholane, n-propanolate, iso-propanolate, n-butanolate, 2-butanolate, iso-butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, n-hexanolate, heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate, nonanolate, decanolate, dodecanolate, n-dodecanolate, cyclo-hexanolate, cycloheptanolate, methylcyclohexanolate, glycolate, glycerate, pinacolate, neopentylglycolate, vinylalkanolate, propargylalkolate, 2-ethyl-1-hexanolate, or R1 and/or R2==methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl,
iso-butyl, tert-butyl, n-pentyl, isopentyl, neo-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, cyclopentyl, cyclohexyl, cyclohexyl, methycyclohexyl, o-toly1, p-tolyl, m-tolyl, xyllyl, ethylphenyl, mesityl, phenyl, benzyl, R2, R3, R4, independent, the same or different: 0, OH, methanol, ethanolate, n-propanolate, iso-propanolate, n-butanol, 2-butanolate, iso-butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, tert-pentanolate, 2-methyl-1-butanol, hexanolate, heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate, nonanolate, decanolate, dodecanolate, n-dodecanolate, cyclopentanolate, cyclohexanolate, cycloheptanolate, methylcyclohexanolate, glycolate, glycinate, picinolate, neopentylglycolate, vinylalcoholate, propargylalcoholate, 2-ethyl-1-hexanolate; or R1= methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, iso-butyl, tert-butyl, n-pentyl, isopentyl, neo-pentyl, tert-pentyl, hexyl, heptyl, n-octyl, iso-octyl, 2,2,4-trimethylpentyl, nonyl, decyl, dodecyl, n-dodecyl, cyclopentyl, cyclohexyl, cycloheptyl, methycyclohexyl, o-tolyl, p-tolyl, m-tolyl, xyllyl, ethylphenyl, mesityl, phenyl, benzyl, R2, R3, R4=OH, OH, methanol, ethanolate, n-propanolate, iso-propanolate, n-butanol, 2-butanolate, iso-butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, tert-pentanolate, 2-methyl-1-butanol, hexanolate, heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate, nonanolate, decanolate, dodecanolate, n-dodecanolate, cyclopentanolate, cyclohexanolate, cycloheptanolate, methylcyclohexanolate, glycolate, glycinate, picinolate, neopentylglycolate, vinylalcoholate, propargylalcoholate, 2-ethyl-1-hexanolate; or R1, R2, R3, R4= independent, the same or different: 0, OH, methanol, ethanolate, n-propanolate, iso-propanolate, n-butanol, 2-butanolate, iso-butanolate, tert-butanolate, n-pentanolate, iso-pentanolate, tert-pentanolate, 2-methyl-1-butanol, hexanolate, heptanolate, n-octanolate, iso-octanolate, 2,2,4-trimethylpentanolate, nonanolate, decanolate, dodecanolate, n-dodecanolate, cyclopentanolate, cyclohexanolate, cycloheptanolate, methylcyclohexanolate, glycolate, glycinate, picinolate, neopentylglycolate, vinylalcoholate, propargylalcoholate, 2-ethyl-1-hexanolate. Especially preferred according to the invention are mixtures with the following examples of compound II: Isobutylisopropyl dimethoxyxyl, disisopropyl dimethoxyxyl, diisobutylidimethoxyxyl, dicyclopropyl dimethoxyxyl, n-propyltrimethoxyxyl, isobutyl-sec-butyl dimethoxyxyl, cyclopropylisobutyl dimethoxyxyl, cyclo-pentylisobutyl dimethoxyxyl, cyclo-hexylisobutyl dimethoxyxyl, isobutyl-ethyl dimethoxyxyl.

[0049] Mixtures of compound I with one or more of the following examples of compound II of formula II are according to the invention preferred (X=Cl or Br or I, with m=1): R1=NH₄, Li, Na, K, Rb, for m=2: R1=Cs, Mg, Ca, Sr, Ba, Zn for m=3: R1=Bi, Al, Sc, Y, for m=4: R1=Ti, Zr, Hf.

