

Description

The present invention is concerned with copolymers containing, as copolymerized monomer units, units of aliphatic monoethylenically unsaturated dicarboxylic acids, such as maleic acid, and units of at least one comonomer selected from monoethylenically unsaturated monocarboxylic acids, such as acrylic acid, and carboxyl-free monoethylenically unsaturated monomers, such as alkyl esters of acrylic acid. This invention is particularly concerned with the use of low levels of copper ions in an aqueous solution polymerization process to promote copolymerization of the above-mentioned monomers at high conversion while maintaining and improving molecular weight control. These copolymers are useful primarily as antiscalants, dispersants, hard surface cleaners, detergent builders and incrustation inhibitors.

Copolymers of monoethylenically unsaturated dicarboxylic acids, monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers are useful as antiscalants, dispersants, incrustation inhibitors and builders in detergents, deflocculants and drilling fluid aids. Several techniques employing aqueous polymerization systems have been previously described in the preparation of these copolymers.

Initially, high molecular weight polymers of this type were produced using a redox system, while the more desirable low molecular weight polymers were produced using a chain transfer agent such as a mercaptan. However, mercaptans are undesirable because of both their expense and unpleasant odor. US-A-4,314,044 ('044) attempted to solve this problem of using mercaptans by describing an aqueous process for the preparation of low molecular weight, water-soluble copolymers of acrylic and methacrylic acid with unsaturated dicarboxylic acids such as itaconic acid, fumaric acid and maleic acid. The '044 patent disclosed the use of a catalytic system comprising an initiator and a metal salt in a molar ratio of initiator to metal ion of from about 10:1 to about 150:1 and the initiator being present in an amount of from 0.5 to about 35 weight percent, based on the weight of the monomers present.

The process of the '044 patent was modified by US-A-4,659,793 ('793) which describes an aqueous batch process for the preparation of copolymers of monoethylenically unsaturated aliphatic dicarboxylic acids with α,β -ethylenically unsaturated monomers, by using one of various metal ions at low levels, such as 1 to 250 ppm, the residual monomer content was claimed to be reduced to 0.5% or less based on the total weight of the dried copolymers, the '793 patent describes a copolymer containing, as copolymerized monomer

units, of from 25 to 55% by weight of the dicarboxylic acid and from 45 to 75% by weight of the ethylenically unsaturated monomers, and said copolymers are claimed to have a weight average molecular weight of from about 2,000 to 1,000,000. However, the lowest level of the dicarboxylic acid exemplified in the '793 patent is 30%, yielding a weight average molecular weight of from 25,000 to 40,000. The metal ions disclosed as suitable for use in the process of the '793 patent are Zn^{++} , Co^{+++} , Co^{++} , Cu^{++} , Mo^{++} , Fe^{+++} , Fe^{++} , Cr^{+++} , Ni^{++} , Ce^{+++} and Ce^{++} . No metal ion is shown to have any advantage over any of the other metal ions and only Fe^{++} is shown in the specific examples of the patent.

Another process for the synthesis of these polymers is a continuous cascade process disclosed in US-A-4,725,655. Described in this patent is the copolymerization of monoethylenically unsaturated dicarboxylic acids in concentrations of from 10 to 60% by weight of the monomers, monoethylenically unsaturated monocarboxylic acids in concentrations of 40 to 90% by weight of the monomers, and optionally carboxyl-free monomers in concentration of not more than 20% by weight of the monomers. This reaction is carried out in the presence of from 0.5 to 6% by weight of a water-soluble, free-radical forming initiator. Multiple reactors are required for this procedure with the preferred number being at least three. This process does not claim the use of any metal salt.

Copending EP 398724A also describes a method of preparation of copolymers of monoethylenically unsaturated aliphatic dicarboxylic acids with comonomers selected from monoethylenically unsaturated monocarboxylic acids and unsaturated carboxyl-free monomers. It describes a continuous or batch process for producing copolymers of more consistent composition by the simultaneous addition of the monomers to a reaction vessel containing an initial charge of water. The monoethylenically unsaturated dicarboxylic acid concentration is from 3 to 65%, preferably from 10 to 60%, by weight of the total monomer concentration, and the comonomer concentration is from 35 to 97%, preferably from 40 to 90%, by weight of the total monomer concentration. This procedure also makes use of a metal salt, e.g. in concentrations from 1 to 200 ppm, preferably from 1 to 25 ppm, based on the total weight of the monomers. The metal ions include water soluble salts of cobalt, iron, copper, nickel, manganese, zirconium and zinc.

Currently, there is no process to control the molecular weight and degree of branching during the preparation of copolymers containing low levels of aliphatic monoethylenically unsaturated dicarboxylic acids of from about 3 to 25%. We have

found that, if any of the previously described techniques are used to synthesize copolymers according to the present invention, the copolymer tends to branch dramatically during synthesis and molecular weight builds. In most circumstances this causes the reaction solution to increase viscosity and eventually gel. When copolymers have been synthesized under these prior art techniques, the molecular weights have generally been too high and, therefore, the copolymers have been undesirable.

The present invention enables the preparation of water-soluble, low molecular weight copolymers containing low levels of monoethylenically unsaturated dicarboxylic acid units, such as maleic acid, and high levels of monoethylenically unsaturated monocarboxylic acid units, such as acrylic acid. Detergent and water treatment formulations containing these novel copolymers are also within the present invention.

