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(54) **POLYMER, PROCESS AND COMPOSITION**

(71) Applicant: **DSM IP ASSETS B.V.**, Heerlen (NL)

(72) Inventors: **Tijs Nabuurs**, Echt (NL); **Gerardus Cornelis Overbeek**, Echt (NL); **Jeffrey Stubbs**, Echt (NL); **Matthew Stewart Gebhard**, Echt (NL)

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(57) **ABSTRACT**

There is described a method of preparing a post-modified polymer the method comprising the steps of: (1) polymerising a monomer composition comprising from 2.5 to 75% by weight of the total monomer composition of at least one itaconic anhydride, precursor thereof and/or derivative thereof in a polymerisation method to obtain an itaconate Polymer A; (2) reacting in a post modification step at least 10 mole-% of the anhydride groups, anhydride precursor groups and/or anhydride derived groups of the Polymer A obtained from step (1) with a Nucleophile B to form a post-modified Polymer C, and optionally using said polymer C as seed or stabiliser in a further step (3) to form a sequential Polymer D.

POLYMER, PROCESS AND COMPOSITION

[0001] The present invention relates to polymers and polymeric materials obtained and/or obtainable from 2-methylidenebutanedioate monomers (also referred to herein as itaconate monomers) and/or related monomers to a process for making such a polymers and their use to prepare for example coatings, inks and/or adhesives. It is preferred that polymers of the invention, and/or the itaconate and related monomers are obtained from bio-renewable sources.

[0002] Itaconate ester monomers have been described for very many years. However they have not been widely used to make commercial vinyl polymers because they are expensive and often difficult to process. The applicant has surprisingly discovered that itaconate ester monomers may be incorporated into polymers of the invention in the manner described herein. The resultant itaconate polymer may then be chemically modified after initial polymerisation in a further step (also referred to herein as post modification) to form further polymers which may exhibit useful properties.

[0003] Advantages of polymers of the invention are described herein. Further problems that may also be addressed by the present invention are described herein and it is an object of the present invention to solve some or all of the problems identified herein.

[0004] In a particularly preferred embodiment post modified polymers of the invention may be obtained and/or obtainable from polymers that comprise anhydride groups (e.g. polymers prepared from copolymerization of an itaconic anhydride monomer). The anhydride groups may react with nucleophilic groups in a post modification step after completion of the first polymerization step. The post modified polymers may be used as a binder and/or as a stabilizer and/or seed in an optional further polymerisation step.

[0005] It would also be advantageous to provide polymers obtainable from itaconate monomers with many functionalised groups as such polymers are likely to have useful properties such as high Tg. Until now it has been found to be very difficult to produce such polymers in practise. Itaconate monomers that contain a single additional functional group (such as for instance an amic acid with one acid group and one amide group) have been described in the literature as being difficult to prepare due to isomerization of the itaconate moiety to the less reactive citraconate moiety. Therefore at present there is no convenient means to prepare such monomers.

[0006] The applicant has now surprisingly found that mono-functional itaconate groups can be introduced into a polymer effectively by copolymerizing a certain concentration of itaconic anhydride monomer and then after completion of the first polymerization, modifying (part of) the anhydride groups on the polymer with a nucleophile.

[0007] Various documents describe polymers prepared from a copolymerisation of an itaconic anhydride monomer.

[0008] WO11/073,417 (DSM) discloses an aqueous emulsion comprising at least a vinyl polymer, said vinyl polymer comprising: a) 45 to 99 wt-% of itaconate ester monomers having formula (I), wherein R and R' are independently an alkyl or an aryl group; b) 0.1 to 15 wt-% of ionic or potentially ionic unsaturated monomers; c) 0 to 54 wt-% of unsaturated monomers, different from a) and b); and 0.9 to 54.9 wt-% by weight of total monomers of a chaser monomer composition added subsequently and polymerised after the polymerisation of monomers a), b) and c); wherein a)+b)+c) and the chaser monomer composition add up to 100 wt-%; and wherein the aqueous emulsion contains less than 0.5 wt-% free itaconate ester monomers of formula I based on the total weight of the aqueous emulsion. Although it is a stated object of the invention to provide a vinyl polymer with a high total concentration of itaconate ester monomers (see page 2, lines 14 to 17) in practise the larger proportion of such itaconate esters are lower itaconate esters (i.e. esters of small alkyl groups such as DMI). This document does not teach that it would be desirable to use a high concentration of higher itaconate esters (i.e. esters of large alkyl groups such as DBI). Indeed '417 states that itaonate esters are difficult to process (see page 2, lines 23 to 25) which combined with the teaching of the examples demotivates a reader to incorporated large amounts of hydrophobic higher itaconate esters like DBI in a copolymer. The only examples in '417 that describe use of a DBI monomer are Examples 2, 4, 5 and 6. It can be seen that DBI is used as co-monomer only at a low concentrations in the final copolymer prepared in these Examples (at a maximum of 22.7 wt-%) which are each also prepared with significant amounts of another hydrophobic monomer butyl acrylate (BA). A styrene chaser monomer is always present in the final product (at least 1.5 wt-%). These examples teach away from using DBI or other higher itaconate esters to replace common hydrophobic monomers such as BA, EHA and/or styrene. No significant improvement is seen in film properties such as hardness and water sensitivity of the copolymers prepared in this document.

[0009] EP103254 (BASF) describes copolymers prepared from a) 10 to 60 wt-% of monoethylenically unsaturated dicarboxylic acid with 4 to 6 carbon atoms; b) 90 to 40 wt-% of a monoethylenically unsaturated monocarboxylic acid with 3 to 10 carbon atoms, and optionally c) up to 20 wt-% of acid free copolymerisable monomer. The copolymerization is performed as precipitation polymerization at a temperature of between 50 and 180° C. EP106991 (BASF) describes similar polymers where the copolymerization is performed at a temperature of between 50 and 180° C. as suspension polymerization in an organic solvent. Neither of these itaconate anhydride polymers are further post modified.

[0010] EP1008913 (Shipley) describes photoresist composition comprising a resin comprising itaconic anhydride units but free of itaconic acid units. These resins do not undergo further chemical modification.

[0011] CN101979417 (University of Beijing) discloses a method of preparing alternating copolymers of itaconic anhydride and styrene. The anhydride groups are not post modified.

[0012] JP20090293683 (Kao Corp) describes a method for producing a cement dispersing agent which is a polymer obtained by polymerizing itaconic anhydride to yield polyitaconic anhydride.

[0013] None of these prior documents suggest that it would be advantageous to further react itaconic anhydride groups in these itaconic anhydride derived polymers. A skilled reader would have no reason to post-modify these polymers and would not know how to do so.

[0014] J. Serb. Chem. Soc., 72 (12) 1507-1514 (2007) (Milovanovic et al) describes preparing and modifying itaconic anhydride-methyl methacrylate copolymers. This document is concerned with providing amphiphilic polymers comprising both hydrophilic and hydrophobic segments that are useful in biological systems. The specific polymers described by Milovanovic are copolymers of itaconic anhydride and methyl methacrylate which are modified by amida-

tion with di-n-butyl amine. From Table II the itaconate copolymers (prior to modification) of Milanoic contain between 12.86 to 66.47 mol % of itaconic anhydride (ITA).

[0015] T. Otsu et al, Polymer International 25, 245-251 (1991) describes a polyitaconic anhydride which is further reacted with amines and with alkanols. However, modifying these polyitaconic anhydride polymers (prepared from high concentrations (30 to 50%) of itaconic anhydride monomer) produces a highly water sensitive coating. These coatings are thus of no practical use and the paper teaches a skilled person away from making post modified itaconic anhydride copolymers of the present invention or using them in coatings. The paper also discloses that alkanols can react with polyitaconic anhydride to produce poly(dialkyl itaconate). These polymers are also very different from the copolymers of the present invention.

[0016] Therefore broadly in accordance with the invention there is provided a method of preparing a post modified polymer (also denoted herein as Polymer C) the method comprising the steps of:

[0017] (1) polymerising a monomer composition comprising from 2.5 to 75% by weight (by weight of the total monomer composition) of at least one itaconic anhydride, suitable precursor therefor and/or suitable derivative thereof in a polymerisation method (optionally an emulsion or solution polymerisation) to obtain an itaconate polymer (also denoted herein as Polymer A); and

[0018] (2) reacting in a post modification step at least 10 mole-% of the anhydride groups, anhydride precursor groups and/or anhydride derived groups of the Polymer A obtained from step (1) with a moiety having a nucleophilic group (also denoted herein as Nucleophile B) to form a post-modified polymer (Polymer C).

with the optional proviso that if the monomer composition of step (1) consists of itaconic anhydride and methyl methacrylate and if the itaconate polymer (Polymer A) is a copolymer obtained solely from itaconic anhydride and methyl methacrylate monomers; then in the post modification step (2) the Nucleophile B is other than di-n-butyl amine.

[0019] The term itaconic anhydride precursor used in steps (1) and (2) denotes an ingredient that under the conditions of the relevant step will transform into an itaconic anhydride.

[0020] The term itaconic anhydride derivative used in steps (1) and (2) denotes an ingredient obtained by reaction of itaconic ahydride (e.g. by hydrolysis) (optionally obtained in situ from itaconic ahydride under the conditions of the relevant step), the derivative under the conditions of the relevant step undergoing the specified reaction in the relevant step.

[0021] In one embodiment of the invention the itaconate anhydride groups, anhydride precursor groups and/or anhydride derived groups are itaconate anhydride (i.e. no precursor or derived groups are used in steps (1) and/or step (2).

[0022] In a further optional proviso if the itaconate copolymer (Polymer A) comprises itaconate anhydride (ITA), the ITA is present in the copolymer in an amount selected from other than: 12.86 mol %, 23.59 mol %, 42.47 mol %, 47.29 mol %, 59.86 mol % and 66.47 mol %, more preferably the ITA is present in an amount other than from 12 to 67 mol %.

[0023] In a further aspect of the invention provides post-modified polymers (Polymer C) obtained and/or obtainable by a method of the present invention.

[0024] In a still further optional proviso the monomer composition does not consist solely of itaconic anhydride and methyl methacrylate and/or the itaconate copolymer (Polymer A) is not obtained solely from itaconic anhydride and methyl methacrylate.

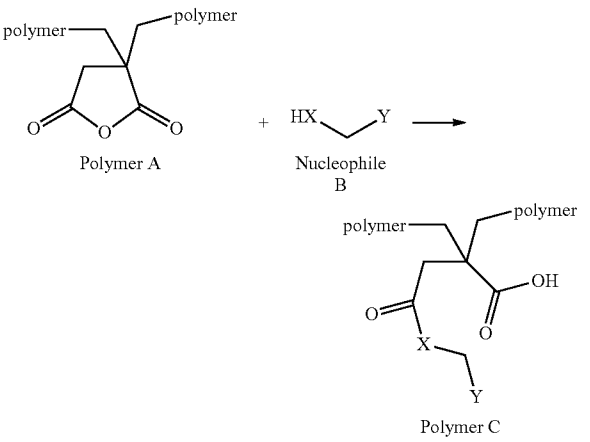
[0025] In a yet further optional proviso the itaconate copolymer (Polymer A) and/or the monomer composition of step (1) is substantially free of (preferably free of) methyl methacrylate.

[0026] In a yet still further optional proviso in the post modification step (2) the Nucleophile B is other than di-n-butyl amine.

[0027] In another optional proviso the polymers of or prepared by the method of the present invention (Polymer C) are other than copolymers of itaconic anhydride and methyl methacrylate modified by amidation with di-n-butyl amine.

[0028] In step (1) an itaconate diester such as diethyl itaconate (DEI) may also be used, in addition to, or instead of the itaconate anhydride. Similarly itaconamides may also be used in step (1) however generally they yield poor leaving groups so they are less preferred.

