

"PROCESS FOR REACTING QUATERNARY AMMONIUM MONOMERS IN THE
PRESENCE OF ANIONIC POLYMERS"

The present invention is directed to a process for reacting quaternary ammonium monomers and optionally monomers copolymerizable therewith in the presence of anionic polymers and forming a coacervate directly in dry form. The process involves forming a concentrated solution of the respective monomer(s), an anionic polymer, initiators and any other reactants, and thereafter simultaneously polymerizing the monomer(s) and drying the solution.

10 The most generally employed prior art processes for producing homo- and co-polymers of quaternary ammonium monomers, particularly quaternized diallyl amines such as dimethyldiallylammonium chloride (DMAAC), yield a final product in the form of a solution or oil-in-water latex. In order to obtain a dry solid, it is then necessary to separate and dry or otherwise isolate the desired fraction. Typical of such methods are those described in U.S. Patent Nos. 2,923,701; 3,284,393; 3,288,770; 3,461,163; and 3,920,599.

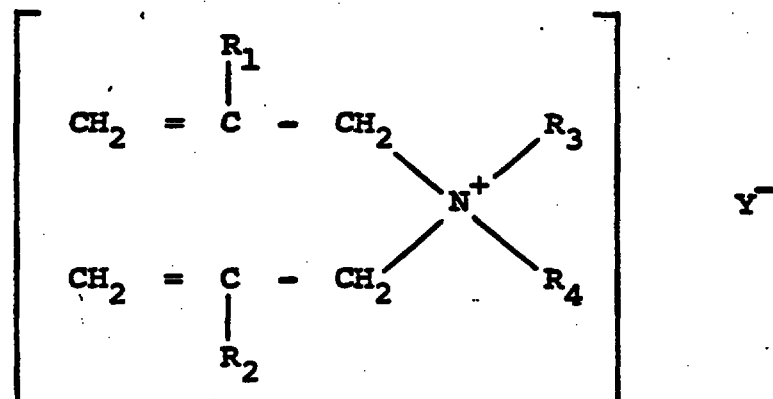
20 There are a number of applications in industry wherein it is desired to utilize a blend of cationic homo- or co-polymers of quaternary ammonium monomers with certain anionic polymers. Thus, U.S. Patent No. 3,539,510 teaches the advantages in flocculating applications of utilizing

high molecular weight anionic polymers which are modified with certain cationic, water-soluble amino polymers. Other potential uses include, for example, as electroconductive agents in photographic, fiber, membrane or paper applications.

While the benefits achieved by using such materials will be apparent, the difficulties inherent in their production, transportation and storage are formidable since the water soluble polymers of opposite charges interact ionically in water solution to form a precipitate or sometimes a gel or pultaceous coacervate. Transportation and/or storage of such polymer solutions is thus very difficult and the drying of such pre-reacted gels or coacervates entails considerable energy and time.

The present invention provides a process for polymerizing a quaternary ammonium monomer in the presence of an anionic polymer so as to form a dry coacervate directly, which comprises:

a) forming a solution dispersion or emulsion of at least one quaternary ammonium monomer having the formula:



where R_1 and R_2 each represent hydrogen, methyl or ethyl;
 R_3 and R_4 each represent alkyl, aryl, cycloalkyl,
hydroxyalkyl or alkoxyalkyl radicals having from 1 to 18
carbon atoms each, and Y^- represents an anion; an anionic
5 polymer which is a homo- or co-polymer of styrene
sulfonate, alkali metal styrene sulfonate, acrylate or
methacrylate, an alkali metal or ammonium salt of a high
copolymer of styrene or substituted styrene with maleic
acid, a water-soluble copolymer of a styrene sulfonate,
10 acrylate or methacrylate with acrylamide, methacrylamide,
acrylonitrile, methacrylonitrile, styrene, vinyl acetate,
vinyl toluene, methyl acrylate, N-vinyl oxazolidinone or
N-vinyl pyrrolidone, a homo- or co-polymer of a sulfoalkyl
acrylate or carboxyalkyl acrylate or a carboxyalkyl
15 cellulose ether or starch, in an amount from 0.1 to 3
parts by weight per part of the monomer(s); solvent, and
free-radical initiator;

b) simultaneously polymerizing the monomers
and drying the solution at a temperature above the boiling
20 point of the solvent; and

c) recovering the resultant dry product.

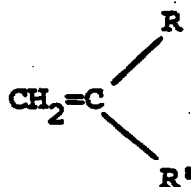
Monomers copolymerizable with the quaternary ammonium monomers may be included in the quaternary ammonium monomer/anionic polymer solution.