It has now been found that polymers, containing low levels of monoethylenically unsaturated aliphatic dicarboxylic acids, can be successfully synthesized and the molecular weight controlled at a desirable level by using low levels of copper salt as polymerization moderator. Surprisingly, copper salt has been found to be unique in its properties among the common metal salts disclosed in the previous art.

According to the present invention there is provided a process for preparing water-soluble copolymers, which comprises polymerizing from 3 to 25% by weight, based on the total amount of the monomers, of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, or salt or anhydride thereof, and 75 to 97% by weight based on the total amount of the monomers, of at least one comonomer comprising monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule or carboxyl-free monoethylenically unsaturated monomers, conducting said reaction in the presence of water-soluble polymerization initiator, copper salt polymerization moderator and neutralizer at elevated temperature, and, after said polymerization, recovering said copolymer, wherein said process comprises:

(a) establishing an initial reactor charge of said monoethylenically unsaturated dicarboxylic acid to which is added the comonomer(s), water-soluble initiator and neutralizer during a period of from 1 to 6 hours and said copper polymerization moderator is contained in said initial charge, added to said reaction as a separate solution, or a combination thereof.

The process of the present invention is run such that at least a portion, for example all, of at

least one, but not all, of the monomers, initiator and neutralizer is added to the reactor, and the remainder of the monomers, initiator and neutralizer is subsequently added to the reactor. For example, the monomers, initiator and neutralizer may not all be substantially initially cofed. In one embodiment of the invention, at least a portion of one of the monomers may be added to the reactor with the remainder of the monomers, the initiator and the neutralizer being subsequently added to the reactor.

The present invention provides an aqueous process, which may be operated in a batch or continuous manner, for the preparation, at high conversions, of copolymers of (i) aliphatic monoethylenically unsaturated dicarboxylic acids, especially maleic acid, and (ii) monoethylenically unsaturated monocarboxylic acids, such as acrylic acid, and/or carboxyl-free monoethylenically unsaturated monomers, such as alkyl esters of acrylic acid. Copolymers with lower levels of aliphatic monoethylenically unsaturated dicarboxylic acid content of controlled molecular weight can be prepared and their molecular weight controlled by using the process of this invention as compared to copolymers made from processes described in the previous art using similar monomers.

In the continuous process the metal salt polymerization moderator may be simultaneously cofed into a reaction vessel along with the monomers. The metal salt may, however, be simultaneously cofed into the reaction vessel along with the remaining reaction components, e.g. along with the monomers, or contained in the initial charge, or both. In the batch process the metal salt polymerization moderator may be contained in an initial charge of monomers in the reaction vessel, or cofed into the reaction vessel along with the monomers, or a combination of both. For example, in the batch process an aqueous solution of the dicarboxylic acid monomer may be placed in a reaction vessel and the copper salt polymerization moderator added thereto. The solution is heated and then an aqueous solution of one or more of the comonomers, a solution of initiator and a neutralizing solution are added to the reaction vessel over a period of several hours. However, two or more of the solutions may be combined prior to addition to the reactor, or the monomers may be added as separate solutions.

We have found that the use of low levels of copper salt in an aqueous polymerization facilitates improved molecular weight control and, in addition, allows for the preparation of a broad range of polymer compositions. Although the mechanism of the process set forth herein is not fully understood, it is believed that the copper salts, used in the reaction of this invention, act as polymerization

moderators, that is they control the molecular weight, the chain length and the degree of branching. The theory of this invention is presented here as a possible explanation of the surprising results obtained and in no way is intended to limit the scope of this invention.

Monomer, initiator and neutralizer streams, e.g. as solutions, may be added at a substantially uniform rate, e.g. a linear rate. Preferably, after addition to the reactor of at least part of at least one of the monomer, initiator and neutralizer components, the remainder of the monomer, initiator and neutralizer components are added to the reactor as three streams, e.g. solutions, the monomer stream, the initiator stream and the neutralizer stream. A satisfactory alternative variation involves combining two or more of these three streams, e.g. solutions, prior to addition to the reactor, and another alternative involves the addition of the monomers as separate streams, e.g. solutions. Further, the remainder of the monomer, initiator and neutralizer streams may be cofed, to the reactor for at least a portion of the total addition time of such streams. The rate and time of addition of the monomers and initiator can be varied to account for the difference in reactivity of the monomers and thereby maximize the conversion of the monomers.

The monomers used in the process comprise monoethylenically unsaturated dicarboxylic acids containing from 4 to 6 carbon atoms per molecule, their salts, e.g. their alkali metal and ammonium salts, and the anhydrides of the cis-dicarboxylic acids. Examples of suitable monomers include maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid and the anhydrides of cis-dicarboxylic acids, such as maleic anhydride. Maleic anhydride is preferred among these monomers. The monoethylenically unsaturated dicarboxylic acid concentration can be from 3 to 25%, and preferably from 5 to 23%, by weight of the total monomer concentration.

The comonomers, used in the present invention, are selected from monoethylenically unsaturated monocarboxylic acids and carboxyl-free monoethylenically unsaturated monomers. The concentration of these monomers is from 75 to 97%, and preferably from 77 to 95%, by weight of the total monomer concentration.

Suitable monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per molecule include acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid. The preferred monoethylenically unsaturated monocarboxylic acid is acrylic acid.

