

Description

The present invention relates to a process for the preparation of a dispersion of a water-soluble cationic polar which is useful as a flocculant or dehydrating agent for waste water disposal or as a papermakers chemical.

Known processes for the preparation of a water-soluble cationic polymer which is useful as a flocculant for waste water disposal or as a papermakers chemical include standing polymerization in an aqueous solution, water-in-oil emulsion polymerization (see, for example, Japanese Patent Laid-Open No. 102388/1979), suspension polymerization in a hydrophobic solvent (see, for example, Japanese Patent Laid-Open No. 69196/1979).

Further, there has been disclosed a process for preparing a water-soluble, nonionic or anionic polymer by precipitation polymerization in an aqueous solution of ammonium sulfate (see, for example, Japanese Patent Laid-Open No. 70489/1975).

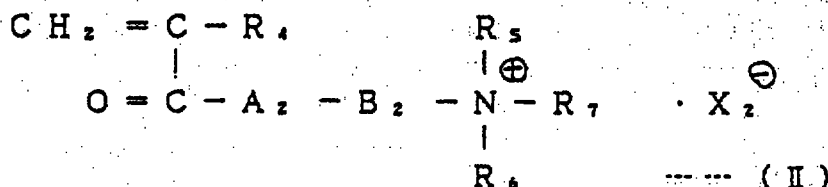
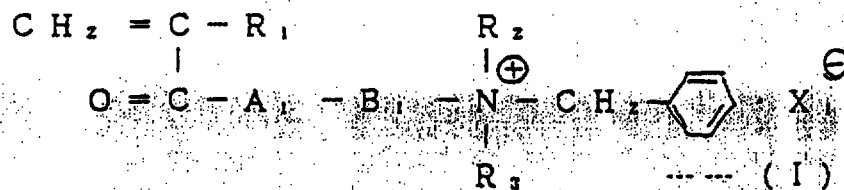
Also there have been disclosed a process for carrying out the polymerization in an aqueous solution of a salt in the presence of a polyhydric alcohol (see, for example Japanese Patent Laid-Open No. 20502/1987) and a process for carrying out the polymerization in an aqueous solution of a salt in the presence of a polyelectrolyte as a dispersant (see, for example, Japanese Patent Laid-Open Nos. 123610/1986, 20511/1987 and EP-A-183 466).

The standing polymerization in an aqueous solution, however, must be carried out with a monomer concentration of at least 10% by weight in order to obtain a high-molecular weight polymer. Therefore, the product is given in a state of water-containing gel, so that it is difficult to dissolve the product as such. Accordingly, the product must be put on the market in a state of a low-concentration solution obtained by further diluting a product or must be dried and powdered. With respect to the low-concentration solution, the transportation cost is disadvantageously enhanced, while with respect to the powdering of the product, much heat energy is necessitated for drying the product and the product disadvantageously causes three-dimensional crosslinking by heating to insolubilize a part thereof.

Meanwhile, the water-in-oil emulsion polymerization has a problem that a flammable and valuable organic solvent is consumed wastefully. Further, the suspension polymerization in a hydrophobic solvent has a problem that the production equipment costs a great deal, because a flammable material such as cyclohexane or toluene is used. The precipitation polymerization in an aqueous solution of ammonium sulfate has a problem that the formed polymers adhere to each other to form big lumps, resulting in difficult handling, though it is a preferable method with a low cost of equipment. Furthermore, it is difficult to prepare a polymer in a state of fine particle by using a conventional dispersant.

The present invention relates to a process for dispersing a water-soluble cationic polymer in an aqueous solution of a polyvalent anion salt in a state of fine particle. In other words, it aims at providing a process for the preparation of a dispersion of a water-soluble cationic polymer which is easily flowable and easily soluble in spite of its high molecular weight.

The present invention provides a process for the preparation of a dispersion of a water-soluble cationic polymer which process comprises polymerizing a water-soluble monomer mixture containing at least 5 mole % of a cationic monomer represented by the following general formula (I) in an aqueous solution of a polyvalent anion salt, characterized in that the polymerization is carried out in the presence of both a water-soluble cationic polymer (A) which is insoluble in said aqueous solution of a polyvalent anion salt and a water-soluble cationic polymer (B) which is soluble in said aqueous solution of a polyvalent anion salt, each polymer being used in an amount of 1 to 10% by weight based on the amount of the water-soluble monomer mixture; in that both water-soluble cationic polymers are coexistent at the beginning of polymerisation; in that said water-soluble cationic polymer contains at least 5 mole % of cationic monomer units represented by the following general formula (I); and in that said water-soluble cationic polymer (B) contains at least 20 mole % of cationic monomer units represented by the following general formula (II):