[0050] Also, mixtures of compound I with one or more of the following examples of compound II of formula III are according to the invention preferred, such as: NaClO₂, KClO₂, HClO₂, HClO₃, KClO₃, NaClO₃, HClO₄, NaClO₄, KClO₄, and, particularly preferred, NaCl, AlCl₃, KCl, NaBr, KBr, NaClO₄, and KClO₄ and their respective hydrates.

[0051] Moreover, mixtures of compound I with one or more of the following examples of compound II of formula III are according to the invention preferred (X=SO₄, KSO₄, MgSO₄, CaSO₄, SrSO₄, BaSO₄, Al₂(SO₄)₃, NaAl(SO₄)₃, NH₄Al(SO₄)₂, KAl(SO₄)₂, Na, and their hydrates, particularly preferred are Al₂(SO₄)₃, NaAl(SO₄)₃, NH₄Al(SO₄)₂.

[0052] The molar ratio of compound I to compound II may by advantage be 1:0.001 to 1:200, preferred is a ratio of 1:0.01 to 1:20.

[0053] The composition of compound I and/or compound II may contain suspension agents or solvents to improve reaction kinetics and yield.

[0054] The invention further provides a process for the continuous or batchwise catalysis of esterification, transesterification, polymerization, polytransfermerification reactions of an alcohol and an acid or acid derivative, e.g. an ester, anhydride or halogenide, characterized by employing a catalytic composition as defined above. This process may include the steps:

[0055] Preparation of a reaction mixture containing a polyvalent alcohol and an acid or ester with at least two carboxylic groups.

[0056] Addition of catalytic composition according to the invention.

[0057] At least two catalytic compounds I and II may be added to the reaction mixture in isolated form, as solid, dissolved in a suitable solvent, as a liquid or as suspension.

[0058] The employed carboxylic acid may be a monocarboxylic acid, di- or polycarboxylic acid. Among dicarboxylic acids, carboxylic acids containing at least two carboxyl groups, dicarboxylic acids such as e.g. terephthalic acid and/or 1,2,6-naphthalenedicarboxylic acid, isophthalic acid, 1,4-cyclohexane dicarboxylic acid, 1,6-naphthalene dicarboxylic acid, 4,4-bisphenyl dicarboxylic acids, adipic acid, phthalic acid, alkane dicarboxylic acids, halogen derivates of the mentioned dicarboxylic acids for example tetrahydrophthalic acid, and copolymers of the mentioned dicarboxylic acids or the esters of the mentioned carboxylic acids for example dimethyl terephthalate, bis(hydroxethyl) terephthalate, 2,6-dimethyl naphthalate, 1,6-dimethyl naphthalate are particularly preferred.

[0059] The alcohols employed in the process according to the invention may be mono-, di- or polyvalent.

[0060] As di- or polyvalent alcohols, alcohols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol and/or 1,4-cyclohexanedimethanol, di-, triethylene glycol, polyglycols with a molecular weight below 1000 or neopentyl glycol, are particularly preferred.

[0061] Further, recycled polyester material might be used as comonomer within the process based on the invention.

[0062] The inventors have shown that compound II, bearing a heteroatom as such neither catalyzes the esterification, nor transesterification, nor the polycondensation reaction. Surprisingly, an unexpected synergism between the metal catalyst (compound I) and the heteroatom compound (compound II) was found. The catalytic activity of selected systems of compound I can be increased according to the invention by approx. 50%.
According to the invention, the polycondensation is catalyzed and accelerated by a new compound system. It has been shown that in comparison to conventional catalytic systems less amounts of catalyst and stabilizer lead to comparable results. Furthermore, even high-viscous polyesters can be manufactured in a direct process in far shorter polycondensation times. The novel mixtures according to the invention are further hydrolysis resistant and may be added either during the esterification phase and/or the precondensation phase as an active composition.

The catalytic composition of the invention shows a lower toxicity in comparison with conventional catalytic systems.

The preferred metal concentration of the catalytically effective metal compound (compound I) is 0.1 to 500 ppm (as Sn), in particular 10-200 ppm (as Sn) in relation to the acid or ester to be reacted.

The preferred concentration of the heteroatom containing compound (compound II) is 0.0001 ppm (as compound I), in particular 10-200 ppm in relation to the acid or ester to be reacted.

Particularly preferred is a process for a polyesterification reaction as defined above, characterized by reacting a dicarboxylic acid or a dicarboxylic acid derivative with a divalent alcohol.