Suitable carboxyl-free monoethylenically unsaturated monomers include alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl

acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrrolidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene; vinyl sulfonic acid and its salts; and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts. The concentration of carboxyl-free monoethylenically unsaturated monomers can be from 0 to about 80% by weight of the total monomer concentration. The concentration is typically up to 35%, and is dependent upon the solubility of the particular monomer in the reaction mixture.

The water-soluble initiators which may be used are the well known peroxy, persulfate and azo initiators, including hydrogen peroxide, t-butyl hydroperoxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perphosphate, ammonium perphosphate, potassium perphosphate and 2,2-azobis(cyanovaleric acid). The initiator concentration is normally from 0.5 to 20%, and preferably from 1 to 10%, based on the total weight of the monomers.

Water-soluble copper salts are preferred at levels of from 1 to 200 ppm, and more preferred from 1 to 50 ppm. Copper salts include all inorganic or organic compounds that will generate copper ions in aqueous solution. These salts include such salts as copper sulfate, copper nitrate, copper chloride, copper acetate and inert, water-soluble copper complexes.

The polymerization is preferably run to about 20 to 80% solids, and most preferably to about 30 to 65% solids, by weight. Polymerization temperatures may be from 80 to 150°C, preferably from 90 to 120°C. When run in the batch mode, monomer addition rates may be from 1 to 10 hours, preferably from 1 to 6 hours, and when run as a continuous process, residence times of at least 30 minutes should be used. If residual monomer levels are higher than desired, a post-polymerization addition of initiator (chaser catalyst), or initiator and a monomer may be used.

The in-process neutralizer, e.g. in the form of a neutralization solution, may be used in an amount of from 20 to 80 equivalent percent of base, preferably 40 to 60 percent base, based on the acid

content of the monomer mixture, and may be added to the reactor linearly throughout the polymerization. Suitable bases include, sodium hydroxide, potassium hydroxide and ammonium hydroxide. The pH of the reaction solution is preferably maintained in the range of from 3 to 7, and most preferably from 4 to 6.

The present invention will now be further described with reference to the accompanying drawings, in which:

FIG. 1 is a graph of the molecular weight of copolymers synthesized from monomer units of maleic acid and acrylic acid (axis "Y" - measured as GPC $M_w \times 1000$) versus the weight percent of maleic acid (axis "X") based on the total weight of the monomers. To furnish a striking comparison, the graph contains two plots, one is the results of the copolymer synthesis without copper (line "A") and one is the result of the copolymer synthesis with copper (line "B" - 6 ppmCu (on monomer)) as the polymerization moderator; and

Figure 2 is a bar graph of copolymer molecular weight (axis "Y" - measured as GPC $M_w \times 1000$) versus the type of metal used for the synthesis of a copolymer of 80/20 acrylic acid/maleic acid (axis "X").

Both figures demonstrate the dramatic superiority of using copper salt as the polymerization moderator. Figure 1 compares the molecular weight of copolymers synthesized using copper to the molecular weight of copolymers synthesized without any metal polymerization moderator. The copper allows for better control of the molecular weight over a wide range of maleic acid content in the copolymer. Without the use of copper salt as the polymerization moderator, the molecular weight of the copolymer increases rapidly to an undesirable level as the amount of maleic acid contained in the copolymer is decreased. Figure 2 compares using copper salt as opposed to other metals (metals used are as indicated - bar (i) is a control utilizing no metal salt) and shows how the phenomenon of stable molecular weight control is unique to copper. Copper is the only metal leading to a copolymer containing 20% maleic acid with a desirable molecular weight. All other metal salts tested lead to gelling of the polymerization solution, except for Fe^{++} which leads to an undesirable, very high molecular weight copolymer.

The Figures demonstrate the superiority of using copper as the polymerization moderator in controlling the molecular weight and degree of branching during the polymerization reaction. None of the other common metal ions control molecular weight to the extent copper does. Copper is surprisingly superior to any of the other metal ions previously used.

The copolymers of this invention can be added to detergent compositions in concentrations of up to about 50% by weight, when used as builders, but only from 0.1 to 5.0% by weight, and more preferably from 0.5 to 5.0% by weight, when used to enhance incrustation inhibition (or anti-redeposition of salts). Detergent compositions normally include as the "active" components both a detergent builder and at least one water-soluble organic surfactant compound; such as the anionic, nonionic, zwitterionic, and ampholytic surfactants. Particular performance characteristics are imported to detergent formulations by the use of a host of optional ingredients which are mainly intended to enhance the aesthetic effect of the product. Among these are optical brighteners, stain removers, softening agents and perfumes. The chemical nature of these optional detergent additives is not an essential feature of the present invention since these are well known to those skilled in the detergent art.

Examples of other builder compounds which may be used in the detergent composition of the current invention can include the alkali metal salts of carboxymethyloxysuccinic acid and oxydiacetic acid, tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium triphosphates, ether polycarboxylates, citrates, starch or cellulose derived from polycarboxylates, polyacrylic acids and the like. The copolymers of the present invention are particularly useful as anti-redeposition agents in detergent formulations containing a precipitant builder such as sodium-carbonate. Other materials which may be present in a liquid or powdered detergent composition are those conventionally present therein. Typical examples thereof include soil suspending agents, hydrotropes, corrosion inhibitors, dyes, perfumes, fillers, abrasives, optical brighteners, enzymes, suds boosters, suds dispersants, germicides, anti-tarnishing agents, cationic detergents, softeners, chlorine releasing agents, buffers and the like. The balance of the detergent composition is water.