[0029] Without wishing to be bound by any mechanism the applicant believes that a possible non-limiting synthetic route for an embodiment of the process of the invention can be shown schematically below: It is believed that during the post modification step of the present invention the itaconate anhydride rings present in Polymer A, undergo ring opening as shown below

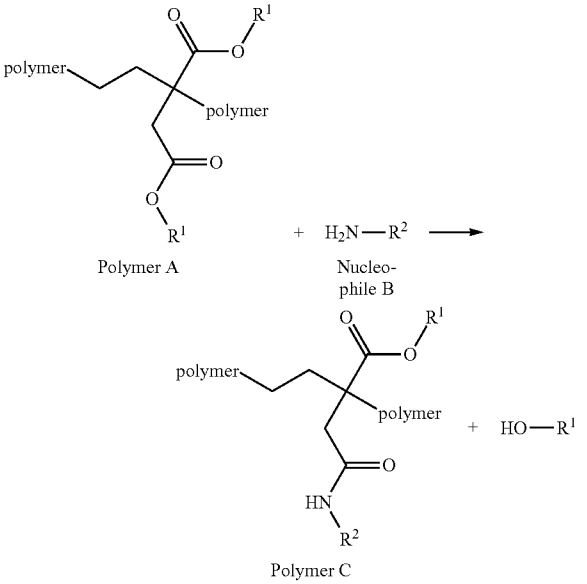


(the reactant B shown as $HXCH_2Y$ above may also be replaced by a compound represented by HXY)

where X denotes a nucleophilic group and Y any other different functionality (detailed preferences are given below).

[0030] The product shown as Polymer C above can also undergo reaction with further nucleophile to form a further post modified Polymer C'.

[0031] In another embodiment of the process of the invention a further non-limiting synthetic route is shown schematically below. In this embodiment Polymer A is now a diester itaconate functional polymer which reacts with a primary amine as the Nucleophile B (which could of course be replaced with another suitable nucleophile).



[0032] In the above scheme R^1 and R^2 represent any suitable organo moieties (for example alkyl in which case the polymer to be post-modified (Polymer A) may be a copolymer obtained from copolymerising a dialkyl itaconate monomer. The polymer reacts with a Nucleophile B (in this embodiment a primary amine) to yield the substituted product Polymer C (in this embodiment an amide-ester of itaconic acid) and an alkanol. The alkanol may conveniently be removed via evaporation.

[0033] Another aspect of the invention provides a polymer obtained and/or obtainable from the method of the invention.

[0034] A further aspect of the present invention provides a process where the polymer obtained and/or obtainable from step (2) is used in a further step (3) as a stabilizer or seed in a subsequent sequential polymerization step to obtain a sequential polymer (also referred to herein as Polymer D). Polymer D is also an aspect of the present invention.

[0035] Another aspect of the invention provides a coating composition that comprises a polymer of the invention.

[0036] Another yet aspect of the invention provides a sequential polymer comprises a polymer of the invention. This aspect also provides a method of preparing a sequential polymer (Polymer D), the method comprising the step of using a Polymer C as described herein as a stabilizer and/or seed in a sequential polymerization and sequential Polymer D obtained and/or obtainable from such a method.

[0037] As used herein the term sequential (co)polymer denotes a polymer or copolymer obtained and/or obtainable by polymerisation of (optionally different) polymer precursors (e.g. monomers) in sequence, for example in a living anionic polymerisation and/or emulsion polymerisation. A sequential polymer may be prepared in separate steps and/or in a single step for example by an all in one polymerisation where all the required ingredients are already present in the same vessel. Sequential copolymers of the invention may have any suitable distribution of monomers within the copolymer, for example be statistic, random, gradient, alternating, periodic and/or block copolymers.

[0038] Preferably the sequential copolymer composition is an emulsion copolymer (usefully an emulsion polymer prepared where no chaser monomer has been used), more preferably an aqueous emulsion copolymer, most preferably an aqueous coating composition. Conventional methods for preparing sequential polymers are well known to those skilled in the art.

[0039] Thus polymers of or used in processes of the present invention may comprise three types:

[0040] i) the itaconate polymer—Polymer A as described in step (1) preferably comprising from 2.5 to 75% by weight of Polymer A of moieties obtained and/or obtainable from at least one monomer selected from itaconic anhydride, itaconate amides and/or dialkyl itaconates, more preferably from itaconic anhydride and/or di(C_{1-10}alkyl) itaconates, most preferably from di(C_{1-4}alkyl) itaconates such as diethyl itaconate (DEI);

the post modified Polymer C obtained and/or obtainable from step (2) by reacting Polymer A with a Nucleophile B and/or the sequential Polymer D obtained and/or obtainable from step (3) using Polymer C as a stabiliser and/or seed in a sequential polymerisation;

[0041] Combinations and/or mixtures of any of Polymers A, C or D also form different aspects of the present invention.

[0042] An aqueous polymer emulsion or solution obtained and/or obtainable from step (2) and a polymer emulsion or solution obtained and/or obtainable from step (3) also form further aspects of the present invention.

[0043] Polymer A can be made via solution polymerization or (continuous) bulk polymerization. Where the Polymer A is prepared from a dialkyl itaconate and emulsion polymerisation method may also be used. Polymer A is preferably used as colloidal stabilizer in a second stage emulsion polymerization. For this purpose, the acid groups of the low molecular weight Polymer Can be (partially) neutralized and the polymer being (partially) emulsified or dissolved prior to starting the second polymerization stage. This second polymerization is preferably an emulsion polymerization step.

[0044] Polymer A of the invention may be obtained from itaconic anhydride monomers and/or precursors therefor and/or derivatives thereof such that Polymer A comprises from 2.5 to 75 wt-%, preferably from 5 to 60 wt-%, more preferably from 5 to 50 wt-%, even more preferably from 7.5 to 50 wt-%, for example from 7.5 to 40% wt-% (based on total weight of Polymer A) of moieties that are derived from itaconic anhydride monomers and/or precursors therefor and/or derivatives thereof.

[0045] In the post-modification step (2) that produces Polymer C at least 10 mole-% of the anhydride groups of Polymer A are converted by reaction with the Nucleophile B. Preferably at least 20 mole-%, more preferably at least 30 mole-%, even more preferably at least 40 mole-%, even yet more preferably at least 50 mole-%, most preferably at least 60 mole-% and for example from 60 to 90 mole-% of the anhydride groups are converted.

[0046] Nucleophile B may be a compound or a moiety part of a compound and/or large macromolecule. Nucleophile B may comprise a species of large molecular weight such as a fatty acid amine or be a species of low molecular weight such as for instance butyl amine.

[0047] Nucleophile B comprises at least one nucleophilic group represented as —XH which can be any group that can react with an anhydride group. Preferably, —XH is —OH, NH_2, —NHR (where R is hydrocarbo), or —SH. More preferably —XH is —OH, —NH_2, or —NHR. Most preferably —XH is —NH_2. Examples of suitable Nucleophiles B comprise primary amines, amides, hydrazines, hydrazides, and semi-carbazides.

[0048] In one useful embodiment preferably Nucleophile B independently comprises a plurality of nucleophilic groups

—XH (each of which may be the same or different), more preferably from 2 to 4 nucleophilic groups —XH.

[0049] Alternatively in another useful embodiment Nucleophile B has from 1 to 4, more usefully one nucleophilic group —XH.

[0050] Nucleophile B may further comprise additional functional groups represented by Y which (under the conditions of the post modification reaction as described herein) are not capable of undergoing a nucleophilic reaction with the itaconic anhydride groups on Polymer A. Each Y may independently comprise H and/or one or more (optionally substituted) C_{1-20} hydrocarbo group(s), preferably H and/or optionally substituted groups selected from C_{1-20}alkyl, C_{3-20} cycloalkyl, C_{3-20} aryl, C_{4-20} aralkyl and/or C_{4-20} alkaryl.

[0051] Nucleophile B may comprise at least one Y group (as defined above) preferably from one to four Y groups, more preferably one Y group.

[0052] Nucleophile B may further comprise substituents that can induce crosslinking, promote adhesion to wet substrates and/or improve colloidal stability. A non-limiting list of components that may be suitable as Nucleophile B comprise any of the following: amines (such as alkyl amines, fatty acid amines, trialkoxy amino silanes, taurine, ureido amines, amine functional perfluoro moieties, cationic functional amines, hydrazine), alcohols (such as alkyl alkanols, diacetone alcohol), amides (such as fatty acid amides); phosphoric acid derived moieties (such as phosphates), sulphonic acid derived moieties (such as sulphates); polyalkylene glycols (such as PEG or PPG) semicarbizides, and/or mercaptans.

[0053] Polymer A may be made via a variety of polymerization processes. Preferred polymerization processes are solution polymerization or (continuous) bulk polymerization. When a bulk polymerisation is used at a temperature above 110° C. itaconic acid may be used in component A as itaconic acid ring closes to form itaconic anhydride.

[0054] Further details for these known polymerisation methods are conventional and are described in many documents for example WO96/19536 the contents of which are hereby incorporated by reference/In case of a solution polymerization, it is preferred to use non-protic solvents. Especially preferred are non-protic solvents that have a boiling point of less than 150° C., most preferred are non-protic solvents having a boiling point of between 75 and 140° C.

[0055] In the case where Polymer A is prepared via solution polymerization, the preferred solids content of the polymer solution before chemical modification is at least 30 wt-%, more preferred between 40 and 95%, even more preferred between 50 and 90 wt-%, and most preferred between 55 and 80 wt-%.

[0056] Residual monomer levels after completion of Polymer A before chemical modification are less than 5000 ppm, more preferred less than 3000 ppm, and most preferred less than 2000 ppm, based on total weight of Polymer A.

[0057] Preferred initiators for bulk and/or solution polymerization are known in the art. Suitable initiators for emulsion polymerisation are described in WO96/19536 (Zeneca) on page 16 line 35 to page 17 line 8, which passage is hereby incorporated herein by reference. Where an aqueous emulsion polymerisation method is used component A is other than Itaconic anhydride as under the conditions of the reaction it will be hydrolysed.

[0058] In one preference in any embodiment of the invention which uses a polymerisation process where an initiator may usually have been required (such as but not limited to a radical polymerisation such as an emulsion polymerisation) the process of the invention uses initiator in the following total amounts relative to the total monomer composition no more than 1 wt-%, preferably no more than 0.5%, more preferably no more than 0.2%, even more preferably no more than 0.1%, most preferably no initiator.

[0059] Initiators for polymerizing the monomers to make vinyl polymers are well known and are any which are normally suitable for free-radical polymerisation of acrylate monomers. They may be oil-soluble and have low solubility in water such as organic peroxides, organic peroxyesters and organic azo initiators and are generally used in an amount of about 0.1 to 2 wt-% based on the total monomer content.

[0060] Chain transfer agents can advantageously be used to control molecular weight. Since mercaptans will react with the anhydride groups, the preferred chain transfer agents are alkyl halogenides, such as tetrabromomethane or tribromoethane, and catalytic chain transfer agents and are well known to those skilled in the art for example as described in WO96/19536 (Zeneca) on page 17 line 16 to page 18 line 34), which passage is hereby incorporated herein by reference. However in an embodiment of the invention where component A comprises itaconic anhydride conveniently chain transfer agents will not be used.

[0061] In one preference in any embodiment of the invention which uses a polymerisation process where a chain transfer agent may usually have been required (such as but not limited to a radical polymerisation, such as an emulsion polymerisation the process of the invention may uses chain transfer agent in the following total amounts relative to the total monomer composition no more than 1 wt-%, preferably no more than 0.5%, more preferably no more than 0.2%, even more preferably no more than 0.1%, most preferably less than 50 ppm, for example no chain transfer agent.