Particularly preferred derivatives of mono-, di-, or polycarboxylic acids are esters or halogenides.

In the process of the invention hydroxycarboxylic acids such as p-hydroxybenzoic acid, salicylic acid, lactic acid, glycol acid or preferably, derivatives thereof such as esters or ethers, and their co-polyesters with dicarboxylic acids and/or diols as described above may be reacted to the respective polyesters.

As a further compound a polyfunctional alcohol can be added to the reaction mixture. The polyfunctional alcohol, such as pentaerythritol can be added favored in a concentration of 0-500 ppm, in particular 50 ppm. The alcohol can be added together with compound I or separately, simultaneously, before or after, latest during the precondensation of the polyester. No influence on the effect of the other compounds occurs in this case.

The compounds I and/or II used for the production of polyester can be added during the period before the beginning of the esterification and/or transesterification until shortly before the end of the polycondensation, favored during the esterification and/or transesterification or before the precondensation.

A solvent or suspending agent may be added to compound I and/or compound II.

As solvents or suspending agents for the compounds I and/or II a mono-, di- or polyvalent alcohol such as e.g. an alkane can be employed. Preferred are 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethylpropan-1,3-diol.

The same solvent and/or suspending agent may be employed during manufacturing of the catalytic composition and said esterification, transesterification, polyesterrification or polytransesterification reaction.

Alternative to this, also a different solvent and/or suspending agent may be employed during manufacturing of the catalytic composition and said esterification, transesterification, polyesterrification or polytransesterification reaction.

Moreover, a solvent or suspending agent may be employed in the manufacturing step of the catalytic composition being selected from the group of mono-, di- or polyvalent alcohols that is reacted in said esterification, transesterification, polyesterrification or polytransesterification reaction.

Further an organic liquid may be employed as solvent or suspending agent for the catalytic composition that is indifferent with respect to the polyester production process. Indifferent organic liquids are e.g. alkanes, cycloalkanes or benzene derivatives (for example benzene, toluene, xylene). Also water or a mixture of water with an alcohol or a polyvalent alcohol is suited as solvent and/or suspending agent according to the invention.

Further additives for a color correction such as cobalt salts or organic dyes or pigments might be added to the reaction mixture, usually in amounts of 0.0001-5% by weight with respect to the acid or ester to be reacted.

Subject of the invention are further polycondensation products, produced by the described process of esterification, transesterification, polyesterrification, polytransesterification with the use of the catalytic compositions according to the invention.

Furthermore, subject of the invention are polyester for bottles, films, foils, yarn, molded padding, resins for powder coatings and technical synthetic materials, obtainable by the process according to the invention.

The polyester available by the process according to the invention shows comparable qualities for the processability in comparison with conventional polyesters for example catalyzed by antimony. In comparison with usual high-viscous melt polymerisations, resins products produced with the compounds described in the invention show a relatively low content of acetic aldehyde. In particular the polyesters synthesized with the process according to the invention show a narrow molecular weight distribution, a high translucency and give a polymer with a high, desired blue shift. A polymer of high viscosity is, unlike the state of the art using Sb catalysts, obtained without difficulty.

In the case of the inventive use of compound I with R1=—X-R^ the organoton catalyst is incorporated into the polymer by the means of an ester bond, that means the organoton species can only be released out of the polymer resin by its total destruction.

The polymers, produced with catalysts based on the invention show a high blue shift (negative b-values; color values are determined by using the CIE-Lab 100 color system with spectral reference beam color measuring instrument LUCI 100, Dr. Lange).

Polyesters, produced according to the invention employing a catalytic composition according to the invention show less by-products such as acetic aldehyde in polyethylene terephthalate (PET) in comparison with conventional techniques.
The polyesters produced according to the process described in the invention are made by esterification or transesterification with the use of the composition of compound I and/or compound II described in the invention and optionally subsequent polycondensation.