By utilizing this process, a number of benefits 5 are achieved. Thus, the direct conversion from monomer to dry solid avoids the need for the plurality of steps required by prior art techniques. Furthermore, since the coacervate forms in situ and is dried immediately the necessity of handling a gelled solution is avoided. By 10 using the heat of polymerization to effect drying, a more energy conserving process is provided. The process also avoids the possibility of dangerous exotherms which may occur in a conventional solution polymerization so there is no need to control the heat of polymerization through 15 heat transfer to a jacket.

Illustrative examples of radicals which may be represented by R_3 and R_4 are methyl to octadecyl alkyl radicals, inclusive: methoxymethyl and various higher alkoxy (e.g. methoxy to octadecoxy, inclusive)-alkyl (e.g. ethyl to octadecyl, inclusive) radicals; and the corresponding hydroxyalkyl and cycloalkyl radicals. Illustrative examples of anions which may be represented by Y are the halide, sulfate, sulfonate, phosphate, hydroxide, borate, cyanide, carbonate, thiocyanate, thiosulfate, isocyanate, sulfide, cyanate, acetate and the other common inorganic and organic ions.

Specific examples of monomers useful herein are the diallyl dimethyl, diallyl di-(beta-hydroxyethyl), dimethallyl dimethyl, dimethallyl di-(beta-hydroxyethyl), diethallyl dimethyl and diethallyl di-(beta-hydroxyethyl) ammonium chlorides, bromides, phosphates, or sulfates.

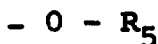
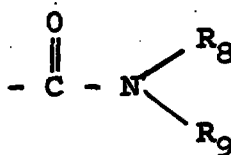
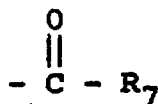
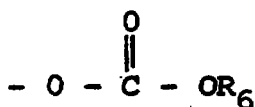
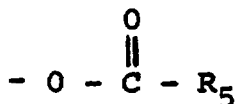
In producing copolymers of the quaternized ammonium monomers, any monomeric entities which are substantially non-volatile at the reaction temperatures and which contain a single $CH_2=C$ grouping and which are typically copolymerizable with the quaternized ammonium monomers may be used. Preferably, the monomers are of the general formula:



where R represents hydrogen, halogen, alkyl, cycloalkyl, aryl, alkaryl or aralkyl and R' represents an aryl or alkaryl radical or a radical of the formula:

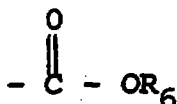


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or

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where R_5 and R_6 each represent a radical selected from alkyl, cycloalkyl, and alkoxyalkyl radicals or hydrogen or an alkali metal cation, R_7 has the same meaning as R_5 and R_6 and may, in addition, be an aryl radical; and R_8 and R_9 each represent hydrogen, alkyl, cycloalkyl, aryl, alkaryl, aralkyl or alkoxyalkyl.

Preferable compounds represented by the above formulas and useful as monomers herein include styrene,

aromatic substituted monomethyl and dimethyl styrene, methyl and other lower alkyl acrylates, acrylic acid, acrylamide, acrylonitrile, methacrylonitrile, vinyl acetate and the like.

- 5 If a copolymer is to be produced using the process of the invention, the quaternary ammonium monomer should be present in an amount of at least 50%, preferably at least about 75% by weight of the monomeric components.

 The particular anionic polymer employed herein
10 depends upon the end use application for which the product is intended. Anionic polymers which may be utilized herein are the homo- and co-polymers of styrene sulphonates, alkali metal styrene sulfonates, acrylates and methacrylates. The comonomers may be water-soluble
15 or water-insoluble mono-ethylenically unsaturated monomers and are copolymerizable with one of the foregoing to produce water-soluble polymers. When water-insoluble comonomers are employed, they are used in amounts insufficient to impair the water-solubility
20 of the resulting copolymer. Comonomers used with the sulphonates, acrylates and methacrylates above are acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, styrene, vinyl acetate, vinyl toluene, methyl acrylate, N-vinyl oxazolidinone, and
25 N-vinyl pyrrolidone. Other anionic polymers which may be used are the alkali metal and ammonium salts of high copolymers of styrene and substituted styrenes with maleic acid; homo- and co-polymers of sulfoalkyl acrylates and carboxyalkyl acrylates such as sodium sulfo-

ethyl acrylate and sodium carboxyethyl acrylate;
carboxyalkyl cellulose ethers such as carboxymethyl
cellulose, carboxymethyl methyl cellulose, carboxymethyl
hydroxyethyl cellulose and starch. Additionally,
5 one may wish to utilize certain anionic polymers which
are not water-soluble, in which case it will be necessary
to utilize either a non-aqueous solvent or a mutual
solvent so as to provide a uniform distribution of the
monomeric components throughout the anionic polymer
10 solution.

