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(54) **Title:** A WATER-SOLUBLE POLYMER DISPERSION AND A METHOD OF PRODUCING A WATER-SOLUBLE POLYMER DISPERSION

(57) **Abstract:** The present invention relates to a water-soluble polymer dispersion comprising a dispersed polymer made up of at least one water-soluble monomer A and at least one water-soluble cationic monomer B, at least one stabiliser C, and at least one cationic polyelectrolyte as co-stabiliser D. It also relates to a method of producing a polymer dispersion and to a paper-making process.

A WATER-SOLUBLE POLYMER DISPERSION AND A METHOD OF PRODUCING A WATER-SOLUBLE POLYMER DISPERSION

The present invention relates to a new polymer dispersion and a method of producing a polymer dispersion. It also relates to a paper-making process.

Cationic polymers, in particular copolymers based on acrylamide, are used commercially on a large scale as process aids for the implementation of separation processes during water processing and waste water treatment, in the coal and ore industry, in particular however in the paper industry in order to improve retention and accelerate de-watering.

The radical polymerisation of commercially relevant cationic monomers, such as for example diallyldimethylammonium chloride (DADMAC), (meth-) acryloyloxyethylrimethylammonium chloride (MADAM or ADAM), (meth-) acryloyloxyethylbenzyldimethylammonium chloride (MADAMBQ or ADAMBO), or trimethylmethacrylamidopropylammonium chloride (TMAPMA) leads to water-soluble cationic polymers, so-called cationic polyelectrolytes. In contrast, a most extensively non-ionic water-soluble polymer results from the radical polymerisation of acrylamide. The co-polymerisation of acrylamide with cationic monomers leads to the formation of copolymers with different charge density, which is dependent upon the proportion of the cationic monomer used for the co-polymerisation, which is incorporated in the polymer chain.

According to the state of the art, the production of these polymers is effected by radical polymerisation in homogeneous, aqueous solution or in heterogeneous phase.

US 5403883 describes the production of aqueous dispersions of water-soluble polymers, formed by polymerisation of a mixture comprising water-soluble, hydrophobic and possibly amphiphilic monomers in the presence of a polymeric dispersing agent.

EP 0 664 302 discloses a process for the production of water-soluble polymer dispersions.

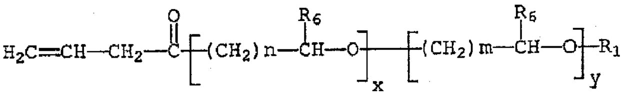
The present invention provides a water-soluble polymer dispersion comprising:

- a dispersed polymer made up of:
- from about 50 to about 99 mole % of at least one water-soluble monomer A and
- from about 1 to about 50 mole % of at least one water-soluble cationic monomer B,
- from about 0.05 to about 10 weight % of at least one copolymer as polymer stabiliser C,
- from about 1 to about 25 weight % of at least one cationic polyelectrolyte as co-stabiliser D, relative respectively to the total mass of the dispersion, the polymer dispersion having no substantial amount of an inorganic polyvalent anion salt present,

the polymer stabiliser C is a co-polymer comprising:

- at least one of compounds of the general formulas III, IV or V, wherein:

(i) general formula III is a monofunctionally allyl-terminal polyether:



$$H_2C{=}CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}\left[(CH_2)_n{-}\overset{\overset{R_6}{|}}{C}H{-}O\right]_x{-}\left[(CH_2)_m{-}\overset{\overset{R_6}{|}}{C}H{-}O\right]_y{-}R_1$$