Preferred polyesters according to the invention are a) polyethylene terephthalate (PET), containing 0.1-10 mass % diethylene glycol and 0-10 mass % of isophthalic acid, 2-hydroxyisophthalic acid, p-hydroxyisophthalic acid, 2,6-naphthalene dicarboxylic acid and/or 1,4-cyclohexane dimethanol as co-monomer; b) polyester for powder coatings mainly poly-2,2-dimethylpropyl-1,3-terephthalate; c) polypropylene terephthalate (PPT); d) polyester polyols as for example polyethylene glycol terephthalate; e) polybutylene terephthalate (PBT); f) polynaphthalene terephthalates (PNT); g) polyethylene naphthalate (PEN).

The following examples further illustrate the invention without, however, limiting the invention. Unless otherwise indicated, parts and percentages relate to the weight, as in the remainder of the description.

**EXAMPLES**

**Example 1**

Preparation of Catalytic Active Mixtures of compound I and compound II

**Apparatus:**

100 ml round bottom flask, magnetic stirrer, rotary evaporator.

**Starting Materials, Quantities:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Molar Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>butyltin tris(neodecanoate)</td>
<td>68.44 g</td>
<td>0.10 mol</td>
</tr>
<tr>
<td>triphenylphosphine</td>
<td>26.23 g</td>
<td>0.10 mol</td>
</tr>
<tr>
<td>triphenylphosphite</td>
<td>31.03 g</td>
<td>0.10 mol</td>
</tr>
<tr>
<td>tributylphosphate oxide</td>
<td>27.83 g</td>
<td>0.10 mol</td>
</tr>
<tr>
<td>dinitrilotrihexanediol</td>
<td>25.03 g</td>
<td>0.10 mol</td>
</tr>
</tbody>
</table>

**Preparation:**

The heteroatom compound II, dissolved in xylene (ethanol in the case of triphenylphosphine oxide) was given into the round bottom flask and stirred for 15 min. Butyltin tris(neodecanoate) dissolved in 50 ml xylene or ethanol, respectively was added to the mixture by the means of a tap funnel and stirred for an additional hour. The catalytic active system was obtained after removal of the solvent under reduced pressure.

**Analysis:**

115Sn-NMR

31P-NMR

catalyst system e)

**Apparatus:**

250 ml three necked round bottom flask, tap funnel, magnetic stirrer, water separator, rotary evaporator.

**Example 2**

Catalyst Test by Synthesis of a Resin for Powder Coatings

**Starting Materials, Quantities:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Molar Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>terephthalic acid</td>
<td>83.07 g</td>
<td>0.50 mol</td>
</tr>
<tr>
<td>neopentylglycol</td>
<td>104.15 g</td>
<td>1.00 mol</td>
</tr>
<tr>
<td>(2,2-Dimethyl-1,3-propandiol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>catalyst:</td>
<td>0.05% [m/m]</td>
<td></td>
</tr>
</tbody>
</table>

**Synthesis:**

Monobutyltin oxide was dissolved in 150 ml xylene, triphenylphosphine, dissolved in 50 ml xylene and neodecanoic acid were added within 10 min. The mixture was heated under reflux until the water-formation stops. The product was obtained after filtration and removal of the solvent under reduced pressure.

**Example 3**

Catalyst Test by Synthesis of a Resin for Powder Coatings with Physical Mixtures of Monobutyltin Oxide, Triphenylphosphine and Triphenylphosphite

**Starting Materials, Quantities:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Molar Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>terephthalic acid</td>
<td>83.07 g</td>
<td>0.50 mol</td>
</tr>
<tr>
<td>neopentylglycol</td>
<td>104.15 g</td>
<td>1.00 mol</td>
</tr>
<tr>
<td>(2,2-Dimethyl-1,3-propandiol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>catalyst:</td>
<td>0.05% [m/m]</td>
<td></td>
</tr>
<tr>
<td>f) 0.165 g monobutyltin oxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.207 g triphenylphosphine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g) 0.165 g monobutyltin oxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.245 g triphenylphosphine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Synthesis:**

Catalyst, neopentyl glycol and terephthalic acid are given into a 250 ml three-necked round bottom flask. The mixture is heated to a maximum by the means of a heating jacket, the reaction water is distilled off and the amount is metered. The reaction time equals the time between the first water formation and the "clear point" of the reaction.
The reaction time equals the time between the first water formation and the "clear point" of the reaction.