The detergent composition of the present invention may be in any of the usual physical forms of such compositions, such as powders, beads, flakes, bars, tablets, noodles, liquids, pastes, and the like. The detergent compositions are prepared and utilized in the conventional manner. An additional advantage of the polymers of this invention is that they are biodegradable.

The present invention will now be further illustrated with reference to the following Examples which are for illustrative purposes only and are not to be construed as imposing any limitation on the scope of the invention. In the Examples, all percentages are by weight unless specified otherwise.

EXAMPLE 1

To a two liter four neck flask equipped with a mechanical stirrer, reflux condenser and addition funnels, were added 190 grams of deionized water, 6 grams of a 0.15% by weight solution of copper (II) sulfate pentahydrate dissolved in deionized water and 42.4 grams of maleic anhydride. This solution was heated to reflux at which time 200 grams of glacial acrylic acid, an initiator solution of 40 grams of deionized water and 12.5 grams of sodium persulfate, and a neutralizing solution of 217 grams of 50% sodium hydroxide, 75 equivalent percent based on the monomers, were fed into the flask linearly and separately over 2 hours while maintaining reflux. When the addition was complete the system was held at reflux for twenty minutes, then cooled to 60°C and the solution pH was adjusted with the addition of 52 grams of a 50% solution of NaOH in water.

The resultant pH 6.7 polymer solution had a solids content of 46.0%. Based on gel permeation chromatography (GPC), the weight average molecular weight (Mw) was 15,200 and the number average molecular weight (Mn) was 7440. Residual maleic acid content was 0.2% and residual acrylic acid content was 0.01%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 2 (Comparative)

The procedure of Example 1 was repeated except that no copper (II) sulfate pentahydrate solution was added to the reactor. The polymerization solution gelled before the additions were completed.

EXAMPLE 3 (Comparative)

The procedure of Example 1 was repeated except that 6 grams of a 0.15% iron (II) sulfate heptahydrate solution was added to the reactor instead of the copper (II) sulfate pentahydrate.

The resultant pH 6.7 polymer solution had a solids content of 47.0%. Based on GPC, the Mw was 91,100 and the Mn was 9420. Residual maleic acid content was 0.1% and residual acrylic acid content was 0.01%, the percentages being based on the total theoretical weight of solids.

EXAMPLE 4 (Comparative)

The procedure of Example 1 was repeated except that 1.08 grams of a 1.0% cerium (III) sulfate solution was added to the reactor instead of the copper (II) sulfate pentahydrate solution. The polymerization solution gelled before the additions were completed.

EXAMPLE 5 (Comparative)

The procedure of Example 1 was repeated except that 6.4 grams of a 0.15% cobalt (II) sulfate heptahydrate solution was added to the reactor instead of the copper (II) sulfate pentahydrate solution. The polymerization solution gelled before the additions were completed.

Example 6

The procedure of Example 1 was repeated except 3 grams of a 0.15% copper sulfate pentahydrate solution and 50 grams of deionized water were initially added to the reactor. The post reaction pH was adjusted with 30.1 grams of a 50% solution of NaOH in water.

The resultant pH 5.9 polymer solution had a solids content of 44.6%. Based on GPC, the Mw was 33,500 and the Mn was 9,990. Residual acrylic acid content was 0.07% and residual maleic acid content was 0.16%, the percentages being based on the total theoretical weight of solids.

Example 7

The procedure of Example 1 was repeated except 12 grams of a 0.15% copper sulfate pentahydrate solution was added to the reactor.

The resultant pH 6.8 polymer solution had a solids content of 45.5%. Based on GPC, the Mw was 15,200 and the Mn was 7,930. Residual acrylic acid content was 1.2% and residual maleic acid content was 1.0%, the percentages being based on the total theoretical weight of solids.

Example 8 (Comparative)

The procedure of Example 1 was repeated except 1.4 grams of a 1.0% ethylenediaminetetraacetic acid iron (III), monosodium salt solution was added to the reactor. Before the gradual additions could be completed, the polymerization reaction gelled due to the increase in molecular weight.

Example 9

The procedure of Example 1 was repeated except 1.4 grams of a 1.0% ethylenediaminetetraacetic acid copper(II), monosodium salt solution was added to the reactor.

The resultant pH 6.8 polymer solution had a solids content of 45.9%. Based on GPC, the Mw was 15,100 and the Mn was 6,090. Residual acrylic acid content was 0.54% and residual maleic acid content was 0.39%, the percentages being based on the total theoretical weight of solids.

Example 10

The procedure of Example 1 was repeated except 10.6 grams of maleic anhydride was added to the reactor. The monomer cofeed was 237.5 grams of glacial acrylic acid and the base cofeed was 211 grams of a 50% solution of NaOH. The post reaction pH was adjusted with 43.3 grams of a 50 % solution of NaOH.

The resultant pH 5.9 polymer solution had a solids content of 42.3%. Based on GPC, the Mw was 37,800 and the Mn was 9,320. Residual acrylic acid content was 0.5 % and residual maleic acid content was 0.1%, the percentages being based in the total theoretical weight of solids.