III

with

R_1 = H or methyl,

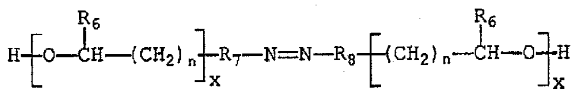
R_6 = independently of each other are H, methyl, or ethyl,

n = 1 or 3,

x = 5 to 50, and

y = 5 to 50,

(ii) general formula IV is a macroinitiator:



$$\mathrm{H}{-}\left[\mathrm{O}{-}\overset{\displaystyle R_6}{\mathrm{CH}}{-}(\mathrm{CH_2})_n\right]_x{-}R_7{-}\mathrm{N}{=}\mathrm{N}{-}R_8{-}\left[(\mathrm{CH_2})_n{-}\overset{\displaystyle R_6}{\mathrm{CH}}{-}\mathrm{O}\right]_x{-}\mathrm{H} \qquad \mathrm{IV}$$

with

R_1 = H or methyl,

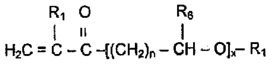
R_6 = independently of each other are H, methyl, or ethyl,

R_7, R_8 = independently of each other are alkyl, cyanoalkyl, or carbalkoxyalkyl (C_1-C_8),

n = 1 or 3, and

x = 5 to 100, and

(iii) general formula V is a monofunctionally vinyl-terminal polyether:



$$H_2C = \overset{\displaystyle R_1}{C} - \overset{\displaystyle O}{\overset{\|}{C}} - [(CH_2)_n - \overset{\displaystyle R_6}{CH} - O]_x - R_1 \qquad \mathrm{V}$$

with

R_1 = H or methyl,

R_6 = H, methyl, or ethyl,

n = 1 or 3,

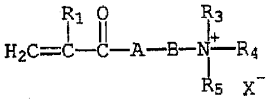
and x = 5 to 50;

and either

- at least one monomer, selected from the group diallyldimethylammonium chloride (DADMAC), vinylpyridinium chloride, N-vinylimidazoline chloride, vinylbenzyltrimethylammonium chloride and mixtures thereof;

or

- compounds of the general formula II:



$$H_2C{=}\overset{R_1}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}A{-}B{-}\underset{\underset{R_5}{|}}{\overset{\overset{R_3}{|}}{N^+}}{-}R_4 \quad X^- \qquad \text{II}$$

II

with

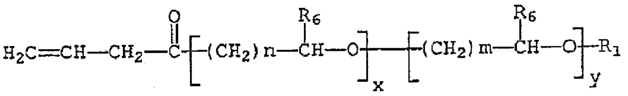
R_1 = H or methyl,
R_3, R_4, R_5 = independently of each other are H, alkyl (C_1-C_8), benzyl, or alkylbenzyl,
A = NH or O,
B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),
X^- = an anionic counterion.

The present invention also provides a method of producing a water-soluble polymer dispersion comprising polymerising from about 50 to about 99 mole % of at least one water-soluble monomer A and from about 1 to about 50 mole % of at least one water-soluble cationic monomer B, in the presence of from about 0.05 to about 10 weight % of a polymer stabiliser C and from about 1 to about 25 weight % of a cationic polyelectrolyte as co-stabiliser D, relative respectively to the total mass of the dispersion, implemented in a reaction medium with no substantial amount of an inorganic polyvalent anion salt present,

the polymer stabiliser C is a co-polymer comprising

- at least one of compounds of the general formulas III, IV or V, wherein:

(i) general formula III is a monofunctionally allyl-terminal polyether:



$$H_2C{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}\left[(CH_2)_n{-}\overset{R_6}{\overset{|}{CH}}{-}O\right]_x{-}\left[(CH_2)_m{-}\overset{R_6}{\overset{|}{CH}}{-}O\right]_y{-}R_1$$

III

with

R_1 = H or methyl,

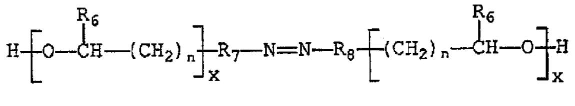
R_6 = independently of each other are H, methyl, or ethyl,

n = 1 or 3,

x = 5 to 50, and

y = 5 to 50,

(ii) general formula IV is a macroinitiator:



$$H\left[O-\overset{R_6}{CH}-(CH_2)_n\right]_x-R_7-N=N-R_8-\left[(CH_2)_n-\overset{R_6}{CH}-O\right]_x-H$$