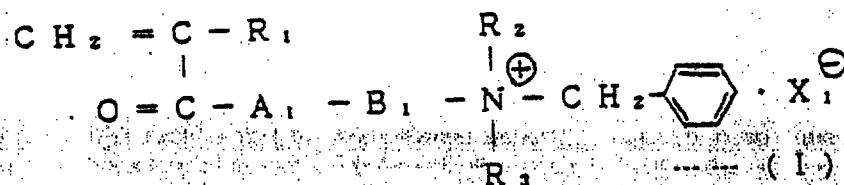
wherein R_1 and R_4 are each H or CH_3 ; R_2 , R_3 , R_5 and R_6 are each an alkyl group having 1 to 2 carbon atoms; R_7 is a hydrogen atom or an alkyl group having 1 to 2 carbon atoms; A_1 and A_2 are each an oxygen atom or NH; B_1 and B_2 are each an alkylene group having 2 to 4 carbon atoms or a hydroxypropylene group and X_1^- and X_2^- are each a counter anion.

According to another aspect of the present invention there is provided a process for the preparation of a dispersion of a water-soluble cationic polymer which comprises polymerizing a water-soluble monomer mixture containing a cationic monomer represented by the general formula (I) in an aqueous solution of a polyvalent anion salt, characterized in that the formed water-soluble cationic polymer is precipitated in a state of fine particles and that the precipitation of the polymer is controlled so as to give fine particles of the polymer.

In a preferred embodiment of the present process, the water-soluble cationic polymer is precipitated in an aqueous solution of a polyvalent anion salt, whereby the viscosity of the resultant dispersion is lowered and the separation of the polymer in the aqueous solution is inhibited.

The process for the preparation of a dispersion of a water-soluble cationic polymer according to the present invention is characterized in that the three components described below are coexistent at the beginning of the polymerization, though other components may, if necessary, be used additionally:

a water-soluble monomer mixture containing at least 5 mole % of a cationic monomer represented by the general formula (I):



wherein R_1 is H or CH_3 ; R_2 and R_3 are each an alkyl group having 1 to 2 carbon atoms; A_1 is an oxygen atom or NH; B_1 is an alkylene group having 2 to 4 carbon atoms or a hydroxypropyl group and X_1^- is a counter anion, an aqueous solution of a polyvalent anion salt in which the above water-soluble monomer mixture is soluble and the polymer of the monomer mixture is insoluble, and

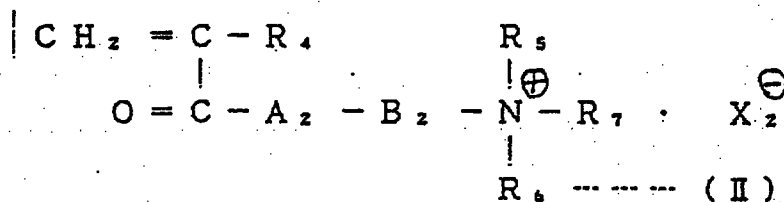
a dispersant comprising a water-soluble cationic polymer insoluble in an aqueous solution of a polyvalent anion salt and a water-soluble cationic polymer soluble in an aqueous solution of a polyvalent anion salt as essential components.

The polyvalent anion salt to be incorporated in the aqueous solution according to the present invention is suitably a sulfate or phosphate and particular examples thereof include ammonium sulfate, sodium sulfate, magnesium sulfate, aluminum sulfate, ammonium hydrogenphosphate, sodium hydrogenphosphate and potassium hydrogenphosphate. In the present invention, these salts may be each used as an aqueous solution thereof having a concentration of 15% or above.

The above cationic monomer represented by the general formula (I) includes quaternary ammonium salts obtained by the reaction of benzyl chloride with dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminohydroxypropyl (meth)acrylate, dimethylaminopropyl (meth)acrylamide or

dimethylaminopropylacrylamide.

The monomer to be copolymerized with the cationic monomer represented by the general formula (I) includes (meth)acrylamide and cationic monomers represented by the general formula (II).



wherein R_4 is H or CH_3 ; R_5 and R_6 are each an alkyl group having 1 to 2 carbon atoms; R_7 is H or an alkyl group having 1 to 2 carbon atoms; A_2 is an oxygen atom or NH; B_2 is an alkylene group having 2 to 4 carbon atoms or a hydroxypropylene group and X_2^- is a counter anion.

Among the cationic monomers represented by the general formula (II), salts and methylated quaternary salts of dimethylaminohydroxypropyl (meth)acrylate or dialkylaminoethyl (meth)acrylate are particularly preferred.

The cationic monomer represented by the general formula (II) is so highly hydrophilic that the excess use thereof hinders the precipitation of the generated polymer. Accordingly, the mol fraction of the cationic monomer represented by the general formula (II) must not exceed that of the monomer represented by the general formula (I). The polymerization concentration thereof is suitably selected in a range of 5 to 30% by weight.