Example 11

The procedure of Example 1 was repeated except 50 grams of itaconic acid was added to the reactor. The base cofeed was 213 grams of a 50% solution of NaOH. The post reaction pH was adjusted with 62.3 grams of a 50% solution of NaOH.

The resultant pH 12.8 polymer solution had a solids content of 42.4%. Based on GPC, the Mw was 39,600 and the Mn was 9,880. Residual acrylic acid content was 0.09% and residual itaconic acid content was <.01%, the percentages being based on the total theoretical weight of solids.

Example 12

The procedure of Example 1 was repeated except the initiator cofeed contained 14.1 grams of azo-bis cyanovaleric acid, 8 grams of a 50% solution of sodium hydroxide and 50 grams of deionized water.

The resultant pH 6.2 polymer solution had a solids content of 47.1%. Based on GPC, the Mw was 24,600 and the Mn was 10,200. Residual acrylic acid content was 0.71% and residual maleic acid content was 0.78%, the percentages being based on the total theoretical weight of solids.

Example 13

The procedure for Example 12 was repeated except no copper sulfate solution was added to the reactor.

The resultant pH 6.9 polymer solution had a solids content of 47.9%. Based on GPC, the Mw was 46,600 and the Mn was 13,900. Residual acrylic acid content was 0.11% and residual maleic acid content was 0.06%, the percentages being based on the total theoretical weight of solids.

Claims

1. A process for preparing water-soluble copolymers, which comprises polymerizing from 3 to 25% by weight, based on the total amount of the monomers, of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, or salt or anhydride thereof, and 75 to 97% by weight based on the total amount of the monomers, of at least one comonomer comprising monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule or carboxyl-free monoethylenically unsaturated monomers, conducting said reaction in the presence of water-soluble polymerization initiator, copper salt polymerization moderator and neutralizer at elevated temperature, and, after said polymerization, recovering said copolymer, wherein said process comprises:

(a) establishing an initial reactor charge of said monoethylenically unsaturated dicarboxylic acid to which is added the comonomer(s), water-soluble initiator and neutralizer during a period of from 1 to 6 hours, and said copper polymerization moderator is contained in said initial charge, added to said reaction as a separate solution, or a combination thereof.

2. A process according to claim 1 wherein said copper is present in an amount of from 1 to 200 ppm based on the total weight of said polymerization.

3. A process as claimed in claim 1 or 2 wherein said monoethylenically unsaturated dicarboxylic acid concentration ranges from 5 to 23% by weight, based on the total amount of the monomers.

4. A process as claimed in any of claims 1 to 3 wherein said monoethylenically unsaturated dicarboxylic acid is selected from maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid, salts thereof, anhydrides thereof, and combinations thereof, and is preferably selected from maleic acid, its salts and its anhydride.

5. A process as claimed in any of claims 1 to 4 wherein the polymerization is run at a solids level in the range of from 20 to 80%, for example in the range of from 30 to 65%.

6. A process as claimed in any of claims 1 to 5 wherein said monoethylenically unsaturated



Example 10

The procedure of Example 1 was repeated except 10.6 grams of maleic anhydride was added to the reactor. The monomer cofeed was 237.5 grams of glacial acrylic acid and the base cofeed was 211 grams of a 50% solution of NaOH. The post reaction pH was adjusted with 43.3 grams of a 50 % solution of NaOH.

The resultant pH 5.9 polymer solution had a solids content of 42.3%. Based on GPC, the Mw was 37,800 and the Mn was 9,320. Residual acrylic acid content was 0.5 % and residual maleic acid content was 0.1%, the percentages being based in the total theoretical weight of solids.

Example 11

The procedure of Example 1 was repeated except 50 grams of itaconic acid was added to the reactor. The base cofeed was 213 grams of a 50% solution of NaOH. The post reaction pH was adjusted with 62.3 grams of a 50% solution of NaOH.

The resultant pH 12.8 polymer solution had a solids content of 42.4%. Based on GPC, the Mw was 39,600 and the Mn was 9,880. Residual acrylic acid content was 0.09% and residual itaconic acid content was <.01%, the percentages being based on the total theoretical weight of solids.

Example 12

The procedure of Example 1 was repeated except the initiator cofeed contained 14.1 grams of azo-bis cyanovaleric acid, 8 grams of a 50% solution of sodium hydroxide and 50 grams of deionized water.

The resultant pH 6.2 polymer solution had a solids content of 47.1%. Based on GPC, the Mw was 24,600 and the Mn was 10,200. Residual acrylic acid content was 0.71% and residual maleic acid content was 0.78%, the percentages being based on the total theoretical weight of solids.

Example 13

The procedure for Example 12 was repeated except no copper sulfate solution was added to the reactor.

The resultant pH 6.9 polymer solution had a solids content of 47.9%. Based on GPC, the Mw was 46,600 and the Mn was 13,900. Residual acrylic acid content was 0.11% and residual maleic acid content was 0.06%, the percentages being based on the total theoretical weight of solids.