[0062] Typical chain transfer agents that have been used in the prior art include mercapto-acids and alkyl esters thereof, carbon tetrabromide, mixtures thereof and cobalt chelate, dodecylmercaptane (DDM) being one of the most commonly used. Mercapto chain transfer agents have been generally used in amounts from to 0.01 to 3.0 wt-% based on the total monomer content. Typically cobalt chelate CTAs are used in amounts from 1 to 200 ppm.

[0063] The preferred Co concentrations are less than 100 ppm Co, more preferred below 60 ppm, and most preferred between 2 and 45 ppm Co on total monomer weight.

[0064] Preferably, Polymer A has a weight average molecular weight—as determined using SEC—of between 500 and 100,000 g/mole, more preferably between 1000 and 80,000, even most preferably between 5000 and 70,000, and most preferably between 10,000 and 60,000 g/mole. Most preferably, the polydispersity, which is defined as M_W/M_N, is between 1 and 6, more preferably between 1.2 and 5, and most preferably between 1.5 and 3.5.

[0065] Polymer A is a copolymer and so comprises at least one other monomer (preferably vinyl monomer) other than itaconic anhydride (and precursors therefor and/or derivatives thereof). These 'other' monomers may be vinyl monomers selected from: (meth)acrylate monomers, vinyl benzene monomer and/or vinyl alkanoate monomer; preferably (meth)acrylate esters of C_{1-20}alcohols, more preferably of C_{1-8}alcohols. Preferably, Polymer A does not contain any acid functional monomer other than itaconic anhydride (and precursors therefor and/or derivatives thereof). In one embodiment amounts of (meth)acrylic acid up to 2 wt-%, more preferably up to 1 wt-% can be used advantageously.

[0066] Polymer A can contain functional monomers that may have an advantageous effect on (wet) adhesion properties of the resulting coating.

[0067] In a preferred embodiment of this invention a dimer fatty acid diamine (for instance Priamine 1071, Priamine

1073, Priamine 1074, or Priamine 1075, all ex. Croda) and/or a fatty acid amide (such as for instance stearic amide) may be used as the Nucleophile B to post modify Polymer A.

[0068] Preferentially in the embodiment of the invention where the Nucleophile B comprises a fatty acid amine, the composition of Polymer A using in the post modification step (2) comprises between 5 and 50 wt-% of moieties derived from itaconic anhydride monomers. In this embodiment preferably, at least 20 mole-%, more preferably at least 40 mole-%, of the anhydride groups are converted using the fatty acid amine.

[0069] Emulsification of the modified Polymer C may be feasible due to the formation of acid groups upon chemical modification with Nucleophile B. In addition if needed (meth)acrylic acid can be used as a (co)monomer in the copolymerisation step (1) so that the resultant Polymer C can emulsify itself (i.e. can be dispersed in water under Standard Conditions without the addition of additional surfactant). However small amounts of additional surfactant can be used to aid emulsification of Polymer C, especially if it is desired to obtain dispersion comprising high concentrations of A is desired.

[0070] Neutralisation of acidic groups for example in an emulsion of Polymer C may be done in any order of mixing the three ingredients, neutralising agent (e.g. base), Polymer C and water. For example: by adding base to Polymer C then adding water; by adding a pre-mix of water and base to Polymer C, by adding Polymer C to a mixture of base and water, and/or by adding a pre-mix of base and Polymer C to water. However it is more preferred that water is added to a mixture of Polymer C and base so Polymer C is emulsified after any acid groups have been neutralized.

[0071] Preferred bases include organic amines and oxide or hydroxide salts of (earth) alkali metals. More preferred bases include ammonia, monoalkyl, dialkyl, and trialkyl amines, and oxide or hydroxide salts of alkali metals (among which the most preferred salts are lithium hydroxide, sodium hydroxide, and potassium hydroxide), for example ammonia.

[0072] Other suitable neutralisation agents or bases are any known in the art for example to also neutralise conventional polyurethane dispersions and for example are described in WO1993-24551 (Zeneca) page 11 (last paragraph) to page 12 (first paragraph) which passage is hereby incorporated herein by reference.

[0073] Preferably, at least 20 mole-% of the acid groups of Polymer C may be neutralized to aid in the emulsification of Polymer C. More preferably, at least 40 mole-% and most preferably between 60 and 90 mole-% of the acid groups of Polymer C may be neutralized.

[0074] To aid in the emulsification, additional surfactant(s) can be used. This can be anionic surfactants, non-ionic surfactants, mixed anionic and non-ionic surfactants, and combinations thereof. In special occasions, Polymer C may be modified using cationic groups, the additional surfactant(s) can be cationic by nature, non-ionic, mixed cationic and non-ionic, and combinations thereof.

[0075] Preferably, the concentration of additional surfactant is less than 5 wt-% on total mass of Polymer C, more preferably less than 3.5 wt-%, even more preferably less than 2.5 wt-%, and most preferably between 0.05 and 1.0 wt-%.

[0076] In another embodiment of the invention, Polymer C is emulsified after sufficient lithium hydroxide is used to neutralize between 30 and 80 mole-% of the acid groups of Polymer C. Next, sufficient water is added to achieve a solids content of between 15 and 75 wt-%, more preferred between 20 and 65 wt-%.

[0077] In yet another embodiment of the invention, Polymer C is used as-is, without neutralization of the acid groups and emulsified using between 0.5 and 5 wt-%, more preferably between 0.5 and 3.5 wt-% on total weight of Polymer C, of anionic, mixed anionic and non-ionic, non-ionic surfactant, or combinations thereof.

[0078] The particle size of an emulsion of Polymer C in water preferably has an average particle size, as determined using dynamic light scattering, of between 10 and 500 nm, more preferably of between 30 and 400 nm, most preferably of between 40 and 300 nm.

[0079] Preferably, the solids content of the emulsion of Polymer C in water is between 10 and 80 wt-%, more preferably between 20 and 70 wt-%, most preferably between 25 and 60 wt-%.

[0080] The emulsion of Polymer C in water preferably has a pH of higher than 6.5, more preferably of between 6.5 and 9.5, most preferably of between 7 and 9.

[0081] Preferably, the solvent, that is used in case Polymer C is prepared via solution polymerization, is removed after emulsification of Polymer C. Preferred levels of solvent in the aqueous emulsion of Polymer C are less than 1000 ppm, more preferably less than 500 ppm, even more preferably less than 250 ppm, and most preferably less than 100 ppm of residual solvent.

[0082] In a preferred embodiment according to the invention an emulsion comprising Polymer C in water is provided having a pH of less than 7, characterized in that the emulsion is stabilized by cationic groups covalently linked to the backbone of Polymer C.

[0083] In yet another preferred embodiment of the invention is provided a polymer emulsion, comprising Polymer C, having a pH of less than 7, further characterized in that the emulsion is stabilized using cationic or non-ionic surfactants, or combinations thereof.

[0084] The process of producing Polymer C via solution polymerization is preferably done via free radical polymerization. However, it is envisaged that controlled radical polymerization can yield advantageous results. Especially controlled radical polymerization procedures such as RAFT, ATRP, RITP and NMP are useful to control the polymerization.

[0085] Polymer C and/or Polymer D can be combined with other polymers to provide a binder system useful in aqueous coatings. Combinations of Polymer C and/or Polymer D and other polymers can be obtained according to several procedures.

[0086] The solution of Polymer C in solvent can be mixed with a second copolymer composition dissolved in organic solvent, prior to simultaneous emulsification of both polymers. Secondly, the emulsion of Polymer C and/or Polymer D can be mixed with an emulsion(s) of a second copolymer composition, thirdly, the emulsion of Polymer C can be used as stabilizer to emulsify a solution of a second copolymer composition or bulk polymer, and fourthly, the emulsion of Polymer C can be used as stabilizer or seed for a sequential polymerization of the second copolymer composition.

[0087] More preferred are the combinations obtained by blending a solution of Polymer C and a solution of a second copolymer prior to emulsification and the use of an emulsion of Polymer C as stabilizer or seed for a sequential polymerization. Especially preferred is using an emulsion of Polymer C as stabilizer or seed for a sequential polymerization.

[0088] The phase ratio between Polymer C and the second copolymer composition(s) is preferably set between 5:95 and 95:5, more preferably between 10:90 and 70:30, and most preferably between 15:85 and 60:40.

[0089] The solids content of the aqueous emulsion comprising Polymer C and the second copolymer composition is preferably between 20 and 60 wt-%, more preferred between 30 and 55 wt-%, and most preferred between 35 and 50 wt-%.

[0090] Preferably, the second copolymer composition has a Tg which is different from that of Polymer C. Preferably, the difference in Tg is at least 15° C., more preferred at least 25° C., and most preferred at least 40° C.

[0091] In a preferred embodiment the Tg of Polymer C is at least 15° C. higher than that of the second copolymer composition, more preferred at least 25° C., and most preferred at least 40° C.

[0092] In another preferred embodiment of the invention the Tg of the second copolymer composition is at least 15° C. higher than that of Polymer C, more preferred at least 25° C. higher, and most preferred at least 40° C. higher.

[0093] In an especially preferred embodiment is provided a process for preparing an emulsion according to the invention comprising Polymer C and a second copolymer composition prepared by emulsion polymerization in the presence of Polymer C, further characterized in that:

[0094] Polymer C and the second copolymer composition have Tg values that differ by at least 15° C., more preferably at least 30° C., and

[0095] at least 10 mole-% of the anhydride groups in Polymer A are modified by reacting with Nucleophile B, and

[0096] the phase ratio of Polymer C to the second copolymer composition is between 5:95 and 95:5, more preferably 10:90 and 70:30.

[0097] In yet another special embodiment of the invention is provided a process of producing an aqueous emulsion according to the invention comprising Polymer C, characterized in that

[0098] Polymer A comprises from 2.5 to 75 wt-% of itaconic anhydride, more preferably between 5 and 60 wt-%, and

[0099] at least 10 mole-% of the anhydride groups in Polymer A are modified by reacting with Nucleophile B, and

[0100] the aqueous emulsion has solids content of from 5 to 65 wt-%, more preferably from 20 to 55 wt-%.

[0101] A still further aspect of the present invention comprises paints obtained, obtainable and/or comprising polymer compositions of the invention, especially where polymers compositions of the invention are emulsion polymers.