The amount and the choice of the particular anionic
polymer to be used will depend upon the properties required
for the end use application. The anionic
polymer is used in amounts of 0.10 to 3 parts by weight
15 per part of the monomeric components. It has been found
that the lower concentrations of polymer result in higher
conversion of the monomer to polymer and hence the desired
degree of conversion should be considered when deciding the
relative amounts employed. The preferred amounts of polymer
20 comprise 0.25 to 1 part per part of the monomeric component(s).

Generally, an aqueous medium is used as the
polymerization vehicle for the reaction although organic
solvents, particularly those which are C₁₋₈ carbon compounds
containing hydroxyl, ketone, aldehyde, ester or halide
25 substitution, may be used. While the use of such solvents
does pose some safety problems in processing, in some cases
they provide advantages over the use of water which may make

them more desirable. Thus, the manufacture of low molecular weight polymers may be accomplished by using a solvent with a greater transfer constant than water. This would eliminate the need for aqueous chain transfer agents
5 coupled with large amounts of catalyst used to make comparable molecular weight compounds in water. Another advantage to the use of nonaqueous solvents is that the particular monomer to be polymerized may have a greater solubility in the solvent than it would have in water. In
10 such cases, higher concentrations of reactants could be employed and greater through-put realized. The latter approach is especially useful for reactants which form high viscosity solutions at low concentrations in water. Additionally, as was discussed above, it may also be
15 necessary or desirable to utilize a non-aqueous solvent and/or a mutual co-solvent in the instances wherein anionic polymers are utilized which are not soluble in water. It is to be noted that by proper choice of solvent mixtures, it is possible to utilize any combination of water-soluble
20 and/or water-insoluble monomers and anionic polymers.

Whether water or other solvents (both hereinafter referred to as "solvents") are used, the reactants should be uniformly dispersed throughout the medium in solute or emulsion form, using dispersants or emulsifiers if necessary.
25 Sufficient solvent should be used to dissolve or disperse the components homogeneously throughout the reaction system

in order to facilitate the polymerization rate and provide a uniform end product. Amounts of solvent in the range of 10 to 90% by weight of the reaction mixture will generally be used. The amount of solvents used will depend, in part, 5 upon the particular drying method employed. Thus, extrusion and calendering processes are usually operated at higher solids levels, e.g. 70 to 90% dry solids, while spray drying and flash drying are usually carried out at 10 to 40% dry solids. Drum drying, the preferred polymerization 10 and drying method, is generally carried out at levels of 30 to 85%, preferably 40 to 65%, solids.

The reaction is carried out using conventional free radical polymerization techniques, most commonly in the presence of a free-radical initiator or free-radical 15 precursor. Initiators which are useful in the embodiment wherein water or aqueous alcoholic solutions are used as solvent include the water-soluble peroxy catalysts, preferably a water-soluble salt of persulfuric (perdisulfuric) acid, which salt is preferably used in 20 combination with a sulfoxy type of reducing agent. Other examples of polymerization initiators which are useful include the inorganic and organic peroxides, e.g. the diacyl peroxides, the primary, secondary and tertiary alkyl peroxides and hydroperoxides and esters thereof, the various 25 water-soluble peracetates, perchlorates, percarbonates, perborates, perphosphates, e.g. the ammonium and alkali-

metal salts of peracetic, percarbonic, perboric, perphosphoric, persulfuric and perchloric acids; and water soluble ferric salts capable of yielding ferric ions, e.g. ferric ammonium sulfate and ferric sodium sulfate. In a preferred embodiment, where polymerization and drying take place on a drum drier, cast iron drums may be used and the residual free ferric ions present thereon will provide the necessary initiating activity.

Such water-soluble initiators as mentioned above by way of example are generally employed in combination with a water-soluble activator, for instance, oxygen-containing, sulfur-containing compounds that are capable of undergoing oxidation. Illustrative examples of such activators or adjuvants include sulfur dioxide, the alkali-metal (e.g. sodium and potassium) bisulfites, hydrosulfites, thiosulfates, sulfurous acid (or compounds which engender sulfurous acid, e.g. alkali-metal sulfites and ethyl and other alkyl sulfites), various organic sulfinic acids, e.g. p-toluene sulfinic acid and formamidine sulfinic acid. If alkali-metal sulfites, e.g. sodium sulfite or similar compounds which engender sulfurous acid are used, the aqueous solution also should contain a strong acid, e.g. sulfuric acid, in an amount which is at least chemically equivalent to the amount of such a compound engendering sulfurous acid that is employed.