Table 1 shows the acceleration of the reaction time in the described resin synthesis with the mixtures of (comparative) examples 1a, 1b, 1c, 1d, 1e and 1f, 1g in comparison with the uncatalyzed reaction or with monobutyltinoxide (0.05%[m/m]) as catalyst.

Example 4
Polycondensation of bis(2-hydroxyethyl) terephthalate (BHET)

Experimental Method:

Polycondensation equipment 1 (glass equipment) for the melt polycondensation of BHET

Tempering-bath (salt bath), polycondensation vessel (glass), screw mixer (glass), vacuum pump, pressure gauge

As a polycondensation equipment, a round glass flask with round bottom was used, (internal diameter 2.6 cm, and 35 cm height, described in T. Johnson, Chem. Fibers International 46 (1996) 280; 49 (1999) 455). A horizontal vapor outlet was integrated into the upper third of the flask wall. A further extension tube near the bottom of the vessel allowed sampling from the polymer melt. The stirrer was a glassware screw mixer, reaching down to the ground (1.8 cm diameters). The mixer was operated with a rotation speed of 100 min⁻¹ and intermixed the melt with axially downward direction.

25.4 g (0.1 mol) BHET was filled into the polycondensation vessel, the catalyst (5 to 200 ppm as metal) was added and the vessel locked. Then the polycondensation vessel filled with the reaction mixture was evacuated three times and rinsed with dry nitrogen before it was immersed in the tempering-bath. The bath temperature was preset so that the desired internal temperature of 280°C was reached in the polycondensation vessel. After the reaction mixture was melted, the stirrer was started and the vessel evacuated within 15 min onto a vacuum of 2x10⁻¹ mbar. The time of the first formation of glycol at the wall of the glass was regarded as t₀. The attainable final pressure for this equip-
TABLE 3-continued

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>temperature [°C]</th>
<th>time [min]</th>
<th>catalyst conc. [ppm]</th>
<th>P₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>antimony</td>
<td>270</td>
<td>30</td>
<td>190</td>
<td>85</td>
</tr>
<tr>
<td>antimony</td>
<td>270</td>
<td>150</td>
<td>190</td>
<td>100</td>
</tr>
<tr>
<td>antimony</td>
<td>270</td>
<td>180</td>
<td>190</td>
<td>115</td>
</tr>
<tr>
<td>antimony</td>
<td>280</td>
<td>30</td>
<td>190</td>
<td>30</td>
</tr>
<tr>
<td>antimony</td>
<td>280</td>
<td>60</td>
<td>190</td>
<td>55</td>
</tr>
<tr>
<td>antimony</td>
<td>280</td>
<td>90</td>
<td>190</td>
<td>75</td>
</tr>
<tr>
<td>antimony</td>
<td>280</td>
<td>120</td>
<td>190</td>
<td>95</td>
</tr>
<tr>
<td>antimony</td>
<td>280</td>
<td>150</td>
<td>190</td>
<td>115</td>
</tr>
<tr>
<td>triacetate</td>
<td>280</td>
<td>180</td>
<td>190</td>
<td>135</td>
</tr>
<tr>
<td>tetrabutyl titanate</td>
<td>280</td>
<td>30</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>tetrabutyl titanate</td>
<td>280</td>
<td>60</td>
<td>20</td>
<td>65</td>
</tr>
<tr>
<td>tetrabutyl titanate</td>
<td>280</td>
<td>90</td>
<td>20</td>
<td>85</td>
</tr>
</tbody>
</table>
| tetrabutyl titanate | 280    | 120        | 20                   | 105
| tetrabutyl titanate | 280    | 150        | 20                   | 125|
| tetrabutyl titanate | 280    | 180        | 20                   | 150|

TABLE 2

<table>
<thead>
<tr>
<th>time [%]</th>
<th>Sn [ppm]</th>
<th>COOH [ug/g]</th>
<th>Mₙ [g/Mol]</th>
<th>Pₙ</th>
<th>L [a]</th>
<th>b [b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>123</td>
<td>0.2766</td>
<td>16</td>
<td>5104</td>
<td>26</td>
<td>34.19</td>
</tr>
<tr>
<td>60</td>
<td>123</td>
<td>0.5216</td>
<td>14</td>
<td>13380</td>
<td>69</td>
<td>33.84</td>
</tr>
<tr>
<td>90</td>
<td>123</td>
<td>0.7152</td>
<td>19</td>
<td>21616</td>
<td>112</td>
<td>37.73</td>
</tr>
<tr>
<td>120</td>
<td>123</td>
<td>0.8359</td>
<td>24</td>
<td>27588</td>
<td>143</td>
<td>36.54</td>
</tr>
</tbody>
</table>