[0102] Paints made from the emulsion polymer compositions of this invention may contain pigment at pigment volume concentrations in the range of 0 to 85%, preferably in the range of 0 to 55%. The pigment volume concentration of a species of pigment particles is the percentage of the volume occupied by that species of pigment particles, based on the total volume of the dried coating prepared from the emulsion polymer compositions. Suitable pigments include inorganic pigments, such as titanium dioxide, iron oxide, zinc oxide, magnesium silicate, calcium carbonate, organic and inorganic coloured pigments, aluminosilicates, silica, and various clays. Titanium dioxide is a preferred for its ability to provide opacity. Suitable organic pigments also include plastic pigments such as solid bead pigments and microsphere pigments containing voids or vesicles. Examples of solid bead pigments include polystyrene and polyvinyl chloride beads. Examples of microsphere pigments, which include polymer particles containing one or more voids and vesiculated polymer particles, are disclosed in for example U.S. Pat. No. 4,427,836, U.S. Pat. No. 4,920,160, U.S. Pat. No. 4,594,363, U.S. Pat. No. 4,469,825, U.S. Pat. No. 4,468,498, U.S. Pat. No. 4,880,842, U.S. Pat. No. 4,985,064; U.S. Pat. No. 5,157,084, U.S. Pat. No. 5,041,464, U.S. Pat. No. 5,036,109, U.S. Pat. No. 5,409,776 and U.S. Pat. No. 5,510,422. Other suitable pigments include, for example, Expancel™ 551 DE20 acrylonitrile/vinyl chloride expanded particles (Expancel Inc. Duluth Ga.); Sil-Cell™ 35/34 sodium potassium aluminium silicate particles (Silbrico Corporation, Hodgkins III.); Dualite™ 27 polyvinylidene chloride copolymer Coated with $CaCO_3$ (Pierce and Stevens Corporation, Buffalo N.Y.); Fillitte™ 150 ceramic spherical particles (Trelleborg Fillite Inc. Norcross Ga.); Microbeads™4A soda lime particles (Cataphote Inc.); Sphericell™ hollow glass particles (Potter Industries Inc. Valley Forge Pa.); Eccosphere™ hollow glass spheres (New Metals & Chemicals Ltd.; Essex England); Z-light™ Zeeospheres W-410 and W-610 ceramic hollow spheres (3M St. Paul Minn.); Scotchlite™ K46 glass bubbles (3M St. Paul Minn.); Vistamer™ UH 1500 polyethylene particles; and Vistamer™ HD 1800 polyethylene particles (Fluoro-Seal Inc., Houston Tex.). Ropaque™ polymer is a preferred component in the coatings. Z-light™ Zeeospheres W-410 and W-610 ceramic hollow spheres are also preferred components. Combinations of the above ingredients are frequently preferred.

[0103] Paints prepared from the emulsion polymer compositions of this invention may be thickened with various aqueous thickening agents. These include but not are limited to hydrophobically-modified alkali swellable emulsions such Acrysol™ TT-935, Acrysol™ TT-615, Acrysol™ RM-6, Polyphobe™ TR-116. Alkali swellable emulsions such as Acrysol™ ASE-60 may also be used. Hydrophobically-modified water soluble polymers may also be used such as Acrysol™ RM-2020, Acrysol™ RM-8, Aquaflow™ XLS-500, Aquaflow™ NHS-310, Rheolate™ CVS-11, and hydrophobically-modified HEC such as Natrosol™ Plus 330. Hydroxyethyl cellulose may also be used such as Natrosol™ HBR, or Cellosize™ QP-3000. Clays such as Attagel™ 50 or Bentone™ DE may also be used for sagging and settling control.

[0104] Paints prepared from the emulsion Polymer Compositions of this invention may utilize dispersants to help stabilize the pigments in the paint. Polyacid dispersants such as Hydropalat™ 44, or hydrophobic copolymer dispersants such as Tamol™ 681, Tamol™ 165, and Tamol™ 731 may be used. Styrene Maleic anhydride copolymers may also be used. Small molecule dispersants such as polyphosphates and citric acid may also be used. Examples of polyphosphates include tetra-potassium Pyrophosphate, Potassium tripolyphosphate, Sodium hexameta phosphate, and higher phosphates sold under the brand name Calgon™. The latter phosphates are used in conjunction with ZnO pigments to help provide stability.

[0105] Paints prepared from the emulsion Polymer Compositions of this invention may utilize coalescing aids to aid in the film formation of the latex emulsion polymers. These coalescing aids can be volatile such as ethoxy and propoxy ethers of common alcohols. Examples would include ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, propylene glycol monobutyl, and dipropylene glycol monobutyl ether. A common and preferred coalescing agent is Texanol™. Paints prepared from the emulsion Polymer Compositions of this invention may also utilize non-volatile coalescing agents which do not contribute volatile organic compounds (VOC). These coalescing agents would include materials like Optifilm™ 400, dioctyl maleate, triethyl citrate, or tributyl phosphate. In some instances oxidatively curing reactive plasticizers such as Oxi-Cure™ 100 may be used. In addition the paint may also contain a humectant

material such as ethylene glycol or propylene glycol. Open time additives such as Rhodaline™ OTE, or Optifilm™ OT1200 may also be used. It is preferred that the paint made from the emulsion polymer compositions contain less than 5% VOC by weight based on total weight of the composition. More preferred are paint compositions containing less than 2% VOC by weight, and most preferred are paint compositions containing less than 0.05% VOC by weight.

[0106] Paints prepared from the emulsion polymer compositions of this invention will also contain added surfactants. These surfactants are used to improve substrate wetting, insure pigment and colorant compatibility, and improve stability. Non-ionic surfactants such as ethoxylated alcohols are frequently added to improve free/thaw stability and colorant compatibility. These would include low HLB non-ionic such as Igepal™ CO-430, Igepal™ CO-630 and higher HLB non-ionic such as Triton X-405. For these surfactants it is also desirable to use analogues based on alkyl alcohols such as tridecyl alcohol, or branched secondary alcohols such as Tergitol™ TMN-10. Triton™ CF-10 is also quite commonly used to aid in pigment wetting. Dioctyl sulfosuccinates are frequently used to enhance substrate wetting such as Aerosol™ OT-100. Acetylenic diols such as Surfynol™ 104 can also be used and are sometimes desired due to their low dynamic surface tension. Phosphate based surfactants can also be employed particularly to improve TiO_2 compatibility and stability. These would include surfactants from the Strodex™ line such as PK-90 or PK-0VOC.

[0107] Paints prepared from the emulsion Polymer Compositions of this invention may also contain additives which can alter the surface blocking characteristics. Such additives would include fluorocarbon surfactants such as Capstone™ FS-61.

[0108] Paints prepared from the emulsion Polymer Compositions of this invention may also contain multivalent metal ions to provide for post film formation crosslinking. These multivalent metal ions will improve the hardness, and scratch resistance of the final paint as well as to improve the chemical resistance. In particular it is seen that this will improve resistance to organic solvents. Examples of multivalent metal ions include Zn, Mg, Zr, and Ca. These are frequently added in the form of water soluble salts such as acetates or carbonates. Zinc Ammonium Carbonate is frequently used to great advantage; however $Mg(OH)_2$ is also effective and sometimes desired.

[0109] It is intended and expected that paints prepared from the emulsion Polymer Compositions of this invention will be prepared in a tint base structure and will be tinted at the point of sale. This would involve the introduction of colour concentrates into the paint such as the Colortrend™ 888 line or the Ultralow VOC NovoColor™ II 8800 line. It would be preferred that the paints of this invention were tinted with Ultralow VOC colorants to yield an ultralow VOC paint.

[0110] Paints prepared from the emulsion polymer compositions of this invention may contain phosphate or borosilicate based corrosion inhibiting pigments such as Heucophos™ ZPO, Halox™ SPZ-391, Halox™ SZP-391 JM, Halox™ 430, or Halox™ CW-291. The paints prepared from the emulsion Polymer Compositions of this invention may contain organic corrosion inhibitors such as Halox™ 510, Halox™ 520 or Halox™ 570. The paints prepared from the emulsion polymer compositions of this invention may contain flash rust inhibitors such as nitrite salts, phosphate salts, benzoic acid salts, or Halox™ Flash-X 330. These ingredients are typically added to a direct to metal coating to reduce flash rusting and long term corrosion.

[0111] Paints prepared from the emulsion polymer compositions of this invention may contain tannin stain blocking additives to block the migration of tannins through the coating. These additives are typically based on multivalent cations such as Zr^{2+} and Zn^{2+} or solid inorganic materials capable of binding negatively charged tannins. The additives would include Stainban™ 185, Stainban™ 186, Stainban™ 187, Halox™ BW-100, Halox™ L-44, and Halox™ 1-66. In addition ZnO is frequently added to these paints to improve tannin stain blocking. In many instances it is particularly desired to prepare paints which contain inorganic pigments with high aspect ratios. An example would be a platy talc such as Vertal™ 7. This is known to improve the tannin blocking character of the paint.

[0112] Paints prepared from the emulsion Polymer Compositions of this invention may contain UV absorbers and free radical scavengers. These are used to improve the long term exterior durability of a coating, or to protect the underlying substrate from UV degradation. This is particularly useful when formulating clear to semi-transparent wood stains. The UV blockers can be organic materials such as benzotriazoles, or can be inorganic UV blockers such as sub 100 nm metal oxides. The free radical scavengers are based on hindered amine light stabilizers. Examples of UV blockers include Tinuvin 1130, trans iron oxides such as Tint-ayd CW5499 or Tint-ayd CW5600, nano zinc oxide, and nano titanium oxide. Combinations of Tinuvin 1130 with Tint-ayd CW5499 are particularly useful for semi-transparent wood stains.

[0113] Paints prepared from the emulsion Polymer Compositions of this invention may contain waxes or surface modification additives such as silicone slip aids. Waxes may be used to reduce the gloss of the paint and maintain a high level of coffee, wine, or tea stain resistance. These waxes also can improve the burnish resistance of the coating. Examples of such waxes include Ceraflour™ 916, Ceraflour™ 920, and Ceraflour™ 962. Waxes may also be used to improve the mar and scratch resistance of the paint. An example would be Michem Emulsion™ 39235. Slicone slip aids may also be used to improve mar and scratch. An example would be Tego Glide™ 410.

[0114] Paints prepared from the emulsion polymer compositions of this invention may contain reactive silanes which contain an epoxy group or an amine group. The silane can be a trialkoxy, a dialkoxy, or a mono alkoxy. The alkoxy groups are typically methoxy, ethoxy, or propoxy. In the case of the dialkoxy, or a mono alkoxy materials the silicon atom is bonded to a methyl group. For example, monomethyldimethoxy silane would be common siloxane group. Trialkoxy, and dialkoxy silanes based on methoxy or ethoxy are preferred. The emulsion polymer may also contain reactive groups such as epoxy or acetoacetoxy which can react with the amine functional portion of the amino silane. An example of a useful amino silane would be Silquest A-1100 which is amino propyl-triethoxysilane. Amino propylmethyldimethoxysilane is a useful coupling agent for adhesion to metal oxides such as aluminium oxide. An example of useful epoxy silanes are Silquest A-186 and Silquest A-187. The silanes are typically used at around 1% and provide for adhesion to metals and metal oxide surfaces. They can also be used to crosslink the paint.

[0115] Coatings according to the invention may be advantageously used as coatings, lacquers and paints in interior and exterior decorative coatings for wood, metal, plastic, masonry, concrete, and wood composites including plastic wood and cement wood composite materials, clear and semi-transparent stains and top coats for wood and wood composites including plastic wood and cement wood composite

materials, clear and pigmented primers and top coats for wood furniture and flooring, road marking paint, coatings to protect and preserve structural metal against corrosion, such as bridges, water towers and tank farms, coatings for flooring including wood, wood composite and concrete flooring, barrier primers for wall board, wood and masonry to block migration of water soluble materials such as nicotine, inorganic salts, and tannins, coatings for paper, primers, coloured base coats and clear top coats for automotive parts including plastics and metals, temporary coatings designed to temporarily protect a substrate, and then be easily removed at a later time, temporary coatings designed to be thermally decomposed after manufacture such as those used in the manufacture of cathode ray tubes or fluorescent lights, sound deadening coatings such as those used on the underside of a car, inks, and overprint varnishes, adhesive primers and structural adhesives.

[0116] Whilst the term vinyl polymer is commonly used to refer to thermoplastic polymers derived by polymerization from compounds containing the vinyl group (CH_2=CH—), the term "vinyl polymer" is used herein more broadly to denote any polymer (whether thermoplastic or not) that comprises (e.g. as repeat units therein) and/or is derived from monomers and/or polymer precursors comprising one or more of the following moieties: activated unsaturated moieties (such as acrylates and/or methacrylates); any olefinically unsaturated moieties (such as vinyl moieties); mixtures thereof; and/or combinations thereof within the same moiety.