The actual initiator concentration necessary to effect polymerization under the process drying conditions depends upon the reaction temperature, the reaction time and the free-radical initiating temperature of the initiator.

5 Accordingly, the initiator level may vary considerably (e.g. from 0.1 to 10% of the monomer weight). Peroxide initiator concentrations are typically greater (e.g. 1-10%) than persulfate initiated systems (e.g. 0.03-3%). In the preferred embodiment wherein drum drying is employed, the

10 persulfate concentration will generally fall within the range of 0.03 to 2.0% by weight monomer and preferably between 0.05 to 1.5% with a persulfate concentration ranging from 0.1 to 1.2% being most preferred.

When redox initiation systems are used, the

15 reducing agent is incorporated into the feed solution in amounts of 20-200% by weight, based on the concentration of the initiator.

It will be recognized that in cases wherein non-aqueous solvents are employed, it will be necessary that

20 the initiator and activator chosen be soluble in the particular solvent. Suitable initiators and activators useful in this embodiment are well known to those skilled in the art.

It may also be desirable in practising the

25 present invention to add a buffer to the feed formulation in order to effectively control the pH of the final product.

Although this is especially desirable in facilitating the production of a dry product having a neutral pH, so as to prevent attack on the processing equipment by any acid generated during decomposition of the initiator, 5 products of other pH values may also be prepared. These ends could not be accomplished by merely raising the initial pH of the feed with caustic since the quaternary amines decompose above pH 10. The particular buffer chosen can be a salt of any polyprotic weak acid, either organic 10 or inorganic in nature. Typical examples of such buffers are salts of carbonic, phosphoric, succinic and phthalic acids. The buffer selected should be compatible with the particular feed formulation and should be used in sufficient concentration to render a neutral pH to the dry product. 15 The amount of buffer needed will vary depending upon the type buffer used, the type initiator used and the desired pH of the dry product. Typical concentrations necessary to produce the neutral pH product are in the order of 20 to 200% of the concentration of the initiator, preferably 20 50 to 100%.

Alternatively, premature polymerization (e.g. without concomitant drying) can be effectively avoided by controlling the stage at which the polymerization initiator is introduced into the aqueous dispersion. In processes 25 which, prior to drying, rely upon relatively high temperatures (e.g. greater than 60°C) for several seconds

or more to achieve homogeneous reactant dispersal, initiator addition may be delayed until immediately before or concurrently with the drying step. Conversely, in those processes wherein homogeneous dispersal can be effectively accomplished without exposing the reactants to polymerization conditions before drying, the polymerized catalyst system can be appropriately selected to generate free-radicals when the reactants are exposed to the elevated temperature of the drying step. In general, processes which rely upon relatively high temperature (e.g. greater than 70°C) at a high solids levels (e.g. less than 40% water) are most suitably conducted under the delayed initiator incorporation techniques whereas the low temperature (e.g. less than 50°C) and low solids processes (e.g. more than 50% water) are most suitably conducted in the presence of a thermally initiated polymerization catalyst system.

The reactants are simultaneously polymerized and dried to yield the resultant solid mixture of quaternary ammonium homo- or co-polymer together with anionic polymer. Illustrative processes for simultaneously polymerizing and drying include extrusion, heat-exchanging, rotating, calendaring, spray-drying, flash-drying and drum-drying. The polymerization rate will depend upon the reactivity of the monomers, reactant concentration, the efficacy of the catalyst system, the reaction temperature and the

polymerization time. The most appropriate thermal conditions depend upon the boiling point of the solvent and also upon the particular apparatus used to simultaneously dry and polymerize the homogeneous dispersion or solution.

5 Usually the simultaneous drying and polymerization temperature will range between 60-250°C, preferably being accomplished at less than 200°C.