Of the two polymers to be added before the beginning of the polymerization for the purpose of obtaining a fine dispersion, the water-soluble cationic polymer insoluble in an aqueous solution of a polyvalent anion salt is preferably a product prepared by the process for the preparation of a water-soluble cationic polymer according to the present invention, which is because the dispersion prepared according to the present invention is easily handleable owing to its low viscosity (as compared with a case of adding the polymer as a viscous solution).

The monomer composition of the polymer to be added need not always be equal to that of the objective polymer.

Meanwhile, the water-soluble cationic polymer soluble in an aqueous solution of a polyvalent anion salt which is the other polymer is a cationic polymer comprising at least 20 mole % of a cationic monomer represented by the general formula (II) and the balance of (meth)acrylamide. These two polymers are each added in an amount of 1 to 10% by weight based on the total amount of the monomers used. The coexistence of a polyhydric alcohol such as glycerin or polyethylene glycol often further improves the state of precipitation.

The polymerization according to the present invention is carried out by the use of a conventional water-soluble free-radical initiator. It is particularly preferable to use a water-soluble azo compound such as 2,2'-azobis(2-amidinopropane) hydrochloride or 2,2'-azobis(N,N-dimethyleneisobutyramidine) hydrochloride. The additional dissolution of various salts in the polymer dispersion after the completion of the polymerization is effective in lowering the viscosity of the polymer dispersion and in making the specific gravity of the aqueous solution equal to that of the polymer particle. It is preferable from the standpoint of workability that the viscosity of the dispersion be 1000 cP or below, while it is effective in inhibiting the separation of the polymer that the polymer particle and the aqueous solution have specific gravities equal to each other.

The process for the preparation of a dispersion of a water-soluble cationic polymer according to the present invention is characterized in that the polymerization is carried out in an aqueous solution of a polyvalent anion salt to precipitate the generated water-soluble cationic polymer and that the precipitation is controlled so as to give the fine particle of the polymer. In this connection, the precipitation of a polymer with an aqueous solution of a polyvalent anion salt is a known phenomenon which is easily illustrated based on the Hofmeister's series.

In the process for the preparation of a dispersion of a water-soluble cationic polymer according to the present invention, the benzyl group-containing cationic monomer unit represented by the general formula (I) is particularly easily salted out and an amide group is next easily salted out. The mechanism how the two polymers added as dispersants exhibit the effects is presumably that a suitable polymerization field is provided and the association is hindered by an electrical repulsive force, though it is not apparent. Particularly, a water-soluble cationic polymer insoluble in an aqueous solution of a polyvalent anion salt

exhibits such complicated behavior as the dissolution thereof in the aqueous solution in the presence of the monomers.

By way of illustration only, examples of the process for the preparation of a dispersion of a water-soluble cationic polymer according to the present invention will now be described. The present invention is not limited to the following Examples, but includes all embodiments as far as they are not deviated from the scope of the technical idea constituted of the matters described in the claim.

Example 1

2.5g of an acryloyloxyethyltrimethylbenzylammonium chloride-acrylamide copolymer having a degree of cationization of 10 mole %, 2.5g of polyacryloyloxyethyltrimethylammonium chloride, 335g of ion-exchanged water, 112.5g of ammonium sulfate, 35.1g of acrylamide and 14.9g of acryloyloxyethyltrimethylbenzylammonium chloride were placed in a 1l five-necked separable flask fitted with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet tube. The resulting system was purged with nitrogen. 1ml of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the flask to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 10µm or below and the viscosity of the dispersion was 500 cP.

Comparative Example 1

335g of ion-exchanged water, 112.5g of ammonium sulfate, 35.1g of acrylamide and 14.9g of acryloyloxyethyltrimethylbenzylammonium chloride were placed in the same five-necked separable flask as that used in Example 1. The resulting system was purged with nitrogen. 1ml of a 1% aqueous solution of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the flask to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the obtained polymer was 2 to 3mm and the polymer immediately settled out.

Example 2

17.5kg of ion-exchanged water, 5kg of ammonium sulfate, 3.2kg of acrylamide, 1.33kg of acryloyloxyethyltrimethylbenzylammonium chloride, 1.1kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride and 1.5kg of the polymer dispersion prepared in Example 1 were placed in a 35l jacketed reaction vessel made of stainless steel and fitted with an agitating blade of a ribbon type. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the vessel to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 10µm or below and the viscosity of the dispersion was 2500 cP. 1.3kg of ammonium sulfate was further added to the dispersion. The viscosity of the resulting dispersion was 230 cP, though the particle size was unchanged.

Comparative Example 2

17.5kg of ion-exchanged water, 5kg of ammonium sulfate, 3.2kg of acrylamide, 1.33kg of acryloyloxyethyltrimethylbenzylammonium chloride and 1.1kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the reaction vessel to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 100µm.