[0117] There is an increasing demand to use bio-renewable monomers in order to improve the sustainability of the polymers used in for example coating applications. In view of concerns about depletion of fossil fuel resources or an increase in carbon dioxide in the air that poses a global-scale environmental problem in recent years, methods for producing raw materials of these polymers from biomass resources have attracted a lot of attention. Since these resources are renewable and therefore have a carbon-neutral biomass, such methods are expected to gain in particular importance in future. It is therefore a preferred feature of the present invention and the aspects described herein that where possible the monomers (especially the higher itaconate diesters such as DBI) as far as possible are biorenewable.

[0118] Preferably at least 20 wt-%, more preferably at least 30 wt-%, and especially 40 wt-% of the olefinically unsaturated monomers used to form the polymers of the invention are derived from at least one bio-renewable olefinically unsaturated monomer. Bio-renewable monomers may be obtained fully or in part from bio-renewable sources. In a preferred embodiment methacrylate monomers are used as monomer (c) where the alcohol is made from biorenewable sources. In yet another preferred embodiment both the (meth)acrylate unit and the possible alcohol are made from biorenewable sources. Thus it is preferred to also measure the carbon-14 content to determine the biorenewability.

[0119] The content of carbon-14 (C-14) is indicative of the age of a bio-based material. It is known in the art that C-14, which has a half-life of about 5,700 years, is found in bio-renewable materials but not in fossil fuels. Thus, "bio-renewable materials" refer to organic materials in which the carbon comes from non-fossil biological sources. Examples of bio-renewable materials include, but are not limited to, sugars, starches, corns, natural fibres, sugarcanes, beets, citrus fruits, woody plants, cellulosics, lignocelluosics, hemicelluloses, potatoes, plant oils, other polysaccharides such as pectin, chitin, levan, and pullulan, and a combination thereof.

[0120] C-14 levels can be determined by measuring its decay process (disintegrations per minute per gram carbon or dpm/gC) through liquid scintillation counting. In one embodiment of the present invention, Polymer A and or polymer B comprise at least about 1.5 dpm/gC (disintegrations per minute per gram carbon) of carbon-14, more preferably at least 2 dpm/gC, most preferably at least 2.5 dpm/gC, and especially at least 4 dpm/gC.

[0121] Acrylic acid can be made from glycerol, as is disclosed by Arkema, or from lactic acid as described by US7687661. Methacrylic acid can be prepared from ethene, methanol and carbon monoxide (all bio-renewable), as disclosed by Lucite International Ltd.

[0122] Olefinically unsaturated bio-renewable monomers which may additionally provide a contribution to improved coating properties include α-methylene butyrolactone, α-methylene valerolactone, α-methylene γ-R^3 butyrolactone (R^3 can be an optionally substituted alkyl or optionally substituted aryl); itaconates such as dialkyl itaconates (including DBI) and monoalkyl itaconates, itaconic acid, itaconic anhydride, crotonic acid and alkyl esters thereof, citraconic acid and alkyl esters thereof, methylene malonic acid and its mono and dialkyl esters, citraconic anhydride, mesaconic acid and alkyl esters thereof.

[0123] Another useful set of useful bio-renewable monomers include N—R^2, α-methylene butyrolactam (R^2 can be an optionally substituted alkyl or optionally substituted aryl); N—R^2, α-methylene γ-R^1 butyrolactam; N-alkyl itaconimids; furfuryl (meth)acrylate; fatty acid functional (meth)acrylates such as DAPRO FX-522 from Elementis and Visiomer® MUMA from Evonik.

[0124] It is appreciated that certain features of the invention, which are for clarity described in the context of separate embodiments may also be provided in combination in a single embodiment. Conversely various features of the invention, which are for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

[0125] The object of the present invention is to solve some or all of the problems or disadvantages (such as identified throughout the application herein) with the prior art.

[0126] Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

[0127] The term "comprising" as used herein will be understood to mean that the list following is non-exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s), ingredient(s) and/or substituent(s) as appropriate.

[0128] The terms 'effective', 'acceptable' 'active' and/or 'suitable' (for example with reference to any process, use, method, application, preparation, product, material, formulation, compound, monomer, oligomer, polymer precursor, and/or polymers described herein as appropriate) will be understood to refer to those features of the invention which if used in the correct manner provide the required properties to that which they are added and/or incorporated to be of utility as described herein. Such utility may be direct for example where a material has the required properties for the aforementioned uses and/or indirect for example where a material has use as a synthetic intermediate and/or diagnostic tool in preparing other materials of direct utility. As used herein these terms also denote that a functional group is compatible with producing effective, acceptable, active and/or suitable end products.

[0129] Preferred utility of the present invention comprises as component of a coating composition.

[0130] In the discussion of the invention herein, unless stated to the contrary, the disclosure of alternative values for

the upper and lower limit of the permitted range of a parameter coupled with an indicated that one of said values is more preferred than the other, is to be construed as an implied statement that each intermediate value of said parameter, lying between the more preferred and less preferred of said alternatives is itself preferred to said less preferred value and also to each less preferred value and said intermediate value.

[0131] For all upper and/or lower boundaries of any parameters given herein, the boundary value is included in the value for each parameter. It will also be understood that all combinations of preferred and/or intermediate minimum and maximum boundary values of the parameters described herein in various embodiments of the invention may also be used to define alternative ranges for each parameter for various other embodiments and/or preferences of the invention whether or not the combination of such values has been specifically disclosed herein.

[0132] Thus for example a substance stated as present herein in an amount from 0 to "x" (e.g. in units of mass and/or weight %) is meant (unless the context clearly indicates otherwise) to encompass both of two alternatives, firstly a broader alternative that the substance may optionally not be present (when the amount is zero) or present only in an de-minimus amount below that can be detected. A second preferred alternative (denoted by a lower amount of zero in a range for amount of substance) indicates that the substance is present, and zero indicates that the lower amount is a very small trace amount for example any amount sufficient to be detected by suitable conventional analytical techniques and more preferably zero denotes that the lower limit of amount of substance is greater than or equal to 0.001 by weight % (calculated as described herein).

[0133] It will be understood that the total sum of any quantities expressed herein as percentages cannot (allowing for rounding errors) exceed 100%. For example the sum of all components of which the composition of the invention (or part(s) thereof) comprises may, when expressed as a weight (or other) percentage of the composition (or the same part(s) thereof), total 100% allowing for rounding errors. However where a list of components is non-exhaustive the sum of the percentage for each of such components may be less than 100% to allow a certain percentage for additional amount(s) of any additional component(s) that may not be explicitly described herein.

[0134] In the present invention, unless the context clearly indicates otherwise, an amount of an ingredient stated to be present in the composition of the invention when expressed as a weight percentage, is calculated based on the total amount of monomers in the composition being equivalent to 100% (thus for example components (a)+(b)+(c)+(d) total 100%). For convenience certain non-monomer ingredients (such as for example chain transfer agents (CTA)) which fall outside the definitions of any of components (a) to (d) may also be calculated as weight percentages based on total monomer (i.e. where the weight of total monomers alone is set at 100%). As the weight % of monomers (for example for components (a) to (d)) by definition total 100% it will be seen that using monomer based weight % values for the non-monomer ingredients (i.e. those components outside (a) to (d)) will mean the total percentages will exceed 100%. Thus amounts of non-monomer ingredients expressed as monomer based weight percentages can be considered as providing a ratio for the weight amounts for these ingredients with respect to the total weight of monomers which is used only as a reference for calculation rather than as a strict percentage. Further ingredients are not excluded from the composition when (a)+(b)+(c)+(d) total 100% and weight percentages based on total monomers should not be confused with weight percentages of the total composition.

[0135] The term "substantially" as used herein may refer to a quantity or entity to imply a large amount or proportion thereof. Where it is relevant in the context in which it is used "substantially" can be understood to mean quantitatively (in relation to whatever quantity or entity to which it refers in the context of the description) there comprises an proportion of at least 80%, preferably at least 85%, more preferably at least 90%, most preferably at least 95%, especially at least 98%, for example about 100% of the relevant whole. By analogy the term "substantially-free" may similarly denote that quantity or entity to which it refers comprises no more than 20%, preferably no more than 15%, more preferably no more than 10%, most preferably no more than 5%, especially no more than 2%, for example about 0% of the relevant whole.

[0136] The terms 'optional substituent' and/or 'optionally substituted' as used herein (unless followed by a list of other substituents) signifies the one or more of following groups (or substitution by these groups): carboxy, sulpho, formyl, hydroxy, amino, imino, nitrilo, mercapto, cyano, nitro, methyl, methoxy and/or combinations thereof. These optional groups include all chemically possible combinations in the same moiety of a plurality (preferably two) of the aforementioned groups (e.g. amino and sulphonyl if directly attached to each other represent a sulphamoyl group). Preferred optional substituents comprise: carboxy, sulpho, hydroxy, amino, mercapto, cyano, methyl, halo, trihalomethyl and/or methoxy.

[0137] The synonymous terms "organic substituent", "moiety", and "organic group" as used herein (also abbreviated herein to "organo") denote any univalent or multivalent moiety (optionally attached to one or more other moieties) which comprises one or more carbon atoms and optionally one or more other heteroatoms. Organic groups may comprise organoheteryl groups (also known as organoelement groups) which comprise univalent groups containing carbon, which are thus organic, but which have their free valence at an atom other than carbon (for example organothio groups). Organic groups may alternatively or additionally comprise organyl groups which comprise any organic substituent group, regardless of functional type, having one free valence at a carbon atom. Organic groups may also comprise heterocyclyl groups which comprise univalent groups formed by removing a hydrogen atom from any ring atom of a heterocyclic compound: (a cyclic compound having as ring members atoms of at least two different elements, in this case one being carbon). Preferably the non carbon atoms in an organic group may be selected from: hydrogen, halo, phosphorus, nitrogen, oxygen, silicon and/or sulphur, more preferably from hydrogen, nitrogen, oxygen, phosphorus and/or sulphur.

[0138] Most preferred organic groups comprise one or more of the following carbon containing moieties: alkyl, alkoxy, alkanoyl, carboxy, carbonyl, formyl and/or combinations thereof; optionally in combination with one or more of the following heteroatom containing moieties: oxy, thio, sulphinyl, sulphonyl, amino, imino, nitrilo and/or combinations thereof. Organic groups include all chemically possible combinations in the same moiety of a plurality (preferably two) of the aforementioned carbon containing and/or heteroatom moieties (e.g. alkoxy and carbonyl if directly attached to each other represent an alkoxycarbonyl group).

[0139] The term 'hydrocarbo group' as used herein is a sub-set of an organic group and denotes any univalent or multivalent moiety (optionally attached to one or more other moieties) which consists of one or more hydrogen atoms and

one or more carbon atoms and may comprise one or more saturated, unsaturated and/or aromatic moieties. Hydrocarbo groups may comprise one or more of the following groups. Hydrocarbyl groups comprise univalent groups formed by removing a hydrogen atom from a hydrocarbon (for example alkyl). Hydrocarbylene groups comprise divalent groups formed by removing two hydrogen atoms from a hydrocarbon, the free valences of which are not engaged in a double bond (for example alkylene). Hydrocarbylidene groups comprise divalent groups (which may be represented by "$R_2C=$") formed by removing two hydrogen atoms from the same carbon atom of a hydrocarbon, the free valences of which are engaged in a double bond (for example alkylidene). Hydrocarbylidyne groups comprise trivalent groups (which may be represented by "$RC\equiv$"), formed by removing three hydrogen atoms from the same carbon atom of a hydrocarbon the free valences of which are engaged in a triple bond (for example alkylidyne). Hydrocarbo groups may also comprise saturated carbon to carbon single bonds (e.g. in alkyl groups); unsaturated double and/or triple carbon to carbon bonds (e.g. in respectively alkenyl and alkynyl groups); aromatic groups (e.g. in aryl groups) and/or combinations thereof within the same moiety and where indicated may be substituted with other functional groups

[0140] The term 'alkyl' or its equivalent (e.g. 'alk') as used herein may be readily replaced, where appropriate and unless the context clearly indicates otherwise, by terms encompassing any other hydrocarbo group such as those described herein (e.g. comprising double bonds, triple bonds, aromatic moieties (such as respectively alkenyl, alkynyl and/or aryl) and/or combinations thereof (e.g. aralkyl) as well as any multivalent hydrocarbo species linking two or more moieties (such as bivalent hydrocarbylene radicals e.g. alkylene).