TABLE 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>temperature [°C]</th>
<th>time [min]</th>
<th>catalyst conc. [ppm]</th>
<th>P₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>antimony</td>
<td>270</td>
<td>30</td>
<td>190</td>
<td>25</td>
</tr>
<tr>
<td>antimony</td>
<td>270</td>
<td>60</td>
<td>190</td>
<td>45</td>
</tr>
<tr>
<td>antimony</td>
<td>270</td>
<td>90</td>
<td>190</td>
<td>65</td>
</tr>
</tbody>
</table>

[0118] The comparative investigations for the catalytic activity of the selected tin compounds show that no noteworthy thermal decomposition is to be expected within 2 h of polycondensation time at temperatures of 280°C. Therefore it is absolutely possible to synthesize even higher molecular weight polyethylene terephthalates by prolongation of the polycondensation time.

[0119] All examined tin compounds proved as high-activity catalysts for the polycondensation of BHET, which show significantly higher activity than stibious compounds. Their polytransterification activity is superior to titanium alkoxides and titanium chelates. If required, they can be employed also in higher concentrations.

1-19. (canceled)

20. A catalytic composition useful for esterification, transesterification and polycondensation reactions, said catalytic composition comprising a mixture of:

(A) at least one organotin compound of the general formula (I):

\[
\text{(formula I)}
\]

wherein

R₁ is selected from the group consisting of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, or substituents selected from the group: −X−R₂, wherein R₂ is −CN, −COOH, −COO-methyl, −COO-ethyl, −COO-n-propyl, −COO-

X is \( \text{CH}_2 \), \( \text{C}_3 \text{H}_7 \), \( \text{C}_3 \text{H}_6 \), \( \text{C}_3 \text{H}_5 \), \( \text{C}_3 \text{H}_4 \), \( \text{C}_3 \text{H}_3 \), \( \text{C}_3 \text{H}_2 \), \( \text{C}_3 \text{H}_1 \), \( \text{C}_3 \text{H}_0 \), \( \text{C}_3 \text{H}_9 \), \( \text{C}_3 \text{H}_{10} \), or \( \text{C}_3 \text{H}_{12} \).

R² is selected from the group consisting of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms and anionic ligands with O-coordination of the group selected from \(-O, -OH, \text{linear, branched or cyclic alkyl or aryloxy groups having 1 to 40 carbon atoms, linear, branched or cyclic alkyl-}, \) and aryl alcoholate groups having 1 to 40 carbon atoms; and

R³ and R⁴ are each independently selected from the group consisting of anionic ligands with O-coordination of the group selected from \(-O, -OH, \text{linear, branched or cyclic alkyl groups or aryloxy groups having 1 to 40 carbon atoms, linear, branched or cyclic alkyl-}, \) and aryl alcoholate groups having 1 to 40 carbon atoms and anions of a mineral acid selected from the group of sulphate, sulphite, phosphate, halogen- or pseudohalogen anion; and

(B) at least one compound according to one of the formulae (II), (III) and/or (IV),

\[
\begin{align*}
\text{(B)} & \quad \text{X} \left( \text{R}_{\text{a}} \right)_m \quad \text{(formula II)} \\
& \quad \text{O} \left( \text{X} \left( \text{R}_{\text{a}} \right)_m \right) \quad \text{(formula III)} \\
& \quad \left( \text{O} \left( \text{X} \left( \text{R}_{\text{a}} \right)_m \right) \right)_q \quad \text{(formula IV)}
\end{align*}
\]

wherein X is a heteroatom selected from the group consisting of N, Si, Cl, Br, I or S,

m is an integer from 1 to 5,

n is an integer from 1 to 5,

o is an integer from 1 to 5,

p is an integer from 0 to 5,

q is an integer from 0 to 5,

r is an integer from 0 to 3,

R¹ in formula (III) denotes q different or identical groups, each being independent from each other and selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, anionic ligands with O-coordination selected from the group of \(-O, -OH, \text{linear, branched or cyclic alkyl-}, \) and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₄⁺ or a metal ion,

R¹ in formula (IV) denotes q different or identical groups, each being independent from each other and selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, anionic ligands with O-coordination selected from the group of \(-O, -OH, \text{linear, branched or cyclic alkyl-}, \) and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₄⁺ or a metal ion.