Example 3

15.7kg of ion-exchanged water, 4.6kg of ammonium sulfate, 2.1kg of acrylamide, 3.1kg of acryloyloxyethyltrimethylbenzylammonium chloride, 0.9kg of acryloyloxyethyltrimethylammonium chloride, 0.1kg of glycerin, 1.5kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride and 1.5kg of the polymer dispersion prepared in Example 1 were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the reaction vessel to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 10µm or below and the viscosity of the dispersion was 3200 cP. 2.1kg of ammonium sulfate was further added to the dispersion. The viscosity

of the resulting dispersion was 280 cP, though the particle size was unchanged.

Comparative Example 3

15.7kg of ion-exchanged water, 4.6kg of ammonium sulfate, 2.1kg of acrylamide, 0.9kg of acryloyloxyethyltrimethylammonium chloride, 0.1kg of glycerin and 1.5kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the reaction vessel at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was about 100µm.

Example 4

17.0kg of ion-exchanged water, 4.2kg of ammonium sulfate, 0.4kg of acrylamide, 3.9kg of acryloyloxyethyltrimethylbenzylammonium chloride, 1.7kg of acryloyloxyethyltrimethylammonium chloride and 2.5kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride were placed in the same reaction vessel as that used in Example 2, followed by the addition of 2.5kg of a fine dispersion of an acrylamide-acryloyloxyethyltrimethylbenzylammonium chloride copolymer having a degree of cationization of 80 mole % (containing 200% by weight of the copolymer and 20% by weight of ammonium sulfate). The resulting system was purged with nitrogen. 1g of 2,2'-azobis(N,N'-dimethyleneisobutyramidine) hydrochloride was added to the reaction vessel to carry out the polymerization at a bulk temperature of 45 °C for 10 hours. After the completion of the polymerization, 0.5kg of ammonium chloride was added to the reaction vessel. The particle size of the polymer in the obtained dispersion was about 10µm or below and the viscosity of the dispersion was 400 cP.

Comparative Example 4

17.0kg of ion-exchanged water, 4.2kg of ammonium sulfate, 0.4kg of acrylamide, 3.9kg of acryloyloxyethyltrimethylbenzylammonium chloride, 1.7kg of acryloyloxyethyltrimethylammonium chloride and 2.5kg of a 20% aqueous solution of polyacryloyloxyethyltrimethylammonium chloride were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(N,N'-dimethyleneisobutyramidine) hydrochloride was added to the reaction vessel to carry out the polymerization at a bulk temperature of 45 °C for 10 hours. After the completion of the polymerization, 0.5kg of ammonium chloride was added to the vessel, followed by mixing. The particle size of the polymer in the obtained dispersion was about 100µm.

Example 5

18.3kg of ion-exchanged water, 1.5kg of anhydrous sodium sulfate, 3.5kg of anhydrous aluminum sulfate, 3.1kg of acrylamide, 1.4kg of acrylamidopropyltrimethylbenzylammonium chloride, 1kg of a 20% aqueous solution of polyacrylamidopropyltrimethylammonium chloride and 0.2kg of an acrylamidopropyltrimethylbenzylammonium chloride/acrylamide copolymer having a degree of cationization of 10 mole % were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the vessel to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 10µm or below and the viscosity of the dispersion was 3000 cP. 1kg of sodium chloride was added to the dispersion. The viscosity of the resulting dispersion was 780 cP, though the particle size was unchanged.

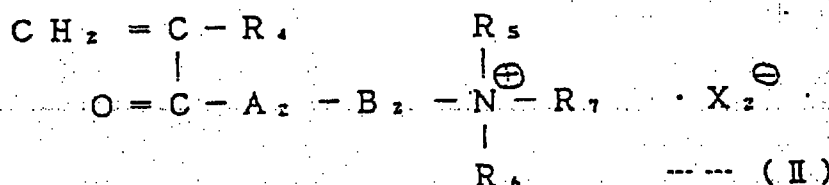
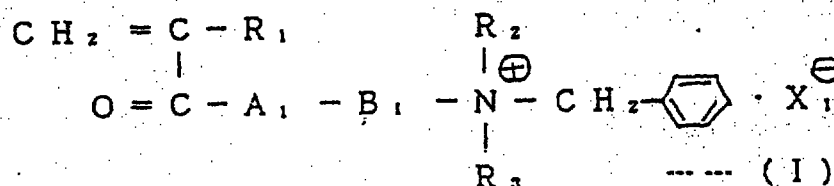
Comparative Example 5

18.3kg of ion-exchanged water, 1.5kg of anhydrous sodium sulfate, 3.5kg of anhydrous aluminum sulfate, 3.1kg of acrylamide, 1.4kg of acrylamidopropyltrimethylbenzylammonium chloride and 1kg of a 20% aqueous solution of polyacrylamidopropyltrimethylammonium chloride were placed in the same reaction vessel as that used in Example 2. The resulting system was purged with nitrogen. 1g of 2,2'-azobis(2-amidinopropane) hydrochloride was added to the reaction vessel to carry out the polymerization at a bulk temperature of 50 °C for 10 hours. The particle size of the polymer in the obtained dispersion was 100µm.