[0141] Any radical group or moiety mentioned herein (e.g. as a substituent) may be a multivalent or a monovalent radical unless otherwise stated or the context clearly indicates otherwise (e.g. a bivalent hydrocarbylene moiety linking two other moieties). However where indicated herein such monovalent or multivalent groups may still also comprise optional substituents. A group which comprises a chain of three or more atoms signifies a group in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings). The total number of certain atoms is specified for certain substituents for example $C_{1\text{-}N}$organo, signifies a organo moiety comprising from 1 to N carbon atoms. In any of the formulae herein if one or more substituents are not indicated as attached to any particular atom in a moiety (e.g. on a particular position along a chain and/or ring) the substituent may replace any H and/or may be located at any available position on the moiety which is chemically suitable and/or effective.

[0142] Preferably any of the organo groups listed herein comprise from 1 to 36 carbon atoms, more preferably from 1 to 18. It is particularly preferred that the number of carbon atoms in an organo group is from 1 to 12, especially from 1 to 10 inclusive, for example from 1 to 4 carbon atoms.

[0143] As used herein chemical terms (other than IUAPC names for specifically identified compounds) which comprise features which are given in parentheses—such as (alkyl) acrylate, (meth)acrylate and/or (co)polymer—denote that that part in parentheses is optional as the context dictates, so for example the term (meth)acrylate denotes both methacrylate and acrylate.

[0144] Certain moieties, species, groups, repeat units, compounds, oligomers, polymers, materials, mixtures, compositions and/or formulations which comprise and/or are used in some or all of the invention as described herein may exist as one or more different forms such as any of those in the following non exhaustive list: stereoisomers (such as enantiomers (e.g. E and/or Z forms), diastereoisomers and/or geometric isomers); tautomers (e.g. keto and/or enol forms), conformers, salts, zwitterions, complexes (such as chelates, clathrates, crown compounds, cyptands/cryptades, inclusion compounds, intercalation compounds, interstitial compounds, ligand complexes, organometallic complexes, non-stoichiometric complexes, π-adducts, solvates and/or hydrates); isotopically substituted forms, polymeric configurations [such as homo or copolymers, random, graft and/or block polymers, linear and/or branched polymers (e.g. star and/or side branched), cross-linked and/or networked polymers, polymers obtainable from di and/or tri-valent repeat units, dendrimers, polymers of different tacticity (e.g. isotactic, syndiotactic or atactic polymers)]; polymorphs (such as interstitial forms, crystalline forms and/or amorphous forms), different phases, solid solutions; and/or combinations thereof and/or mixtures thereof where possible. The present invention comprises and/or uses all such forms which are effective as defined herein.

[0145] Polymers of the present invention may be prepared by one or more suitable polymer precursor(s) which may be organic and/or inorganic and comprise any suitable (co) monomer(s), (co)polymer(s) [including homopolymer(s)] and mixtures thereof which comprise moieties which are capable of forming a bond with the or each polymer precursor (s) to provide chain extension and/or cross-linking with another of the or each polymer precursor(s) via direct bond(s) as indicated herein.

[0146] Polymer precursors of the invention may comprise one or more monomer(s), oligomer(s), polymer(s); mixtures thereof and/or combinations thereof which have suitable polymerisable functionality. It will be understood that unless the context dictates otherwise term monomer as used herein encompasses the term polymer precursor and does not necessarily exclude monomers that may themselves be polymeric and/or oligomeric in character.

[0147] A monomer is a substantially monodisperse compound of a low molecular weight (for example less than one thousand g/mole) which is capable of being polymerised.

[0148] A polymer is a polydisperse mixture of macromolecules of large molecular weight (for example many thousands of g/mole) prepared by a polymerisation method, where the macromolecules comprises the multiple repetition of smaller units (which may themselves be monomers, oligomers and/or polymers) and where (unless properties are critically dependent on fine details of the molecular structure) the addition or removal one or a few of the units has a negligible effect on the properties of the macromolecule.

[0149] A oligomer is a polydisperse mixture of molecules having an intermediate molecular weight between a monomer and polymer, the molecules comprising a small plurality of monomer units the removal of one or a few of which would significantly vary the properties of the molecule.

[0150] Depending on the context the term polymer may or may not encompass oligomer.

[0151] The polymer precursor of and/or used in the invention may be prepared by direct synthesis or (if the polymeric precursor is itself polymeric) by polymerisation. If a polymerisable polymer is itself used as a polymer precursor of and/or used in the invention it is preferred that such a polymer precursor has a low polydispersity, more preferably is substantially monodisperse, to minimise the side reactions, number of by-products and/or polydispersity in any polymeric

material formed from this polymer precursor. The polymer precursor(s) may be substantially un-reactive at normal temperatures and pressures.

[0152] Except where indicated herein polymers and/or polymeric polymer precursors of and/or used in the invention can be (co)polymerised by any suitable means of polymerisation well known to those skilled in the art. Examples of suitable methods comprise: thermal initiation; chemical initiation by adding suitable agents; catalysis; and/or initiation using an optional initiator followed by irradiation, for example with electromagnetic radiation (photo-chemical initiation) at a suitable wavelength such as UV; and/or with other types of radiation such as electron beams, alpha particles, neutrons and/or other particles.

[0153] The substituents on the repeating unit of a Polymer And/or oligomer may be selected to improve the compatibility of the materials with the polymers and/or resins in which they may be formulated and/or incorporated for the uses described herein. Thus the size and length of the substituents may be selected to optimise the physical entanglement or interlocation with the resin or they may or may not comprise other reactive entities capable of chemically reacting and/or cross linking with such other resins as appropriate.

[0154] Another aspect of the invention broadly provides a coating composition comprising the polymers and/or beads of the present invention and/or as described herein.

[0155] A further aspect of the invention provides a coating obtained or obtainable from a coating composition of the present invention.

[0156] A yet other aspect of the invention broadly provides a substrate and/or article having coated thereon an (optionally cured) coating composition of the present invention.

[0157] A yet further aspect of the invention broadly provides a method of using polymers of the present invention and/or as described herein to prepare a coating composition.

[0158] A still further aspect of the invention broadly provides a method for preparing a coated substrate and/or article comprising the steps of applying a coating composition of the present invention to the substrate and/or article and optionally curing said composition in situ to form a cured coating thereon. The curing may be by any suitable means, such as thermally, by radiation and/or by use of a cross-linker.

[0159] Preferred coating compositions are solvent coating compositions or aqueous coating compositions, more preferably are aqueous coating compositions.

[0160] Optionally aqueous coating compositions may also comprise a co-solvent. A co-solvent, as is well known in the coating art, is an organic solvent employed in an aqueous composition to ameliorate the drying characteristics thereof, and in particular to lower its minimum film forming temperature. The co-solvent may be solvent incorporated or used during preparation of polymers of the invention or may have been added during formulation of the aqueous composition.

[0161] The compositions of the invention are particularly useful as or for providing the principle component of coating formulations (i.e. composition intended for application to a substrate without further treatment or additions thereto) such as protective or decorative coating compositions (for example paint, lacquer or varnish) wherein an initially prepared composition optionally may be further diluted with water and/or organic solvents, and/or combined with further ingredients or may be in more concentrated form by optional evaporation of water and/or organic components of the liquid medium of an initially prepared composition.

[0162] The compositions of the invention may be used in various applications and for such purposes may be optionally further combined or formulated with other additives and/or components, such as defoamers, rheology control agents, thickeners, dispersing and/or stabilizing agents (usually surfactants and/or emulsifiers), wetting agents, fillers, extenders, fungicides, bactericides, coalescing and wetting solvents or co-solvents (although solvents are not normally required), plasticisers, anti-freeze agents, waxes, colorants, pigments, dyes, heat stabilisers, levelling agents, anti-cratering agents, fillers, sedimentation inhibitors, UV absorbers, antioxidants, reactive diluents, neutralising agents, adhesion promoters and/or any suitable mixtures thereof.

[0163] The aforementioned additives and/or components and the like may be introduced at any stage of the production process or subsequently. It is possible to include fire retardants (such as antimony oxide) to enhance fire retardant properties.

[0164] The compositions of the invention may also be blended with other polymers such as vinyl polymers, alkyds (saturated or unsaturated), polyesters and or polyurethanes.

[0165] The coating composition of the invention may be applied to a variety of substrates including wood, board, metals, stone, concrete, glass, cloth, leather, paper, plastics, foam and the like, by any conventional method including brushing, dipping, flow coating, spraying, and the like. The coating composition of the invention may also be used to coat the interior and/or exterior surfaces of three-dimensional articles. The coating compositions of the invention may also be used, appropriately formulated if necessary, for the provision of films, polishes, varnishes, lacquers, paints, inks and adhesives. However, they are particularly useful and suitable for providing the basis of protective coatings for substrates that comprise wood (e.g. wooden floors), plastics, polymeric materials, paper and/or metal.

[0166] The carrier medium may be removed from the compositions of the invention once they have been applied to a substrate by being allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat. Crosslinking can be developed by standing the coating for a prolonged period at ambient temperature (several days) or by heating at an elevated temperature (e.g. 50° C.) for a much shorter period of time.

[0167] Many other variations embodiments of the invention will be apparent to those skilled in the art and such variations are contemplated within the broad scope of the present invention. Further aspects of the invention and preferred features thereof are given in the claims herein.

Tests

Minimum Film Forming Temperature

[0168] The minimum film forming temperature (MFFT) of a dispersion as used herein is the temperature where the dispersion forms a smooth and crack free coating or film using DIN 53787 and when applied using a Sheen MFFT bar SS3000.

Koenig Hardness

[0169] Koenig hardness as used herein is a standard measure of hardness, being a determination of how the viscoelastic properties of a film formed from the dispersion slows down a swinging motion deforming the surface of the film, and is measured according to DIN 53157 NEN5319.

Glass transition temperature (Tg)

[0170] As is well known, the glass transition temperature of a polymer is the temperature at which it changes from a glassy, brittle state to a plastic, rubbery state. The glass transition temperatures may be determined experimentally using

Differential Scanning calorimetry (DSC), taking the peak of the derivative curve as Tg, or calculated from the Fox equation. Thus the Tg, in degrees Kelvin, of a copolymer having "n" copolymerised comonomers is given by the weight fractions W of each comonomer type and the Tgs of the homopolymers (in degrees Kelvin) derived from each comonomer according to the equation:

$$1 = W_1 + W_2 + \ldots W_n$$

$$Tg\ Tg_1\quad Tg_2\qquad Tg_n$$

[0171] The calculated Tg in degrees Kelvin may be readily converted to ° C.

Solids Content

[0172] The solids content of an aqueous dispersion of the invention is usually within the range of from about 20 to 65 wt-% on a total weight basis, more usually 30 to 55 wt-%. Solids content can, if desired, be adjusted by adding water or removing water (e.g. by distillation or ultrafiltration).

pH Value

[0173] The pH value of the dispersion of the invention can be from 2 to 10 and mostly is from 6 to 9.5.