Claims

1. A process for preparing water-soluble copolymers, which comprises polymerizing from 3 to 25% by weight, based on the total amount of the monomers, of at least one monoethylenically unsaturated dicarboxylic acid containing from 4 to 6 carbon atoms per monomer molecule, or salt or anhydride thereof, and 75 to 97% by weight based on the total amount of the monomers, of at least one comonomer comprising monoethylenically unsaturated monocarboxylic acids containing from 3 to 6 carbon atoms per monomer molecule or carboxyl-free monoethylenically unsaturated monomers, conducting said reaction in the presence of water-soluble polymerization initiator, copper salt polymerization moderator and neutralizer at elevated temperature, and, after said polymerization, recovering said copolymer, wherein said process comprises:
 - (a) establishing an initial reactor charge of said monoethylenically unsaturated dicarboxylic acid to which is added the comonomer(s), water-soluble initiator and neutralizer during a period of from 1 to 6 hours, and said copper polymerization moderator is contained in said initial charge, added to said reaction as a separate solution, or a combination thereof.
2. A process according to claim 1 wherein said copper is present in an amount of from 1 to 200 ppm based on the total weight of said polymerization.
3. A process as claimed in claim 1 or 2 wherein said monoethylenically unsaturated dicarboxylic acid concentration ranges from 5 to 23% by weight, based on the total amount of the monomers.
4. A process as claimed in any of claims 1 to 3 wherein said monoethylenically unsaturated dicarboxylic acid is selected from maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid, salts thereof, anhydrides thereof, and combinations thereof, and is preferably selected from maleic acid, its salts and its anhydride.
5. A process as claimed in any of claims 1 to 4 wherein the polymerization is run at a solids level in the range of from 20 to 80%, for example in the range of from 30 to 65%.
6. A process as claimed in any of claims 1 to 5 wherein said monoethylenically unsaturated



monocarboxylic acid monomer is selected from acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid, and is preferably acrylic acid.

7. A process as claimed in any of claims 1 to 6 wherein said carboxyl-free monoethylenically unsaturated monomer is selected from alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate; acrylamide; methacrylamide; N-tertiary butyl acrylamide; N-methyl acrylamide; N,N-dimethyl acrylamide; acrylonitrile; methacrylonitrile; allyl alcohol; allyl sulfonic acid; allyl phosphonic acid; vinylphosphonic acid; dimethylaminoethyl acrylate; dimethylaminoethyl methacrylate; phosphoethyl methacrylate; N-vinyl pyrrolidone; N-vinylformamide; N-vinylimidazole; ethylene glycol diacrylate; trimethylolpropane triacrylate; diallyl phthalate; vinyl acetate; styrene, vinyl sulfonic acid and its salts; and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts.
8. A process as claimed in any of claims 1 to 7 wherein the initiator concentration ranges from 0.5 to 20% by weight, preferably from 1 to 10% by weight, based on the weight of the monomers, and/or wherein the initiator is selected from hydrogen peroxide, t-butyl hydroperoxide, sodium persulfate, potassium persulfate, ammonium persulfate, sodium perphosphate, ammonium perphosphate, potassium perphosphate and 2,2-azobis(cyanovaleric acid).
9. A process as claimed in any of claims 1 to 8 wherein the polymerization pH is maintained in the range of 4 to 6 by the addition of from 30 to 80 equivalent percent of base, based on the acid content of the monomer mixture.
10. A process as claimed in any of claims 1 to 9, wherein the copolymer has a molecular weight of less than 25,000 M_w .
11. A detergent composition, which comprises a water-soluble detergent compound selected from anionic, nonionic, zwitterionic, ampholytic detergent compounds and mixtures thereof; a builder selected from the alkali metal salts of carboxymethyloxysuccinic acid and ox-

ydilactic acid, tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphates, ether polycarboxylates, citrates, starch or cellulose derived from polycarboxylate, polyacrylic acids; and up to about 35% by weight, for example from 0.1 to 20% by weight, and preferably from 0.5 to 5.0% by weight, of a copolymer produced by a process as claimed in any of claims 1 to 10.

Patentansprüche

1. Verfahren zum Herstellen wasserlöslicher Copolymere, welches umfaßt: ein Polymerisieren von 3 bis 25 Gew.-%, bezogen auf die Gesamtmenge der Monomeren, von mindestens einer monoethylenisch ungesättigten Dicarbonsäure, welche von 4 bis 6 Kohlenstoffatome pro Monomermolekül enthält, oder eines Salzes oder Anhydrides davon, und 75 bis 97 Gew.-%, bezogen auf die Gesamtmenge der Monomeren, von mindestens einen, Comonomer, umfassend monoethylenisch ungesättigte Monocarbonsäuren, welche von 3 bis 6 Kohlenstoffatome pro Monomermolekül enthalten, oder Carboxyl-freie, monoethylenisch ungesättigte Monomere, Ausführen der Umsetzung in Gegenwart eines wasserlöslichen Polymerisationsinitiators, Kupfersalz-Polymerisationsmoderators und Neutralisierungsmittels bei erhöhter Temperatur, und, nach der Polymerisation, Gewinnen des Copolymers, wobei das Verfahren umfaßt:
 - (a) Aufstellen einer Reaktoranzugscharge der monoethylenisch ungesättigten Dicarbonsäure, welcher das (die) Comonomer(e), der wasserlösliche Initiator und das Neutralisierungsmittel während einer Zeitspanne von 1 bis 6 Stunden zugegeben werden, und wobei der Kupfer-Polymerisationsmoderator in der Anfangscharge enthalten ist, der Umsetzung als eine eigene Lösung zugegeben wird, oder eine Kombination davon.
2. Verfahren nach Anspruch 1, wobei das Kupfer in einer Menge von 1 bis 200 ppm, bezogen auf das Gesamtgewicht der Polymerisation, vorhanden ist.
3. Verfahren, wie in Anspruch 1 oder 2 beansprucht, wobei die Konzentration an monoethylenisch ungesättigter Dicarbonsäure von 5 bis 23 Gew.-%, bezogen auf das Gesamtgewicht der Monomere, reicht.
4. Verfahren, wie in einem der Ansprüche 1 bis 3 beansprucht, wobei die monoethylenisch unge-