Claims

1. A process for the preparation of a dispersion of a water-soluble cationic polymer which process comprises polymerizing a water-soluble monomer mixture containing at least 5 mole % of a cationic monomer represented by the following general formula (I) in an aqueous solution of a polyvalent anion salt, characterized in that the polymerisation is carried out in the presence of both a water-soluble cationic polymer (A) which is insoluble in said aqueous solution of a polyvalent anion salt and a water-soluble cationic polymer (B) which is soluble in said aqueous solution of a polyvalent anion salt, each polymer being used in an amount of 1 to 10% by weight based on the amount of the water-soluble monomer mixture; in that both water-soluble cationic polymers are coexistent at the beginning of polymerisation; in that said water-soluble cationic polymer (A) contains at least 5 mole % of cationic monomer units represented by the following general formula (I); and in that said water-soluble cationic polymer (B) contains at least 20 mole % of cationic monomer units represented by the following general formula (II):



wherein R_1 and R_4 are each H or CH_3 ; R_2 , R_3 , R_5 and R_6 are each an alkyl group having 1 to 2 carbon atoms; R_7 is a hydrogen atom or an alkyl group having 1 to 2 carbon atoms; A_1 and A_2 are each an oxygen atom or NH; B_1 and B_2 are each an alkylene group having 2 to 4 carbon atoms or a hydroxypropylene group and X_1 and X_2 are each a counter anion.

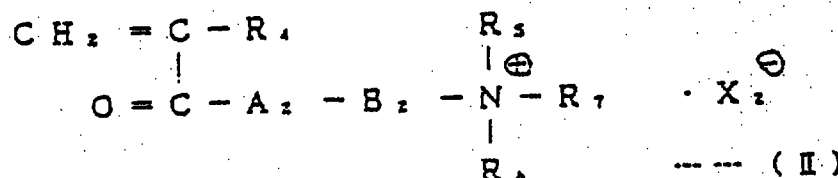
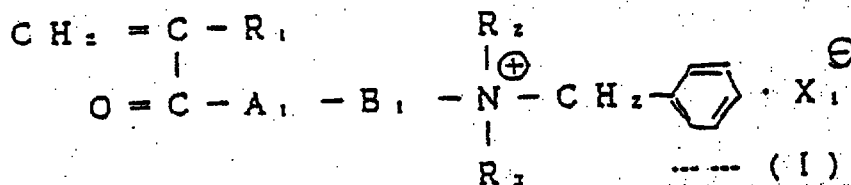
2. A process according to claim 1, wherein the cationic monomer represented by the general formula (II) is selected from salts and methylated quaternary ammonium salts of dimethylaminohydroxypropyl-(meth)acrylate, dialkylaminoethyl (meth)acrylate and mixtures thereof.
3. A process according to claim 1, wherein the cationic monomer represented by the general formula (II) is (meth)acryloyloxyethyltrimethylammonium chloride.
4. A process according to any one of claims 1 to 3, wherein the water-soluble monomer to be copolymerized with the cationic monomer represented by the general formula (I) is selected from (meth)acrylamide, cationic monomers represented by the general formula (II) and mixtures thereof, with the proviso that the mol fraction of the cationic monomer represented by the general formula (II) is lower than that of the cationic monomer represented by the general formula (I).
5. A process according to any one of the preceding claims, wherein said water-soluble cationic polymer insoluble in an aqueous solution of a polyvalent anion salt comprises at least 5 mole % of cationic monomer units represented by the general formula (I) and the balance of one-member selected from (meth)acrylamide, cationic monomers represented by the general formula (II) and mixtures thereof.
6. A process according to any one of the preceding claims, wherein the monomer units constituting said water-soluble cationic polymer soluble in an aqueous solution of a polyvalent anion salt are all represented by the general formula (II).