IV

with

R_1 = H or methyl,

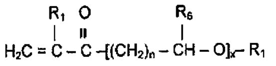
R_6 = independently of each other are H, methyl, or ethyl,

R_7, R_8 = independently of each other are alkyl, cyanoalkyl, or carbalkoxyalkyl, (C_1-C_8),

n = 1 or 3, and

x = 5 to 100, and

(iii) general formula V is a monofunctionally vinyl-terminal polyether:



$$H_2C=\overset{R_1}{C}-\overset{\overset{O}{\|}}{C}-[(CH_2)_n-\overset{R_6}{CH}-O]_x-R_1$$

V

with

R_1 = H or methyl,

R_6 = H, methyl, or ethyl,

n = 1 or 3,

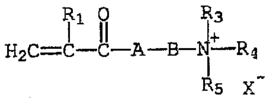
and x = 5 to 50;

and either

- at least one monomer, selected from the group diallyldimethylammonium chloride (DADMAC), vinylpyridinium chloride, N-vinylimidazoline chloride, vinylbenzyltrimethylammonium chloride and mixtures thereof;

or

- compounds of the general formula II:



$$H_2C{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-A-B-\underset{\underset{R_5}{|}}{\overset{\overset{R_3}{|}}{N^+}}-R_4 \quad X^-$$

II

with

R_1 = H or methyl,
R_3, R_4, R_5 = independently of each other are H, alkyl (C_1-C_8), benzyl, or alkylbenzyl,
A = NH or O,
B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),
X^- = an anionic counterion.

Preferably the polymer dispersion or method further comprises from about 75 to about 99 mole % of the at least one water-soluble monomer A and from about 1 to about 25 mole % of the at least one water-soluble cationic monomer B.

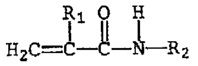
Preferably the polymer dispersion or method is further characterised in that the polymer dispersion comprises from about 5 to about 40 weight % of the dispersed polymer.

Preferably the mass ratio of stabilisers and co-stabilisers to the dispersed polymer is:

$$\frac{C + D}{A + B} < 1$$

Preferably the dispersed polymer has a weight average molecular weight of at least 1.000.000 g/mole.

Preferably the monomer A is a compound of the general formula I:



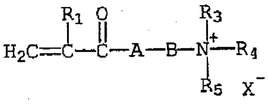
$$H_2C{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_2 \qquad \mathrm{I}$$

with

R_1 = H or methyl,

R_2 = H, methyl, ethyl, isopropyl, methyloyl, hydroxyethyl, or 2-hydroxypropyl.

Preferably the monomer B is a compound of the general formula II:



$$H_2C{=}\overset{R_1}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-A-B-\underset{R_5}{\overset{R_3}{\overset{|}{\underset{|}{N^+}}}}-R_4 \quad X^- \qquad \mathrm{II}$$

with

R_1 = H or methyl,

R_3, R_4, R_5 = independently of each other are H, alkyl (C_1-C_8), benzyl, or alkylbenzyl,

A = NH or O,

B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),

X^- = an anionic counterion.

Preferably the dispersed polymer is present in a concentration between 10 to about 30% by weight relative to the total mass of the dispersion.

Preferably the polymer stabiliser C has a molecular weight between 20.000 and 3.000.000 g/mole.

Preferably the polymer stabiliser C has a molecular weight between 100.000 and 2.000.000 g/mole.

Preferably the polymer stabiliser C has a molecular weight between 200.000 and 800.000 g/mole.

Preferably the polymer stabiliser C is present in a concentration between from about 0.1 to about 5 weight %.

Preferably the polymer stabiliser C is present in a concentration between from about 0.5 to about 2 weight %.

Preferably the polymer stabiliser C is a block co-polymer.

Preferably the polymer stabiliser C is a random co-polymer.