Drum drying processes employing double drums and capable of drying and polymerizing the reactants
10 within 1 minute to 15 minutes time interval at reaction temperature ranging from 60-170°C are preferred depending upon the boiling point of the solvent. The temperature and reaction time is appropriately maintained so as to provide the desired final homo- or co-polymer. The polymerization
15 and drying conditions are effectively controlled by the operational drum speed, the amount of solution retained at any time in the reservoir formed at the nip between the drums and the drum temperature. Most effective manufacture and improved product functionality is accomplished by
20 dissolving the reactants in water and maintaining the solution in the reservoir for a period of 5-15 minutes. The surface temperature of the drum-drier should range from 120-160°C. Excessive drum speed or excessively low temperatures may result in incomplete polymerization
25 whereas excessively slow speeds at the elevated temperatures can char the product and are uneconomical.

The homogeneous dispersion or solution application to the drier is at a rate sufficient to permit its drying and polymerization into the desired homo- or co-polymer. Excessively thick films or non-uniform application can result in incomplete or non-uniform polymerization and drying of the product. Conversely, too thin an application can result in product charring (especially at elevated temperatures) or inefficient production. In general, the drum drying processes typically provide a dried film of a thickness ranging from 1 mil to 50 mils (0.025 to 1.25 mm) with 8 mil to 10 mils (0.2 to 0.25 mm) being optimal. If desired, products which are produced in sheet or film form may be ground to a suitable particle size as desired. Particles of size 30 mesh (U.S.S.S.) (sieve opening 0.59 to 0.074 mm) have been found to be particularly useful in end use applications such as flocculating wherein these homo- and co-polymers are conventionally employed.

The dried product will either disperse in the aqueous system or will form a coacervate therein depending upon the degree of conversion of the monomeric components. While it is difficult to characterize the precise chemical composition of the final product, analysis, to date, indicates that the resultant product may comprise homo- or co-polymer of the monomers mixed with the anionic polymer or graft copolymers of the monomeric components and the anionic polymer. It will be recognized that the specific

product formed will depend, in part, on the reactivity of the monomers as well as the ratio of monomer to polymer in the feed solution.

The following examples are exemplary of the 5 process herein.

EXAMPLE I

This example illustrates the reaction of dimethyldiallyl ammonium chloride in the presence of sulfonated polystyrene. A 61 cm. (24 in.) wide (diameter) cast iron 10 double roll drum drier was cleaned to remove surface rust and dirt. The drums were then pre-set with 586 kPa (85 psig) steam pressure and rotated at 1.5 RPM. The gap was set at minimum and the blade at 138 kPa (20 psig).

15 Two mixtures, designated Mix 1 and Mix 2, were prepared using the components and amounts shown below.

	<u>Ingredient</u>	<u>Amount (g.)</u>
20	Mix 1 Deionized water	44.8
	Sodium thiosulfate	0.98
	Sodium carbonate	0.83
	Sodium persulfate	1.2
25	Mix 2 Sulfonated polystyrene (28% in water)	1265
	Dimethyldiallyl ammonium chloride (63% in water)	187

Both mixtures were prepared in separate containers and purged of dissolved oxygen using a 15 minute subsurface nitrogen injection.

A feed mixture was then prepared using equal parts of Mix 1 and Mix 2 and the feed mixture fed into the nip between the rollers at a rate of 50 ml. per min. so as to ensure a residence time of at least about 5 min. 5 in the reservoir. As the dried product formed on the drums, it was scraped off and the resulting sheet ground on a Cumberland Granulator using a 16 mesh screen (sieve opening 1.2 mm).

Analysis of the product (with pH and Brookfield 10 Viscosity measured at 25% solution in water) gave the following results:

Moisture (Cenco - 90 - 10 min.)	2.2%
pH	6.0
Brookfield Viscosity at 22°C	0.074 Pa.s
15 (Spindle No.2 at RPM)	(74 cps.)
Residual monomer	15.9%
Color (Gardner)	2

EXAMPLE II

In a manner similar to that described in Example 20 I using a 25.4 cm. (10 in.) wide, 20.3 cm. (8 in.) diameter drum, two additional samples were prepared.

	<u>A (g.)</u>	<u>B (g.)</u>
Mix 1 Sodium Persulfate	2.74	2.51
Deionized Water	11.8	10.9
25 Mix 2 Dimethyldiallyl ammonium chloride (63% in water)	274	251
Sulfonated Polystyrene (26% in water)	72	132

Analysis of the product as in Example I gave the following results:

	<u>A</u>	<u>B</u>
pH	2.5	2.5
5 Brookfield Viscosity	2.200 Pa.s (2200 cps.)	4.700 Pa.s (4700 cps.)
Residual monomer	11.0%	10.9%
Moisture	4.2%	5.0%