Blocking

[0174] Block Resistance Measurement [Includes Blocking and Early Blocking]:

Step 1: Blocking:

[0175] A 100 micron wet film of the aqueous emulsion of the invention to which 10% butyldiglycol is added is cast on to a paper substrate and dried for 16 hours at 52° C.

Step 1: Early Blocking:

[0176] A 250 micron wet film of the aqueous emulsion of the invention to which 10% butyldiglycol was added, is cast on to a paper substrate and dried for 24 hours at room temperature.

Step 2: Blocking and Early Blocking:

[0177] After cooling down to room temperature two pieces of coated film are placed with the coated side against each other under a load of 1 Kg/cm.sup.2 for 4 hours at 52° C. After this time interval the load on the samples is removed and the samples are left to cool down to room temperature (22+-2° C.). When the two coatings can be removed from each other without any damage to the film (do not stick) the block resistance is very good and assessed as a 5. When they however completely stick together, block resistance is very bad and assessed as a 0.

Gas Chromatography Mass Spectrometry (GCMS)

[0178] to confirm polymerisation is substantially complete the content of free itaconate ester monomers content can be determined by GCMS. The GCMS analyses were performed on a Trace GC—DSQ MS (Interscience, Breda, the Netherlands) equipped with a CTC combi Pal robotic autosampler for head space has been used. The carrier gas was Helium and a CP Sil 5 low bleed/MS, 25 m×0.25 mm i.d., 1.0 pm (CP nr. 7862) column has been used.

[0179] The GC-oven was programmed from 50° C. (5 min) followed by different sequential temperature ramps of 5° C./min to 70° C. (0 min), 15° C./min to 220° C. (0 min), and ending with 25° C./min to 280° C. (10 min). A continuous Helium flow of 1.2 ml/min was used. A hot split injection at 300° C. was performed on a programmed temperature vaporizer (PTV). The injection volume was 1 μl. The MS transfer line and ion source were both kept at 250° C. The samples were measured with single ion monitoring (SIM). For the specific case of dibutyl itaconate (DBI) the masses 127.0 and 59.0 Da were used, for the internal standard (iso butyl acrylate) the masses 55.0 and 73.0 were applied. The sample solutions were approximately 500 mg in 3 ml of internal standard solution (iso butyl acrylate in acetone). The calibration was performed with 5 different concentration levels from 0 to 500 ppm. The calculation was performed using Microsoft Excel with a linear calibration curve.

Molecular Weight

[0180] Unless the context clearly dictates otherwise the term molecular weight of a polymer or oligomer as used herein denotes weight average molecular weight (also denoted as M_w). M_w may be measured by any suitable conventional method for example by Gas Phase Chromatography (GPC—performed similarly to the GCMS method described above) and/or by the SEC method described below. GPC method is preferred

Determination of Molecular Weight of a Polymer Using SEC

[0181] The molecular weight of a polymer may also be determined using Size Exclusion Chromatography (SEC) with tetrahydrofuran as the eluent or with 1,1,1,3,3,3 hexafluoro isopropanol as the eluent.

1) Tetrahydrofuran

[0182] The SEC analyses were performed on an Alliance Separation Module (Waters 2690), including a pump, auto injector, degasser, and column oven. The eluent was tetrahydrofuran (THF) with the addition of 1.0 vol % acetic acid. The injection volume was 150 μl. The flow was established at 1.0 ml/min. Three PL MixedB (Polymer Laboratories) with a guard column (3 μm PL) were applied at a temperature of 40° C. The detection was performed with a differential refractive index detector (Waters 410). The sample solutions were prepared with a concentration of 20 mg solids in 8 ml THF (+1 vol % acetic acid), and the samples were dissolved for a period of 24 hours. Calibration is performed with eight polystyrene standards (polymer standard services), ranging from 500 to 4,000,000 g/mol. The calculation was performed with Millennium 32 software (Waters) with a third order calibration curve. The obtained molar masses are polystyrene equivalent molar masses (g/mol).

2) 1,1,1,3,3,3 hexafluoro isopropanol

[0183] The SEC analyses were performed on a Waters Alliance 2695 (pump, degasser and autosampler) with a Shodex RI-101 differential refractive index detector and Shimadzu CTO-20AC column oven. The eluent was 1,1,1,3,3,3 hexafluoro isopropanol (HFIP) with the addition of 0.2M potassium trifluoro acetate (KTFA). The injection volume was 50 μl. The flow was established at 0.8 ml/min. Two PSS PFG Linear XL columns (Polymer Standards Service) with a guard column (PFG PSS) were applied at a temperature of 40° C. The detection was performed with a differential refractive index detector. The sample solutions were prepared with a concentration of 5 mg solids in 2 ml HFIP (+0.2M KTFA), and the samples were dissolved for a period of 24 hours.

Calibration is performed with eleven polymethyl methacrylate standards (polymer standard services), ranging from 500 to 2,000,000 g/mol. The calculation was performed with Empower Pro software (Waters) with a third order calibration curve. The molar mass distribution is obtained via conventional calibration and the molar masses are polymethyl methacrylate equivalent molar masses (g/mol).

standard conditions

[0184] As used herein, unless the context indicates otherwise, standard conditions (e.g. for drying a film) means a relative humidity of 50%±5%, ambient temperature (which denotes herein a temperature of 23° C.).±2° and an air flow of ≤(less than or equal to) 0.1 m/s.

[0185] The following examples are provided to further illustrate the processes and compositions of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way. Unless otherwise specified all parts, percentages, and ratios are on a weight basis. The prefix C before an example indicates that it is comparative.

[0186] Various registered trademarks, other designations and/or abbreviations are used herein to denote some of ingredients used to prepare polymers and compositions of the invention. These are identified below by chemical name and/or trade-name and optionally their manufacturer or supplier from whom they are available commercially. However where a chemical name and/or supplier of a material described herein is not given it may easily be found for example in reference literature well known to those skilled in the art: such as: 'McCutcheon's Emulsifiers and Detergents', Rock Road, Glen Rock, N.J. 07452-1700, USA, 1997 and/or Hawley's Condensed Chemical Dictionary (14th Edition) by Lewis, Richard J., Sr.; John Wiley & Sons.

[0187] In the examples of the present invention or elsewhere herein the following ingredients are described abbreviated as follows:

AMBN is 2,2'-azodi(2-methylbutyronitrile)

BA denotes butyl acrylate (may be (partly) bio-renewable)

BAm denotes butyl amine

DBI denotes dibutyl itaconate (may be (partly) bio-renewable)

DEI denotes diethyl itaconate (may be (partly) bio-renewable)

DMI denotes dimethyl itaconate (may be (partly) bio-renewable)

DEAm denotes di-ethyl amine

EHA denotes 2-ethyl hexyl acrylate

EXAMPLES

[0188] The invention can be illustrated by the following non-limiting examples.

Preparation of Solution Polymers

Example 1

[0189] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 287.1 parts of methylethyl ketone. The reactor contents are heated to 79° C.

[0190] At reaction temperature, a solution of 2.6 parts of AMBN in 28.6 parts of methylethyl ketone is added. Next, a monomer feed, consisting of 186.5 parts of methyl methacrylate, 140.7 parts of butyl acrylate, and 36.4 parts of itaconic anhydride, is added over a period of 150 minutes. Simultaneously a catalyst feed, comprising 8 parts of AMBN and 59.3 parts of methylethyl ketone, is added, also over a period of 150 minutes.

[0191] At the end of the monomer feed, reaction temperature is maintained for 60 minutes. 30 minutes after the end of the monomer feed 0.9 parts of AMBN are added to the reactor.

[0192] The reactor contents are cooled to room temperature.

[0193] The resulting polymer solution has a solids content of 50%. The polymer has an itaconic anhydride concentration of 10 wt-%.

Example 2

[0194] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 287.1 parts of methylethyl ketone. The reactor contents are heated to 79° C.

[0195] At reaction temperature, a solution of 2.6 parts of AMBN in 28.6 parts of methylethyl ketone is added. Next, a monomer feed, consisting of 165.8 parts of methyl methacrylate, 125.0 parts of butyl acrylate, and 72.7 parts of itaconic anhydride, is added over a period of 150 minutes. Simultaneously a catalyst feed, comprising 8 parts of AMBN and 59.3 parts of methylethyl ketone, is added, also over a period of 150 minutes.

[0196] At the end of the monomer feed, reaction temperature is maintained for 60 minutes. 30 minutes after the end of the monomer feed a solution of 0.9 parts of AMBN in 106.3 parts of methylethyl ketone is added to the reactor.

[0197] The reactor contents are cooled to room temperature. The resulting polymer solution has a solids content of 47%. The polymer has an itaconic anhydride concentration of 20 wt-%.

Example 3

[0198] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 287.1 parts of methylethyl ketone. The reactor contents are heated to 79° C.

[0199] At reaction temperature, a solution of 2.6 parts of AMBN in 28.6 parts of methylethyl ketone is added. Next, a monomer feed, consisting of 145.0 parts of methyl methacrylate, 109.4 parts of butyl acrylate, and 109.0 parts of itaconic anhydride, is added over a period of 150 minutes. Simultaneously a catalyst feed, comprising 8 parts of AMBN and 59.3 parts of methylethyl ketone, is added, also over a period of 150 minutes.

[0200] At the end of the monomer feed, reaction temperature is maintained for 60 minutes. 30 minutes after the end of the monomer feed a solution of 0.9 parts of AMBN in 209.9 parts of methylethyl ketone is added to the reactor.

[0201] The reactor contents are cooled to room temperature.

[0202] The resulting polymer solution has a solids content of 41%. The polymer has an itaconic anhydride concentration of 30 wt-%.

Post Modification

Example 4

[0203] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 479.8 parts of the polymer solution obtained from Example 1. To this solution are added at room temperature, over a period of 15 minutes, 30 mole-% (based on anhydride) of butyl amine. The mixture is stirred for 60 minutes at room temperature

after which the conversion of amine groups was >98% as determined by titration of the amine number. The solution was diluted to a solids content of 40% with methylethyl ketone.

Examples 5 to 21

[0204] Examples 5 to 21 can be made by the analogous procedure described in Example 4 with reference to the following table where the polymer solution from Example 1 is substituted with the (same amount of) the polymer solution of the example given in Table 1 and the 30 mol % of butyl amine is substituted with the amine in the mol % given in Table 1.

TABLE 1

Ex	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
PS	1	1	2	2	2	3	3	3	1	1	1	2	2	2	3	3	3
Bam	60	90	30	60	90	30	60	90									
EAm									30	60	90	30	60	90	30	60	90

PS—polymer solution from Example # (number given in Table 1)
BAm—mole-% of butyl amine
EAm—mole-% of ethanol amine

Example 22

[0205] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 479.8 parts of the polymer solution obtained from Example 1. To this solution are added, at 50° C., over a period of 15 minutes, 30 mole-% (based on anhydride) of butyl amine. The mixture is stirred for 60 minutes at 50° C. after which the conversion of amine groups was >98% as determined by titration of the amine number. The solution was cooled to room temperature and diluted to a solids content of 40% with methylethyl ketone.

Examples 23 to 39

[0206] Examples 23 to 39 can be made by the analogous procedure described in Example 22 with reference to the following table where the polymer solution from Example 1 is substituted with the (same amount of) the polymer solution of the example given in Table 2 and the 30 mol % of butyl amine is substituted with the amine in the mol % given in Table 2.