Preferably the co-stabiliser D is a cationic polyelectrolyte with a molecular weight between from about 1.000 to about 500.000 g/mole.

Preferably the co-stabiliser D is a cationic polyelectrolyte with a molecular weight between from about 2.000 to about 100.000 g/mole.

Preferably the co-stabiliser D is a DADMAC polymer.

Preferably the polymer dispersion comprises from about 3 to about 15 weight % of the co-stabiliser D.

Preferably the monofunctionally vinyl-terminal polyether according to general formula V is a PEG acrylate.

Preferably the polymer stabiliser C is a co-polymer of the monomers DADMAC, ADAM MQ and PEG acrylate.

Preferably the polymer stabiliser C is a block copolyether modified poly-DADMAC.

Preferably the method is implemented in one stage.

The invention also provides a water-soluble dispersion obtained by a method as described above.

The invention also provides use of a water-soluble polymer dispersion as described above as retention aid for paper manufacturing, as thickening agent and/or as soil improvement agent.

The invention also provides a process for the production of paper from an aqueous suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a water-soluble polymer dispersion as described above, forming and draining the suspension on a wire.

The subject according to the preferred embodiments of the invention is now intended to be explained in more detail with reference to the following examples without restricting said subject to the breadth of these embodiments.

Examples

Example 1:

142 g 50% aqueous AAM solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 2:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10g stabiliser poly-(DADMAC/ADAM-MQ/PEG-acrylate) (45/45/10 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 3:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ/PEG-acrylate) (45/45/10 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 4:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 5:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 6:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ/PEG-acrylate) (45/45/10 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 7:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ) (70/30 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 8:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ) (50/50 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 9:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser

poly-(DADMAC/ADAM-MQ) (70/30 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 10:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ) (50/50 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 695 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 11:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ) (70/30 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 505.5 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 12:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ/PEG-acrylate) (45/45/10 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 555.5 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 13:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ/PEG-acrylate) (45/45/10 mole %), 112.5 g 40% aqueous poly-DADMAC solution, 150 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 443 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 14:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(DADMAC/ADAM-MQ) (70/30 mole %), 112.5 g 40% aqueous poly-DADMAC solution, 150 g 30% aqueous poly-TMAPMA solution, 5 g 1% EDTA solution, 10 g glycerine and 443 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 15:

142 g 50% aqueous AAM solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 16:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 17:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 200 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 595 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 18:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9. 10 mole %), 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 19:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 10 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 20:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyester-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 150 g 40% aqueous poly-DADMAC solution, 5 g 10% EDTA solution, 10 g glycerine and 645 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 21:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 75 g 40% aqueous poly-DADMAC solution, 100 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 530.5 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 22:

213 g 50% aqueous AAm solution, 45 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 112.5 g 40% aqueous poly-DADMAC solution, 150 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 443 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 1, 2, 3, 4, 5 hours, respectively 2.1 g 80% aqueous ADAM-BQ solution are added in doses. After 6 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 23:

142 g 50% aqueous AAm solution, 37 g 80% aqueous ADAM-BQ solution, 5 g stabiliser poly-DADMAC, block copolyether-modified (HLB 6.9, 10 mole %), 5 g stabiliser poly-(ADAM-MQ/ADAM-BQ)-b-PEG, 112.5 g 40% aqueous poly-DADMAC solution, 150 g 30% aqueous poly-TMAPMA solution, 5 g 10% EDTA solution, 10 g glycerine and 353.5 g water are degassed in a reactor with argon and heated to 50°C during agitation. Next, 1 ml 1% aqueous V50 solution is added. After 5 hours, a mixture of 142 g 50% aqueous AAm solution and 37 g 80% aqueous ADAM-BQ solution are added in doses over 10 hours. After 18 hours, the temperature is increased to 60°C and 3 ml 10% V50 solution are added. The polymerisation is ended after a further 2 hours.