7. A process according to any one of the preceding claims, wherein said cationic monomer represented by the general formula (I) is selected from benzylated quaternary ammonium salts of dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminohydroxypropyl (meth)acrylate, dimethylaminopropyl (meth)acrylamide, dimethylaminopropylacrylamide and mixtures thereof.
8. A process according to any one of claims 1 to 6, wherein said cationic monomer represented by the general formula (I) is (meth)acryloyloxyethyltrimethylbenzylammonium chloride.
9. A process according to any one of the preceding claims, wherein the water-soluble cationic polymer insoluble in an aqueous solution of a polyvalent anion salt is added to the monomer solution as fine particles dispersed in an aqueous solution of a polyvalent anion salt.
10. A process according to any one of the preceding claims, wherein the polyvalent anion salt concentration of the aqueous solution is 15% by weight or more.
11. A process according to any one of the preceding claims, wherein said polyvalent anion salt is a sulfate, a phosphate or a mixture thereof.
12. A process according to claim 11, wherein said polyvalent anion salt is ammonium sulfate.
13. A process according to any one of the preceding claims, wherein a salt is additionally dissolved in the dispersion after the completion of the polymerization.
14. A process according to any one of the preceding claims, wherein the specific gravity of the polymer in the dispersion is equal to that of the aqueous solution.
15. A process according to any one of the preceding claims, wherein the viscosity of the polymer dispersion is 1000 cP or below.
16. A process according to any one of the preceding claims, wherein the water-soluble monomer concentration based on the total amount of the aqueous solution is 5 to 30% by weight.
17. A process according to any one of the preceding claims, wherein a water-soluble azo free-radical initiator is used as a polymerization initiator.
18. A process according to claim 17, wherein the polymerization initiator is selected from 2,2'-azobis(2-amidinopropane) hydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) hydrochloride and mixtures thereof.
19. A process according to any one of the preceding claims, wherein the particle size of the polymer is 10 μm or below.

Patentansprüche

1. Verfahren zur Herstellung einer Dispersion eines wasserlöslichen kationischen Polymers, welches Verfahren ein Polymerisieren eines wasserlöslichen Monomergemisches, welches mindestens 5 Mol-% eines kationischen Monomers, für welches die folgende allgemeine Formel (I) steht, enthält, in einer wäßrigen Lösung eines mehrwertigen Anionensalzes umfaßt, dadurch gekennzeichnet, daß die Polymerisation in Gegenwart von sowohl einem wasserlöslichen kationischen Polymer (A), welches in der wäßrigen Lösung eines mehrwertigen Anionensalzes unlöslich ist, als auch von einem wasserlöslichen kationischen Polymer (B), welches in der wäßrigen Lösung eines mehrwertigen Anionensalzes löslich ist, ausgeführt wird, wobei jedes Polymer in einer Menge von 1 bis 10 Gew.-%, bezogen auf die Menge des wasserlöslichen Monomergemisches, verwendet wird; daß beide wasserlöslichen kationischen Polymere zu Beginn der Polymerisation koexistent sind; daß das wasserlösliche kationische Polymer (A) mindestens 5 Mol-% kationische Monomereinheiten, für welche die folgende allgemeine Formel (I) steht, enthält; und daß das wasserlösliche kationische Polymer (B) mindestens 20 Mol-% kationische Monomereinheiten enthält, für die die allgemeine Formel (II)



steht, worin R_1 und R_4 H oder CH_3 sind; R_2 , R_3 , R_5 und R_6 eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen sind; R_7 ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen ist; A_1 und A_2 ein Sauerstoffatom oder NH sind; B_1 und B_2 eine Alkylengruppe mit 2 bis 4 Kohlenstoffatomen oder eine Hydroxypropylengruppe sind, und X_1 und X_2 ein Gegenion sind.