- sättigte Dicarbonsäure aus Maleinsäure, Itaconsäure, Mesaconsäure, Fumarsäure, Citraconsäure, ihren Salzen, ihren Anhydriden, und Kombinationen davon gewählt ist und vorzugsweise aus Maleinsäure, ihren Salzen und ihrem Anhydrid gewählt ist.
5. Verfahren, wie in einem der Ansprüche 1 bis 4 beansprucht, wobei die Polymerisation bei einem Feststoffpegel im Bereich von 20 bis 80%, zum Beispiel im Bereich von 30 bis 65%, gefahren wird. 5
 6. Verfahren, wie in einem der Ansprüche 1 bis 5 beansprucht, wobei das Monomer der monoethylenisch ungesättigten Monocarbonsäure aus Acrylsäure, Methacrylsäure, Vinyllessigsäure, Crotonsäure und Acryloxypropionsäure gewählt ist und vorzugsweise Acrylsäure ist. 10
 7. Verfahren, wie in einem der Ansprüche 1 bis 6 beansprucht, wobei das Carboxyl-freie, monoethylenisch ungesättigte Monomer gewählt ist aus: Alkylester der Acryl- oder Methacrylsäure, wie z.B. Methylacrylat, Ethylacrylat, Butylacrylat, Methylmethacrylat, Ethylmethacrylat, Butylmethacrylat und Isobutylmethacrylat, Hydroxyalkylester der Acryl- oder Methacrylsäure, wie z.B. Hydroxyethylacrylat, Hydroxypopylacrylat, Hydroxyethylmethacrylat und Hydroxypropylmethacrylat; Acrylamid; Methacrylamid; N-tert-Butylacrylamid; N-Methylacrylamid; N,N-Dimethylacrylamid; Acrylnitril; Methacrylnitril; Allylalkohol; Allylsulfonsäure; Allylphosphonsäure; Vinylphosphonsäure; Dimethylaminoethylacrylat; Dimethylaminoethylmethacrylat; Phosphoethylmethacrylat, N-Vinylpyrrolidon; N-Vinylformamid; N-Vinylimidazol; Ethylenglycolbisacrylat; Trimethylolpropantriacrylat; Diallylphthalat; Vinylacetat; Styrol; Vinylsulfonsäure und ihren Salze; und 2-Acrylamido-2-methylpropansulfonsäure (AMPS) und ihren Salze. 15
 8. Verfahren, wie in einem der Ansprüche 1 bis 7 beansprucht, wobei die Initiatorkonzentration von 0,5 bis 20 Gew.-%, vorzugsweise von 1 bis 10 Gew.-%, bezogen auf das Gewicht der Monomere, reicht, und/oder wobei der Initiator aus Wasserstoffperoxid, tert-Butylhydroperoxid, Natriumpersulfat, Kaliumpersulfat, Ammoniumpersulfat, Natriumperphosphat, Ammoniumperphosphat, Kaliumperphosphat und 2,2-Azobis(cyanovaleriansäure) gewählt ist. 20
 9. Verfahren, wie in einem der Ansprüche 1 bis 8 beansprucht, wobei der pH der Polymerisation durch die Zugabe von 30 bis 80 Äquivalentprozent Base, bezogen auf den Säuregehalt des Monomergemisches, in, Bereich von 4 bis 6 gehalten wird. 25
 10. Verfahren, wie in einem der Ansprüche 1 bis 9 beansprucht, wobei das Copolymer ein Molekulargewicht von weniger als 25.000 M_w aufweist. 30
 11. Detergenezusammensetzung, welche umfaßt: eine wasserlösliche Detergensverbindung, ausgewählt aus anionischen, nichtionischen, zwitterionischen, ampholytischen Detergensverbindungen und ihren Gemischen; einen Builder, ausgewählt aus den Alkalimetallsalzen der Carboxymethyloxybernsteinsäure und Oxydiessigsäure, Tetranatrium- und Tetrakaliumpyrophosphat, Pentanatrium- und Pentakaliumtripolyphosphaten, Etherpolycarboxylaten, Citraten, Stärke oder Zellulose, abgeleitet von Polycarboxylatex, Polyacrylsäuren; und bis zu etwa 35 Gew.-%, z.B. von 0,1 bis 20 Gew.-%, und vorzugsweise von 0,5 bis 5,0 Gew.-%, eines Copolymers, welches mittels eines Verfahrens hergestellt wurde, wie es in einem der Ansprüche 1 bis 10 beansprucht ist. 35
- ### Revendications
1. Procédé pour préparer des copolymères hydrosolubles, qui consiste à polymériser de 3 à 25% en poids, par rapport à la quantité totale des monomères, d'au moins un acide dicarboxylique monoéthyléniquement insaturé contenant de 4 à 6 atomes de carbone par molécule monomère, ou bien son sel ou anhydride, et 75 à 97% en poids par rapport à la quantité totale des monomères, d'au moins un comonomère comprenant des acides monocarboxyliques monoéthyléniquement insaturés contenant de 3 à 6 atomes de carbone par molécule monomère ou des monomères monoéthyléniquement insaturés exempts de carboxyle, à conduire ladite réaction en présence d'amorceur de polymérisation hydrosoluble, de modérateur de polymérisation à base de sel de cuivre et de neutralisant à température élevée, et après ladite polymérisation, à récupérer ledit copolymère, dans lequel ledit procédé consiste à: 40
 - (a) établir une charge initiale de réacteur dudit acide dicarboxylique monoéthyléniquement insaturé à laquelle est ajouté le ou les comonomères, l'amorceur hydrosoluble et le neutralisant pendant une durée de 1 à 6 heures, et ledit modérateur de polymérisation à base de cuivre est contenu dans ladite charge initiale, ajoutée à ladite réaction sous forme de solution séparée, ou une 45