Example 24 (application test):

Application tests regarding retention and dewatering in papermaking processes were made. To a furnish of 4g/L with a conductivity of 7 mS/cm was added a polymer dispersion both according to the invention and a similar commercial available polymer dispersion as a reference which contained no co-stabiliser D.

The turbidity (NTU) and the retention time (s) was measured at different polymer loads.

Two different polymer dispersions (I) and (II) according to the invention were tested. The first polymer dispersion (I) was produced according to the procedure described in Example 2, but with an aqueous poly-DADMAC solution used instead of the poly-TMAPMA solution, and the amount monomers A and B, and stabilisers C and co-stabilisers D, selected so that the ratio C+D/A+B is about 0.5. The active content was 32 weight %

The second polymer dispersion (II) was produced according to the general procedure described in, Example 2, but with the amount monomers A and B, and stabilisers C and co-stabilisers D, selected so that the ratio C+D/A+B is about 0.5. according to Example 22. The active content was 26 weight %.

The retention/dewatering tests were made at two different test occasions, thus with different furnish batches.

Table 1. Tests with polymer dispersion (I).

Polymer dispersion	Ratio stabiliser(s) /polymer, (C+D)/(A+B)	Polymer load (kg/t)	Application test	
			Turbidity (NTU)	Retention time (s)
I	0.5	0.5	47	11.8
I	0.5	1.0	27	7.2
Reference (comparative)	1.2	0.5	52	12.5
Reference (comparative)	1.2	1.0	34	10.0

Table 2. Tests with polymer dispersion (II).

Polymer dispersion	Ratio stabiliser(s) /polymer, (C+D)/(A+B)	Polymer load (kg/t)	Application test	
			Turbidity (NTU)	Retention time (s)
II	0.5	0.5	60	11.6
II	0.5	1.0	48	7.8
Reference (comparative)	1.2	0.5	70	14.2
Reference (comparative)	1.2	1.0	66	12.0

The process viscosity was lower than 3000 mPas for both dispersions according to the invention. It is concluded that the dispersions using dispersants according to the invention show excellent results in retention and dewatering.

Example 25:

The shelf life, measured as sedimentation stability, was tested for the polymer dispersions (I) and (II) of Example 24. Samples of the dispersions were centrifuged for 30 minutes at 3000 rpm. The amount of polymer sediment was determined for each sample.

Table 3. Sedimentation stability

Polymer dispersion	Active content (%)	Amount polymer sediment (%)
I	32	0
II	26	0

It is concluded that polymer dispersions with long shelf life can be obtained by the present invention, also at high active contents.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

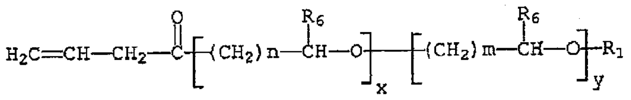
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A water-soluble polymer dispersion comprising:
- a dispersed polymer made up of:
- from about 50 to about 99 mole % of at least one water-soluble monomer A and
- from about 1 to about 50 mole % of at least one water-soluble cationic monomer B,
- from about 0.05 to about 10 weight % of at least one copolymer as polymer stabiliser C,
- from about 1 to about 25 weight % of at least one cationic polyelectrolyte as co-stabiliser D, relative respectively to the total mass of the dispersion, the polymer dispersion having no substantial amount of an inorganic polyvalent anion salt present.

the polymer stabiliser C is a co-polymer comprising:

- at least one of compounds of the general formulas III, IV or V, wherein:

(i) general formula III is a monofunctionally allyl-terminal polyether:

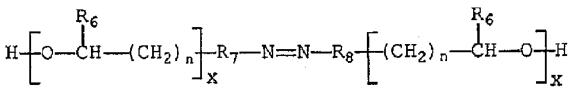


$$H_2C{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}\left[(CH_2)_n{-}\overset{R_6}{\overset{|}{C}H}{-}O\right]_x{-}\left[(CH_2)_m{-}\overset{R_6}{\overset{|}{C}H}{-}O\right]_y{-}R_1$$