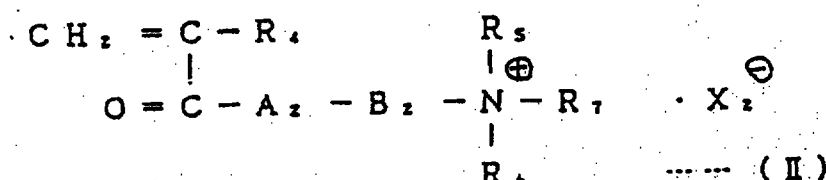
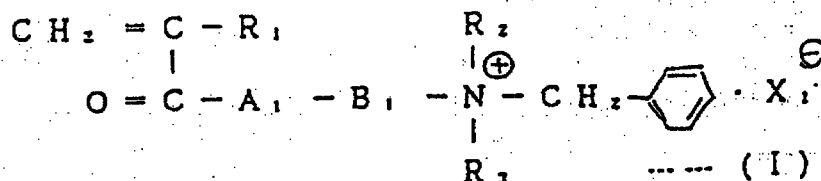
2. Verfahren nach Anspruch 1, worin das kationische Monomer, für welches die allgemeine Formel (II) steht, aus Salzen und methylierten quaternären Ammoniumsalzen von Dimethylaminohydroxypropyl(meth)acrylat, Dialkylaminoethyl(meth)acrylat und ihren Gemischen ausgewählt ist.
3. Verfahren nach Anspruch 1, worin das kationische Monomer, für welches die allgemeine Formel (II) steht, (Meth)acryloyloxyethyltrimethylammoniumchlorid ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin das wasserlösliche Monomer, welches mit dem kationischen Monomer, für das die allgemeine Formel (I) steht, copolymerisiert werden soll, aus (Meth)acrylamid, kationischen Monomeren, für welche die allgemeine Formel (II) steht, und ihren Gemischen ausgewählt ist, mit der Maßgabe, daß die Molfraktion des kationischen Monomers, für welches die allgemeine Formel (II) steht, kleiner ist als jene des kationischen Monomers, für welches die allgemeine Formel (I) steht.
5. Verfahren nach einem der vorhergehenden Ansprüche, worin das wasserlösliche kationische Polymer, welches in einer wäßrigen Lösung eines mehrwertigen Anionensalzes unlöslich ist, mindestens 5 Mol-% kationische Monomereinheiten, für welche die allgemeine Formel (I) steht, und als Rest einen Stoff, ausgewählt aus (Meth)acrylamid, kationischen Monomeren, für welche die allgemeine Formel (II) steht, und Gemischen davon, umfaßt.
6. Verfahren nach einem der vorhergehenden Ansprüche, worin für alle Monomereinheiten, welche das wasserlösliche kationische Polymer, das in einer wäßrigen Lösung eines mehrwertigen Anionensalzes löslich ist, aufbauen, die allgemeine Formel (II) steht.
7. Verfahren nach einem der vorhergehenden Ansprüche, worin das kationische Monomer, für welches die allgemeine Formel (I) steht, aus benzylierten quaternären Ammoniumsalzen von Dimethylaminoethyl(meth)acrylat, Diethylaminoethyl(meth)acrylat, Dimethylaminohydroxypropyl(meth)acrylat, Dimethylaminopropyl(meth)acrylamid, Dimethylaminopropylacrylamid und deren Gemischen ausgewählt ist.
8. Verfahren nach einem der Ansprüche 1 bis 6, worin das kationische Monomer, für welches die allgemeine Formel (I) steht, (Meth)acryloyloxyethyltrimethylbenzylammoniumchlorid ist.
9. Verfahren nach einem der vorhergehenden Ansprüche, worin das wasserlösliche kationische Polymer, welches in einer wäßrigen Lösung eines mehrwertigen Anionensalzes unlöslich ist, der Monomerlösung als feine Partikel, die in einer wäßrigen Lösung eines mehrwertigen Anionensalzes dispergiert sind, zugegeben wird.



10. Verfahren nach einem der vorhergehenden Ansprüche, worin die Konzentration an mehrwertigem Anionensalz der wäßrigen Lösung 15 Gew.-% oder mehr ist.
11. Verfahren nach einem der vorhergehenden Ansprüche, worin das mehrwertige Anionensalz ein Sulfat, ein Phosphat oder ein Gemisch davon ist.
12. Verfahren nach Anspruch 11, worin das mehrwertige Anionensalz Ammoniumsulfat ist.
13. Verfahren nach einem der vorhergehenden Ansprüche, worin ein Salz in der Dispersion nach der Beendigung der Polymerisation zusätzlich gelöst wird.
14. Verfahren nach einem der vorhergehenden Ansprüche, worin das spezifische Gewicht des Polymers in der Dispersion gleich jenem der wäßrigen Lösung ist.
15. Verfahren nach einem der vorhergehenden Ansprüche, worin die Viskosität der Polymerdispersion 1 000 cP oder geringer ist.
16. Verfahren nach einem der vorhergehenden Ansprüche, worin die Konzentration an wasserlöslichem Monomer, bezogen auf die Gesamtmenge der wäßrigen Lösung, 5 bis 30 Gew.-% ist.
17. Verfahren nach einem der vorhergehenden Ansprüche, worin ein wasserlöslicher Azo-Radikalinitiator als Polymerisationsinitiator verwendet wird.
18. Verfahren nach Anspruch 17, worin der Polymerisationsinitiator aus 2,2'-Azobis(2-amidinopropan)-hydrochlorid, 2,2'-Azobis(N,N'-dimethylenisobutyramidin)hydrochlorid und Gemischen davon ausgewählt ist.
19. Verfahren nach einem der vorhergehenden Ansprüche, worin die Partikelgröße des Polymers 10 µm oder geringer ist.

Revendications

1. Procédé pour la préparation d'une dispersion d'un polymère cationique soluble dans l'eau, lequel procédé comporte la polymérisation d'un mélange de monomères solubles dans l'eau contenant au moins 5% en mole d'un monomère cationique représenté par la formule générale (I) suivante dans une solution aqueuse d'un sel anion polyvalent, caractérisé en ce que la polymérisation est effectuée en présence à la fois d'un polymère cationique (A) soluble dans l'eau qui est insoluble dans ladite solution aqueuse d'un sel anion polyvalent et d'un polymère cationique (B) soluble dans l'eau qui est soluble dans ladite solution aqueuse d'un sel anion polyvalent, chaque polymère étant utilisé en quantité de 1 à 10% en poids par rapport à la quantité du mélange de monomères solubles dans l'eau ; en ce que les deux polymères cationiques solubles dans l'eau sont coexistants au début de la polymérisation ; en ce que ledit polymère cationique (A) soluble dans l'eau contient au moins 5% en mole d'unités de monomères cationiques représentés par la formule générale (I) suivante ; et en ce que ledit polymère cationique (B) soluble dans l'eau contient au moins 20% en mole d'unités de monomères cationiques représentés par la formule générale (II) suivante :