TABLE 2

Ex	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
PS	1	1	2	2	2	3	3	3	1	1	1	2	2	2	3	3	3
PAm	60	90	30	60	90	30	60	90									
DEAm									30	60	90	30	60	90	30	60	90

PS—polymer solution from Example # (number given in Table 2)
PAm—mole-% of propyl amine
DEAm—mole-% of diethyl amine

Emulsification of Modified Polymer Solutions

Examples 40 to 60

Emulisfication Method

[0207] Polymer emulsions Examples 40 to 60 can be made by the general procedure described below with reference to the following tables (Tables 3 and 4) where the polymer solution from Example and the amount of ammonia is given. To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 400.0 parts by weight (g) of the polymer solution obtained as described in the respective example given in the table below (Tables 3 and 4). The temperature of the solution is set at 35° C. after which ammonia is added according to the amounts (g) shown in the tables (Tables 3 and 4). Next, enough demineralised water is added over a period of 15 minutes to reach a solids content of 45% after removal of methylethyl ketone. By heating the emulsions to 40° C. and reducing pressure, methylethyl ketone is removed by evaporation. Next, the pH is correct to a value of between 8.5 and 9.0 and the solids content is corrected to 45% using demineralised water.

TABLE 3

Ex	41	42	43	44	45	46	47	48	49
PS (Ex#)	4	5	6	7	8	9	10	11	12
Ammonia	9.73	7.86	6.06	22.24	17.65	13.39	32.75	25.56	19.08

TABLE 4

Ex	50	51	52	53	54	55	56	57	58
PS (Ex#)	13	14	15	16	17	18	19	20	21
Ammonia	9.76	7.91	6.12	22.39	17.87	13.62	33.05	26.01	19.56

PS—polymer solution from Example # (number given in Table 3 or 4)

Further Examples 58 to 120

Preparation of Solution Polymers Example 58

[0208] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 329.7 parts of 2-butanone. The reactor contents are heated to 79° C.

[0209] At reaction temperature, a solution of 11.1 parts of azobis(2-methyl butyronitrile) in 110.5 parts of 2-butanone is added. Next, a monomer feed, consisting of 190.9 parts of methyl methacrylate, 333.2 parts of butyl acrylate, and 224.6

parts of itaconic anhydride, is added over a period of 240 minutes. Simultaneously a catalyst feed, comprising 50.7 parts of azobis(2-methyl butyronitrile) and 245.5 parts of 2-butanone, is added, also over a period of 240 minutes. At the end of the monomer feed, reaction temperature is maintained for 90 minutes. 30 minutes after the end of the monomer feed 3.8 parts of azobis(2-methyl butyronitrile) are added to the reactor. The reactor contents are cooled to room temperature. The resulting polymer solution has a solids content of 54%. The polymer has an itaconic anhydride concentration of 30 wt-% on polymer composition and a theoretical Tg of 30° C.

Example 59

[0210] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 329.7 parts of 2-butanone. The reactor contents are heated to 79° C. At reaction temperature, a solution of 18.5 parts of azobis(2-methyl butyronitrile) in 110.5 parts of 2-butanone is added. Next, a monomer feed, consisting of 306.3 parts of methyl methacrylate, 217.9 parts of butyl acrylate, and 224.6 parts of itaconic anhydride, is added over a period of 240 minutes. Simultaneously a catalyst feed, comprising 43.2 parts of azobis(2-methyl butyronitrile) and 245.5 parts of 2-butanone, is added, also over a period of 240 minutes. At the end of the monomer feed, reaction temperature is maintained for 90 minutes. 30 minutes after the end of the monomer feed 3.8 parts of azobis(2-methyl butyronitrile) are added to the reactor. The reactor contents are cooled to room temperature. The resulting polymer solution has a solids content of 54%. The polymer has an itaconic anhydride concentration of 30 wt-% on polymer composition and a theoretical Tg of 60° C.

Example 60

[0211] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 329.7 parts of 2-butanone. The reactor contents are heated to 79° C. At reaction temperature, a solution of 11.1 parts of azobis(2-methyl butyronitrile) in 110.5 parts of 2-butanone is added. Next, a monomer feed, consisting of 374.4 parts of butyl acrylate, and 374.4 parts of itaconic anhydride, is added over a period of 240 minutes. Simultaneously a catalyst feed, comprising 50.7 parts of azobis(2-methyl butyronitrile) and 245.5 parts of 2-butanone, is added, also over a period of 240 minutes. At the end of the monomer feed, reaction temperature is maintained for 90 minutes. 30 minutes after the end of the monomer feed 3.8 parts of azobis(2-methyl butyronitrile) are added to the reactor. The reactor contents are cooled to room temperature. The resulting polymer solution has a solids content of 54%. The polymer has an itaconic anhydride concentration of 50 wt-% on polymer composition and a theoretical Tg of 30° C.

Post Modification

[0212] The polymers of Examples 58 to 60 may also be post modified as described below.

Post-Modification Method a

[0213] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 479.8 parts of the polymer solution (PS) obtained from Example number (#) given in the tables below. To this solution are added at 45° C., over a period of 15 minutes, M mole-% (based on anhydride) of an amine (A) as identified in the tables below. The mixture is stirred for 60 minutes at 45° C. until the conversion of amine groups was >98% as determined by titration of the amine number. The solution is diluted to a solids content of 40% with 2-butanone. Then the mixture is diluted with water after which 70 mole-% of the remaining acid groups are neutralized with ammonia and the polymer is emulsified. The 2-butanone is removed by evaporation under reduced pressure at 50° C.

Examples 61 to 72

Butyl Amine (BAm)

[0214] Examples 61 to 72 may be prepared according to Postmodification Method A described above with the polymer solution (PS) of the Example number (#) given in Table 5 and the amine A being butyl amine (BAm) used in the amount M (mol %) given in Table 5.

TABLE 5

Post Mod (Ex #)	61	62	63	64	65	66	67	68	69	70	71	72
PS (Ex #)	58	58	58	58	59	59	59	59	60	60	60	60
A = BAm (M mol %)	25	50	75	100	25	50	75	100	25	50	75	100

Examples 73 to 84

Di-ethyl amine (DEAm)

[0215] Examples 73 to 84 may be prepared according to Postmodification Method A described above with the polymer solution (PS) of the Example number (#) given in Table 6 and the amine A being di-ethyl amine (DEAm) used in the amount M (mol %) given in Table 6.

TABLE 6

Post Mod (Ex #)	73	74	75	76	77	78	79	80	81	82	83	84
PS (Ex #)	58	58	58	58	59	59	59	59	60	60	60	60
A = DEAm (M mol %)	25	50	75	100	25	50	75	100	25	50	75	100

Post-Modification Method B

[0216] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 500 parts of the polymer solution (PS) obtained from Example number (#) given in the tables below. The solution is diluted with 100 parts of methanol. To this solution are added at 45° C., over a period of 15 minutes, M' mole-% (based on anhydride) of an amine (A') as identified in the tables below. The

mixture is stirred for 60 minutes at 30° C. until the conversion of amine groups was >98% as determined by titration of the amine number. The solution is diluted to a solids content of 40% with methanol. The mixture is diluted with water after which 70 mole-% of the remaining acid groups are neutralized with ammonia and the polymer is emulsified. The methanol and any 2-butanone (from the PS) are removed by evaporation under reduced pressure at 50° C.

Examples 85 to 96

(3-Aminopropyl) trismethoxy silane (ATMS)

[0217] Examples 85 to 96 may be prepared according to Postmodification Method B described above with the polymer solution (PS) of the Example number (#) given in Table 7 and the amine A' being (3-aminopropyl) trismethoxy silane (ATMS) used in the amount M' (mol %) given in Table 7.

TABLE 7

Post Mod (Ex #)	85	86	87	88	89	90	91	92	93	94	95	96
PS (Ex #)	58	58	58	58	59	59	59	59	60	60	60	60
A' = ATMS (M' mol %)	25	50	75	100	25	50	75	100	25	50	75	100

Examples 97 to 108

2-Aminoethyl piperazine (AEP)

[0218] Examples 97 to 108 may be prepared according to Postmodification Method B described above with the polymer solution (PS) of the Example number (#) given in Table 8 and the amine A' being 2-aminoethyl piperazine (AEP) used in the amount M' (mol %) given in Table 8.

TABLE 8

Post Mod (Ex #)	97	98	99	100	101	102	103	104	105	106	107	108
PS (Ex #)	58	58	58	58	59	59	59	59	60	60	60	60
A' = AEP (M' mol %)	25	50	75	100	25	50	75	100	25	50	75	100

Post-Modification Method C

[0219] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer are added 500 parts of the polymer solution (PS) obtained from Example number (#) given in the tables below. To this solution are added at 60° C., over a period of 15 minutes, M" mole-% (based on anhydride) of an amine (A") as identified in the tables below. The mixture is stirred for 90 minutes at 60° C. until the conversion of amine groups was >98% as determined by titration of the amine number. The solution is diluted to a solids content of 40% with 2-butanone. The mixture is diluted with water after which 70 mole-% of the remaining acid groups are neutralized with ammonia and the polymer is emulsified. The 2-butanone is removed by evaporation under reduced pressure at 50° C.

Examples 109 to 120

Adipic Dihydrazide (ADH)

[0220] Examples 109 to 120 may be prepared according to Postmodification Method C described above with the polymer solution (PS) of the Example number (#) given in Table 9 and the amine A" being adipic dihydrazide (ADH) used in the amount M" (mol %) given in Table 9.

TABLE 9

Post Mod (Ex #)	109	110	111	112	113	114	115	116	117	118	119	120
PS (Ex #)	58	58	58	58	59	59	59	59	60	60	60	60
A' = ADH (M' mol %)	25	50	75	100	25	50	75	100	25	50	75	100

1. A method for preparing a post modified polymer (Polymer C) the method comprising the steps of:

(1) polymerising a monomer composition comprising from 2.5 to 75% by weight (by weight of the total monomer composition) of at least one itaconic anhydride, precursor thereof and/or derivative thereof in a polymerisation method (optionally an emulsion or solution polymerisation) to obtain an itaconate polymer (Polymer A); and

(2) reacting in a post modification step at least 10 mole-% of the anhydride groups, anhydride precursor groups and/or anhydride derived groups of the Polymer A obtained from step (1) with a moiety having a nucleophilic group (Nucleophile B) to form a post-modified polymer (Polymer C).

2. A method as claimed in claim **1**, where if the monomer composition of step (1) consists of itaconic anhydride and methyl methacrylate and if the itaconate polymer (Polymer A) is a copolymer obtained solely from itaconic anhydride and methyl methacrylate monomers; then in the post modification step (2) the Nucleophile B is other than di-n-butyl amine.

3. A method according to claim **1** in which the monomer composition of step (1) comprises itaconic anhydride, itaconamide, and/or dialkyl itaconate.

4. A method according to claim **3**, in which the monomer composition of step (1) comprises itaconic anhydride and/or di(C_{1-10}alkyl) itaconate.

5. A method according to claim **4** in which the monomer composition of step (1) comprises di(C_{1-4}alkyl) itaconate.

6. A method according to claim **5** in which the monomer composition of step (1) comprises diethyl itaconate (DEI).

7. A post modified Polymer C obtained and/or obtainable from a method as claimed in claim **1**.

8. A method of preparing a sequential polymer (Polymer D), the method comprising the step of using a Polymer C as claimed in claim **7** as a stabilizer and/or seed in a sequential polymerization.

9. A sequential Polymer D obtained and/or obtainable from a method as claimed in claim **8**.

10. A coating composition comprising a post modified Polymer C as claimed in claim **7**.

11. A substrate and/or article having coated thereon an (optionally cured) coating composition of claim **10**.

12. A method of using a post modified Polymer C as claimed in claim **7** to prepare a coating composition.

13. A method for preparing a coated substrate and/or article comprising the steps of applying a coating composition of claim **10** to the substrate and/or article and optionally curing said composition in situ to form a cured coating thereon.

14. A coated substrate and/or article obtained and/or obtainable by a method as claimed in claim **13**.

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