III

with
R_1 = H or methyl,
R_6 = independently of each other are H, methyl, or ethyl,
n = 1 or 3,
x = 5 to 50, and
y = 5 to 50,

(ii) general formula IV is a macroinitiator:

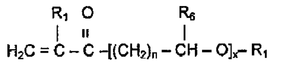


$$H{-}\left[O{-}\overset{R_6}{\overset{|}{C}H}{-}(CH_2)_n\right]_x{-}R_7{-}N{=}N{-}R_8{-}\left[(CH_2)_n{-}\overset{R_6}{\overset{|}{C}H}{-}O\right]_x{-}H$$

IV

with
R_1 = H or methyl,
R_6 = independently of each other are H, methyl, or ethyl,
R_7, R_8 = independently of each other are alkyl, cyanoalkyl, or carbalkoxyalkyl (C_1-C_8),
n = 1 or 3, and
x = 5 to 100, and

(iii) general formula V is a monofunctionally vinyl-terminal polyether:



$$H_2C=C(R_1)-C(=O)-[(CH_2)_n-CH(R_6)-O]_x-R_1$$

V

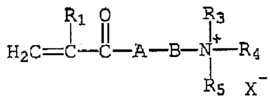
with
R_1 = H or methyl,
R_6 = H, methyl, or ethyl,
n = 1 or 3,
and x = 5 to 50;

and either

- at least one monomer, selected from the group diallyldimethylammonium chloride (DADMAC), vinylpyridinium chloride, N-vinylimidazoline chloride, vinylbenzyltrimethylammonium chloride and mixtures thereof;

or

- compounds of the general formula II:



$$H_2C=C(R_1)-C(=O)-A-B-N^{+}(R_3)(R_4)(R_5)\ X^{-}$$

II

with

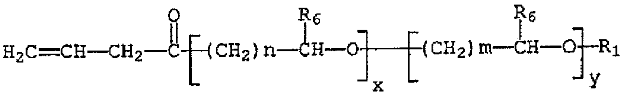
R_1 = H or methyl,
R_3, R_4, R_5 = independently of each other are H, alkyl (C_1-C_6), benzyl, or alkylbenzyl,
A = NH or O,
B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),
X^- = an anionic counterion.

2. A method of producing a water-soluble polymer dispersion comprising polymerising from about 50 to about 99 mole % of at least one water-soluble monomer A and from about 1 to about 50 mole % of at least one water-soluble cationic monomer B, in the presence of from about 0.05 to about 10 weight % of a polymer stabiliser C and from about 1 to about 25 weight % of a cationic polyelectrolyte as co-stabiliser D, relative respectively to the total mass of the dispersion, implemented in a reaction medium with no substantial amount of an inorganic polyvalent anion salt present,

the polymer stabiliser C is a co-polymer comprising:

- at least one of compounds of the general formulas III, IV or V, wherein:

(i) general formula III is a monofunctionally allyl-terminal polyether:

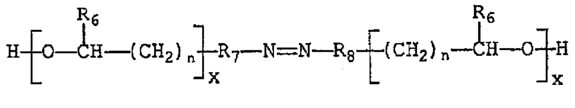


$$H_2C{=}CH{-}CH_2{-}\overset{\overset{\Large O}{\|}}{C}{-}\left[(CH_2)_n{-}\overset{\overset{\Large R_6}{|}}{CH}{-}O\right]_x{-}\left[(CH_2)_m{-}\overset{\overset{\Large R_6}{|}}{CH}{-}O\right]_y{-}R_1$$

III

with
R_1 = H or methyl,
R_6 = independently of each other are H, methyl, or ethyl,
n = 1 or 3,
x = 5 to 50, and
y = 5 to 50,

(ii) general formula IV is a macroinitiator:

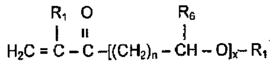


$$H\left[O-\overset{R_6}{CH}-(CH_2)_n\right]_x-R_7-N{=}N-R_8-\left[(CH_2)_n-\overset{R_6}{CH}-O\right]_x-H$$

IV

with
R_1 = H or methyl,
R_6 = independently of each other are H, methyl, or ethyl,
R_7, R_8 = independently of each other are alkyl, cyanoalkyl, or carbalkoxyalkyl (C_1-C_8),
n = 1 or 3, and
x = 5 to 100, and

(iii) general formula V is a monofunctionally vinyl-terminal polyether:



$$H_2C=\overset{R_1}{C}-\overset{O}{\overset{\|}{C}}-[(CH_2)_n-\overset{R_6}{CH}-O]_x-R_1$$

V

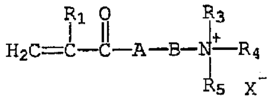
with
R_1 = H or methyl,
R_6 = H, methyl, or ethyl,
n = 1 or 3,
and x = 5 to 50;

and either

- at least one monomer, selected from the group diallyldimethylammonium chloride (DADMAC), vinylpyridinium chloride, N-vinylimidazoline chloride, vinylbenzyltrimethylammonium chloride and mixtures thereof;

or

- compounds of the general formula II:



$$H_2C{=}C(R_1){-}C({=}O){-}A{-}B{-}N^{+}(R_3)(R_4)(R_5)\ X^{-}$$

II

with

R_1 = H or methyl,
R_3, R_4, R_5 = independently of each other are H, alkyl (C_1-C_8), benzyl, or alkylbenzyl,
A = NH or O,
B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),
X^- = an anionic counterion.

3. A water-soluble polymer dispersion according to claim 1 or a method according to claim 2, characterised in that it comprises from about 75 to about 99 mole % of the at least one water-soluble monomer A and from about 1 to about 25 mole % of the at least one water-soluble cationic monomer B.

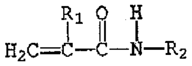
4. A water-soluble polymer dispersion according to any one of the claims 1 or 3, or a method according to any one of the claims 2-3, characterised in that the polymer dispersion comprises from about 5 to about 40 weight % of the dispersed polymer.

5. A water-soluble polymer dispersion according to any one of the claims 1 or 3-4, or a method according to any one of the claims 2-4, characterised in that the mass ratio of stabilisers and co-stabilisers to the dispersed polymer is:

$$\frac{C + D}{A + B} < 1$$

6. A water-soluble polymer dispersion according to any one of the claims 1 or 3-5, or a method according to any one of the claims 2-5, characterised in that the dispersed polymer has an weight average molecular weight of at least 1.000.000 g/mole.

7. A water-soluble polymer dispersion according to any one of the claims 1 or 3-6, or a method according to any one of the claims 2-6, characterised in that the monomer A is a compound of the general formula I



$$H_2C{=}C(R_1){-}C({=}O){-}N(H){-}R_2$$

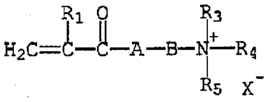
I

with

R1 = H, or methyl,

R2 = H, methyl, ethyl, isopropyl, methyloyl, hydroxyethyl, or 2-hydroxypropyl.

8. A water-soluble polymer dispersion according to any one of the claims 1 or 3-7, or a method according to any one of the claims 2-7, characterised in that the monomer B is a compound of the general formula II



$$H_2C=C(R_1)-C(=O)-A-B-N^{+}(R_3)(R_4)(R_5)\ X^{-}$$

II

with

R_1 = H or methyl,

R_3, R_4, R_5 = independently of each other H, alkyl (C_1-C_8), benzyl, or alkylbenzyl,

A = NH or O,

B = alkyl (C_1-C_{10}) or hydroxyalkyl (C_1-C_{10}),

X^- = an anionic counterion.

9. A water-soluble polymer dispersion according to any one of the claims 1 or 3-8, or a method according to any one of the claims 2-8, characterised in that the dispersed polymer is present in a concentration between 10 to about 30% by weight relative to the total mass of the dispersion.