où R_1 et R_4 représentent chacun H ou CH_3 ; R_2 , R_3 , R_5 et R_6 représentent chacun un groupe alkyle ayant 1 à 2 atomes de carbone ; R_7 est un atome d'hydrogène ou un groupe alkyle ayant 1 à 2 atomes de carbone ; A_1 et A_2 représentent chacun un atome d'oxygène ou NH ; B_1 et B_2 représentent chacun un groupe alkylène ayant 2 à 4 atomes de carbone ou un groupe hydroxypropylène et X_1 et X_2 représentent chacun un contre-anion.

2. Procédé selon la revendication 1, dans lequel le monomère cationique représenté par la formule générale (II) est choisi parmi des sels et les sels ammonium quaternaires méthylés de diméthylaminohydroxypropyl(méth)acrylate, de (méth)acrylate de dialkylaminoéthyle et leurs mélanges.
3. Procédé selon la revendication 1, dans lequel le monomère cationique représenté par la formule générale (II) est le chlorure de (méth)acryloyloxyéthyltriméthylammonium.
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le monomère soluble dans l'eau à copolymériser avec le monomère cationique représenté par la formule générale (I) est choisi parmi le (méth)acrylamide, les monomères cationiques représentés par la formule générale (II) et leurs mélanges, à condition que la fraction de mole des monomères cationiques représentés par la formule générale (II) soit inférieure à celle du monomère cationique représenté par la formule générale (I).
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit polymère cationique soluble dans l'eau, insoluble dans une solution aqueuse d'un sel anion polyvalent comporte au moins 5% en mole d'unités de monomères cationiques représentés par la formule générale (I) et l'équilibre d'un membre choisi parmi le (méth)acrylamide, les monomères cationiques représentés par la formule générale (II) et leurs mélanges.
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel les unités de monomères constituant ledit polymère cationique soluble dans l'eau, solubles dans une solution aqueuse d'un sel anion polyvalent sont toutes représentées par la formule générale (II).
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère cationique représenté par la formule générale (I) est choisi parmi les sels ammonium quaternaires benzylés de (méth)acrylate de diméthylaminoéthyle, de (méth)acrylate de diéthylaminoéthyle, de (méth)acrylate de diméthylaminohydroxypropyle, de (méth)acrylate de diméthylaminopropyle, de diméthylaminopropylacrylamide et leurs mélanges.
8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit monomère cationique représenté par la formule générale (I) est le chlorure de (méth)acryloyloxyéthylidiméthylbenzylammonium.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère cationique soluble dans l'eau, insoluble dans une solution aqueuse d'un sel anion polyvalent est ajouté à la solution de monomères sous la forme de fines particules dispersées dans une solution aqueuse d'un sel anion polyvalent.



10. Procédé selon l'une quelconque des revendications précédentes, dans lequel la concentration de sel anion polyvalent de la solution aqueuse est au moins de 15% en poids.
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit sel anion polyvalent est un sulfate, un phosphate ou un mélange de ceux-ci.
12. Procédé selon la revendication 11, dans lequel ledit sel anion polyvalent est le sulfate d'ammonium.
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel un sel est en outre dissous dans la dispersion après l'achèvement de la polymérisation.
14. Procédé selon l'une quelconque des revendications précédentes, dans lequel la gravité spécifique du polymère dans la dispersion est égale à celle de la solution aqueuse.
15. Procédé selon l'une quelconque des revendications précédentes, dans lequel la viscosité de la dispersion des polymères est de 1000 cP au plus.
16. Procédé selon l'une quelconque des revendications précédentes, dans lequel la concentration de monomères solubles dans l'eau par rapport à la quantité totale de la solution aqueuse est de 5 à 30% en poids.
17. Procédé selon l'une quelconque des revendications précédentes, dans lequel un initiateur radical libre azoïque soluble dans l'eau est utilisé comme initiateur de polymérisation.
18. Procédé selon la revendication 17, dans lequel l'initiateur de polymérisation est choisi parmi l'hydrochlorure de 2,2'-azobis(2-amidinopropane), l'hydrochlorure de 2,2'-azobis(N,N'-diméthylèneisobutyramine) et leurs mélanges.
19. Procédé selon l'une quelconque des revendications précédentes, dans lequel la grosseur des particules du polymère est de 10 μm au plus.