EXAMPLE III

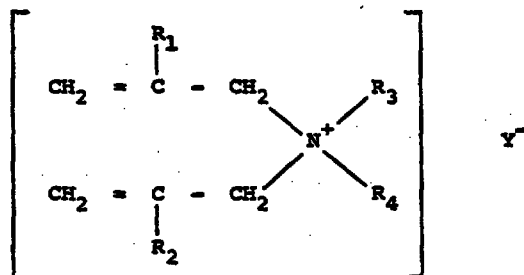
10 Using the procedure described in Example I,
additional products may readily be prepared using other
quaternary ammonium monomers as the sole monomeric
component or combined with other copolymerizable monomers
as, for example, acrylamide or acrylic acid. Similarly,
15 the monomeric components may be reacted in the presence
of other anionic polymers as, for example, polyvinyl
toluene sulfonate. Finally, if desired, solvents other
than water may be employed. Particularly useful is a
methanol/water mixture.



CLAIMS

1. A process for polymerizing a quaternary ammonium monomer in the presence of an anionic polymer so as to form a dry coacervate directly, which comprises:

- a) forming a solution dispersion or emulsion of
5 at least one quaternary ammonium monomer having the formula:



where R_1 and R_2 each represent hydrogen, methyl or ethyl; R_3 and R_4 each represent alkyl, aryl, cycloalkyl, hydroxyalkyl or alkoxyalkyl radicals having from 1 to 18 carbon atoms
10 each, and Y^- represents an anion; an anionic polymer which is a homo- or co-polymer of styrene sulfonate, alkali metal styrene sulfonate, acrylate or methacrylate, an alkali metal or ammonium salt of a high copolymer of styrene or substituted styrene with maleic acid, a water-soluble
15 copolymer of a styrene sulfonate, acrylate or methacrylate with acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, styrene, vinyl acetate, vinyl toluene, methyl acrylate, N-vinyl oxazolidinone or N-vinyl pyrrolidone, a homo- or co-polymer of a sulfoalkyl acrylate or carboxyalkyl acrylate or a carboxyalkyl cellulose ether or
20 starch, in an amount from 0.1 to 3 parts by weight per part of the monomer(s); solvent, and free-radical initiator;

- b) simultaneously polymerizing the monomers and drying the solution at a temperature above the boiling point
25 of the solvent; and

c) recovering the resultant dry product.

2. A process according to claim 1, in which the quaternary ammonium monomer is diallyl dimethyl, diallyl di-(beta-hydroxyethyl), dimethallyl dimethyl, dimethallyl
30 di-(beta-hydroxyethyl), diethallyl dimethyl or diethallyl di-(beta-hydroxyethyl) ammonium chloride, bromide, phosphate, or sulfate.



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3. A process according to claim 1 or 2, in which a copolymerizable monomer selected from styrene, aromatically substituted monomethyl and dimethyl styrene, methyl and lower alkyl acrylates, acrylic acid, acrylamide, methacrylonitrile, acrylonitrile and vinyl acetate is added to the solution in an amount up to about 50% by weight of the combined monomers.

4. A process according to any of claims 1 to 3 in which the anionic polymer is a carboxyalkyl cellulose ether, an alkali metal or ammonium salt of a high copolymer of styrene with maleic acid, an alkali metal or ammonium salt of a high copolymer of a substituted styrene with maleic acid, a homopolymer of an alkali metal styrene sulfonate, alkali metal acrylate, or alkali metal methacrylate, or a water-soluble copolymer of a said sulfonate, acrylate or methacrylate with acrylamide, methacrylamide, acrylonitrile, styrene, vinyl acetate, vinyl toluene or methacrylonitrile.

5. A process according to claim 1, in which the quaternary ammonium monomer is dimethyldiallyl ammonium chloride and the anionic polymer is sulfonated polystyrene.

6. A process according to any of claims 1 to 7 in which water, methanol, or a mixture thereof is used as the solvent.

7. A process according to any of claims 1 to 6, in which the simultaneous polymerizing and drying are carried out using a double drum drier at levels of 30



- 21 -

to 85% solids.

8. A process according to any of claims 1 to 7,
in which a buffer is added to the solution in an amount
of 20 to 200% by weight, based on the amount of the
5 initiator, and/or a redox initiator system is employed by
additionally incorporating a reducing agent in the feed
solution in an amount of 20 to 200% by weight, based on
the weight of the initiator.

9. A process according to claim 1 substantially
10 as described in any one of the Examples.

10. A dry polymeric product produced by the
process of any of the preceding claims.

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