combinaison de ceux-ci.

2. Procédé selon la revendication 1, dans lequel ledit cuivre est présent à raison de 1 à 200 ppm par rapport au poids total de ladite polymérisation. 5
3. Procédé selon la revendication 1 ou 2, dans lequel ladite concentration en acide dicarboxylique monoéthyléniquement insaturé est comprise entre 5 et 23% en poids, par rapport à la quantité totale des monomères. 10
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel ledit acide dicarboxylique monoéthyléniquement insaturé est choisi parmi l'acide maléique, l'acide itaconique, l'acide mésoaconique, l'acide fumarique, l'acide citraconique, leurs sels, leurs anhydrides et leurs combinaisons, et est de préférence choisi parmi l'acide maléique, ses sels et son anhydride. 15 20
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel la polymérisation est réalisé à une teneur en solides comprise entre 20 et 80%, par exemple, comprise entre 30 et 65%. 25
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ledit monomère d'acide monocarboxylique monoéthyléniquement insaturé est choisi parmi l'acide acrylique, l'acide méthacrylique, l'acide vinylacétique, l'acide crotonique et l'acide acryloxypropionique, et est de préférence l'acide acrylique. 30
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit monomère monoéthyléniquement insaturé exempt de carboxyle est choisi parmi les esters alkyls d'acides acrylique ou méthacrylique tels que l'acrylate de méthyle, l'acrylate d'éthyle, l'acrylate de butyle, le méthacrylate de méthyle, le méthacrylate d'éthyle, le méthacrylate de butyle et le méthacrylate d'isobutyle; les esters hydroxyalkyls d'acides acrylique ou méthacrylique tels que l'acrylate d'hydroxyéthyle, l'acrylate d'hydroxypropyle, le méthacrylate d'hydroxyéthyle et le méthacrylate d'hydroxypropyle; l'acrylamide; le méthacrylamide; le N-tertio-butylacrylamide; le N-méthylacrylamide; le N,N-diméthylacrylamide; l'acrylonitrile; le méthacrylonitrile; l'alcool allylique; l'acide allylsulfonique; l'acide allylphosphonique; l'acide vinylphosphonique; l'acrylate de diméthylaminoéthyle; le méthacrylate de diméthylaminoéthyle; le méthacrylate de phosphoéthyle; la N-vinylpyrrolidone; le N-vinylformamide; le N-vinylimidazole; le bisacrylate d'éthylèneglycol; le triacrylate de triméthylolpropane; le phtalate de diallyle; l'acétate de vinyle; le styrène, l'acide vinylsulfonique et ses sels; et l'acide 2-acrylamido-2-méthylpropanesulfonique (AMPS) et ses sels. 35 40 45 50 55

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la concentration en amorceur est comprise entre 0,5 et 20% en poids, de préférence entre 1 et 10% en poids, par rapport au poids des monomères, et/ou dans lequel on choisit l'amorceur parmi le peroxyde d'hydrogène, l'hydroperoxyde de t-butyle, le persulfate de sodium, le persulfate de potassium, le persulfate d'ammonium, le perphosphate de sodium, le perphosphate d'ammonium, le perphosphate de potassium et le 2,2-azobis(acide cyanovalérique). 10
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le pH de la polymérisation est maintenu entre 4 et 6 en ajoutant de 30 à 80 pourcent d'équivalent de base, par rapport à la teneur en acide du mélange monomère. 15
10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel le copolymère possède une masse moléculaire inférieure à 25 000 Mm. 20
11. Composition détergente, qui comprend un composé détergent hydrosoluble choisi parmi les composés détergents anioniques, non ioniques, zwitterioniques, ampholytiques et leurs mélanges; un adjuvant choisi parmi les sels de métal alcalin d'acide carboxyméthylloxysuccinique et d'acide oxydiacétique, le pyrophosphate tétrasodique et tétrapotassique, les tripolyphosphates pentasodiques et pentapotassiques, les étherpolycarboxylates, les citrates, l'amidon ou la cellulose extraite de polycarboxylates, les acides polyacryliques; et jusqu'à environ 35% en poids, par exemple, de 0,1 à 20% en poids, et de préférence, de 0,5 à 5,0% en poids d'un copolymère produit par un procédé selon l'une quelconque des revendications 1 à 10. 25 30 35 40 45 50 55