R¹ in formula (III) denotes q different or identical groups, each being independent from each other and selected from the group of linear, branched or cyclic alkyl groups having 1 to 40 carbon atoms, aryl groups having 1 to 40 carbon atoms, anionic ligands with O-coordination selected from the group of \(-O, -OH, \text{linear, branched or cyclic alkyl-}, \) and aryl alcoholate groups having 1 to 40 carbon atoms, H, Cl, Br, NH₄⁺ or a metal ion.

21. The catalytic composition according to claim 20, wherein the metal ion is selected from the group consisting of NH₄⁺, Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Zn, B, Al, Sc and Y.

22. The catalytic composition according to claim 20, wherein (B) is a phosphite, a phosphine, a phosphonic acid.
ester, a pyrophosphate, an alkaline halogenide, an earth alkaline halogenide or aluminum halogenide.

23. The catalytic composition according to claim 20, comprising a molar ratio of (A) to (B) of 1.0001 to 1:200, in particular 1:0.01 to 1:20, respectively.

24. The catalytic composition according to claim 20, further comprises a suspension agent or solvent.

25. A process for the continuous or batchwise catalysis of esterification, transesterification, polyesterification, polytransesterification reactions of an alcohol and an acid or acid derivative, such as an ester, anhydride or halogenide, said process employing the catalytic composition as defined in claim 20.

26. The process according to claim 25, employing an amount of (A) in the range of 0.1 to 1% by weight, in particular 10 to 200 ppm, with respect to the acid or ester to be reacted.

27. The process according to claim 26, employing a concentration of (B) in the range of 0.0001 ppm to 1% by weight, in particular 10 to 200 ppm, with respect to the acid or ester to be reacted.

28. The process according to claim 25, employing a concentration of (B) in the range of 0.0001 ppm to 1% by weight, in particular 10 to 200 ppm, with respect to the acid or ester to be reacted.

29. The process according to claim 25, comprising reacting a dicarboxylic acid or a dicarboxylic acid derivative with a divalent alcohol in the polyesterification reaction.

30. The process according to claim 25, employing derivatives of mono-, di- or polycarboxylic acids selected from esters or halogenides.

31. The process according to claim 25, comprising reacting hydroxydicarboxylic acids or derivatives of hydroxydicarboxylic acids in the esterification, transesterification, polyesterification or polytransesterification reaction.

32. The process according to claim 31, employing derivatives of hydroxydicarboxylic acids selected from esters or ethers.

33. The process according to claim 25, employing a solvent or suspending agent added to (A) and (B).

34. The process according to claim 33, employing an alkane mono-, di- or polyvalent alcohol as the solvent or suspending agent.

35. The process according to claims 33, employing the same solvent and/or suspending agent during manufacturing of the catalytic composition and said esterification, transesterification, polyesterification or polytransesterification reaction.

36. The process according to claim 35, employing a solvent selected from the group consisting of mono-, di- or polyvalent alcohols reacted in said esterification, transesterification, polyesterification or polytransesterification reaction.

37. The process according to claim 33, employing a different solvent and/or suspending agent during manufacturing the catalytic composition and said esterification, transesterification, polyesterification or polytransesterification reaction.

38. A composition comprising polyester for bottles, films, foils, yarn and/or molded padding, or resin for powder coatings or technical synthetic materials, obtained by the process according to claim 25.

39. The polyester or resin composition according to claim 38, wherein said polyester is selected from the group consisting of polyethylene terephthalate, poly-2,2-dimethylpropyl-1,3-terephthalate, polypropylene terephthalate, polyethylene glycol terephthalate, polybutylene terephthalate, polynaphthalene terephthalate, polyethylene naphthalate, and mixtures thereof.

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