10. A water-soluble polymer dispersion according to any one of the claims 1 or 3-9, or a method according to any one of the claims 2-9, characterised in that the polymer stabiliser C has a molecular weight between 20.000 and 3.000.000 g/mole.

11. A water-soluble polymer dispersion according to any one of the claims 1 or 3-10, or a method according to any one of the claims 2-10, characterised in that the polymer stabiliser C has a molecular weight between 100.000 and 2.000.000 g/mole.

12. A water-soluble polymer dispersion according to any one of the claims 1 or 3-11, or a method according to any one of the claims 2-11, characterised in that the polymer stabiliser C has a molecular weight between 200.000 and 800.000 g/mole.

13. A water-soluble dispersion according to any one of the claims 1 or 3-12, or a method according to any one of the claims 2-12, characterised in that the polymer stabiliser C is present in a concentration between from about 0.1 to about 5 weight %.

14. A water-soluble dispersion according to any one of the claims 1 or 3-13, or a method according to any one of the claims 2-13, characterised in that the polymer stabiliser C is present in a concentration between from about 0.5 to about 2 weight %.

15. A water-soluble polymer dispersion according to any one of the claims 1 or 3-14, or a method according to any one of the claims 2-14, characterised in that the polymer stabiliser C is a block co-polymer.

16. A water-soluble polymer dispersion according to any one of the claims 1 or 3-14, or a method according to any one of the claims 2-14, characterised in that the stabiliser C is a random co-polymer.

17. A water-soluble polymer dispersion according to any one of the claims 1 or 3-16, or a method according to any one of the claims 2-16, characterised in that the co-stabiliser D is a cationic polyelectrolyte with a molecular weight between from about 1.000 to about 500.000 g/mole.

18. A water-soluble polymer dispersion according to any one of the claims 1 or 3-17, or a method according to any one of the claims 2-17, characterised in that the co-stabiliser D is a cationic polyelectrolyte with a molecular weight between from about 2.000 to about 100.000 g/mole.

19. A water-soluble polymer dispersion according to any one of the claims 1 or 3-18, or a method according to any one of the claims 2-18, characterised in that the co-stabiliser D is a DADMAC polymer.

20. A water-soluble dispersion according to any one of the claims 1 or 3-19, or a method according to any one of the claims 2-19, characterised in that the polymer dispersion comprises from about 3 to about 15 weight % of the co-stabiliser D.

21. A water-soluble dispersion according to any one of the claims 1 or 3-20, or a method according to any one of the claims 2-20, characterised in that the monofunctionally vinyl-terminal polyether according to general formula V is a PEG acrylate.

22. A water-soluble dispersion according to any one of the claims 1 or 3-21, or a method according to any one of the claims 2-21, characterised in that the polymer stabiliser C is a co-polymer of the monomers DADMAC, ADAM MQ and PEG acrylate.

23. A water-soluble dispersion according to any one of the claims 1 or 3-20, or a method according to any one of the claims 2-20, characterised in that the polymer stabiliser C is a block copolyether modified poly-DADMAC.

24. A method according to any one of the claims 2-23, characterised in that it is implemented in one stage.

25. A water-soluble polymer dispersion obtained by a method according to any one of the claims 2-24.

26. Use of a water-soluble polymer dispersion according to any one of the claims 1, 3-23 or 25 as retention aid for paper manufacturing, as thickening agent and/or as soil improvement agent.

27. A process for the production of paper from an aqueous suspension containing cellulosic fibres, and optional fillers, which comprises adding to the suspension a water-soluble polymer dispersion according to any one of the claims 1, 3-23 or 25, forming and draining the suspension on a wire.

28. A water-soluble polymer dispersion, a method of producing a water-soluble polymer dispersion or a process for the production of paper comprising the water-soluble polymer dispersion, substantially as herein described with reference to the accompanying examples.