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(72) Inventeurs/Inventors:
SHEEHAN, MICHAEL T., US;
SMITH, BRAD L., US

(73) Propriétaire/Owner:
TRIQUEST, L.P., US

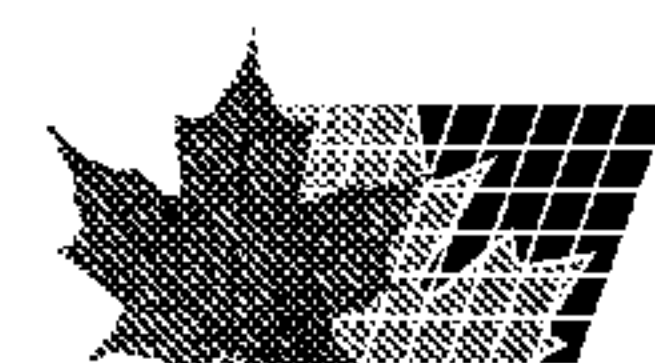
(74) Agent: SMART & BIGGAR

(54) Titre : PROCEDE POUR LA PREPARATION DE POLYMERES DE TYPE 4-HYDROXYSTYRENE A PARTIR DE
POLYMERES DE TYPE ACETOXYSTYRENE

(54) Title: PROCESS FOR THE PREPARATION OF 4-HYDROXYSTYRENE POLYMERS FROM 4-ACETOXYSTYRENE
POLYMERS

(57) Abrégé/Abstract:

Homopolymers and/or copolymers of 4-hydroxystyrene are produced by hydrolyzing homopolymers and/or copolymers of 4-acetoxystyrene with hydroxylamine.



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Abstract of the Disclosure.

Homopolymers and/or copolymers of 4-hydroxystyrene are produced by hydrolyzing homopolymers and/or copolymers of 4-acetoxystyrene with hydroxylamine.

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1 PROCESS FOR THE PREPARATION OF 4-HYDROXYSTYRENE
2 POLYMERS FROM 4-ACETOXYSTYRENE POLYMERS

3 Technical Field of the Invention.

4 - The present invention relates to the field of
5 polymers of 4-hydroxystyrene and, more particularly, to a
6 process for the preparation of such polymers. Still more
7 particularly, the present invention discloses a method of
8 preparing polymers of 4-hydroxystyrene by hydrolyzing
9 polymers of 4-acetoxystyrene with hydroxylamine.

10 Background of the Invention.

11 Homopolymers and copolymers of 4-hydroxystyrene,
12 a compound which is also known as p-vinylphenol, are well
13 known compositions which are used in the manufacturing of
14 metal treatment compositions, photoresists, epoxy resins
15 and epoxy resin curing agents. Polymers of
16 4-hydroxystyrene can be produced by polymerizing the
17 4-hydroxystyrene monomer. That monomer, however, is an
18 unstable compound under room temperature and must be stored
19 under low temperatures provided by refrigeration to prevent
20 its spontaneous polymerization. Even under low
21 temperatures, the monomer slowly polymerizes to low
22 molecular weight polymers.

23 Because of the instability of the
24 4-hydroxystyrene monomer, alternative routes for preparing
25 polymers of 4-hydroxystyrene have been utilized using
26 4-acetoxystyrene, the acetic acid ester of

1 4-hydroxystyrene, as the starting compound.
2 4-Acetoxystyrene is a stable monomer which can be readily
3 polymerized and copolymerized to low, medium and high
4 molecular weight polymers. Those processes involve the
5 polymerization of the 4-acetoxystyrene monomer, followed by
6 the hydrolysis of the phenolic ester groups of the
7 4-acetoxystyrene polymers to produce 4-hydroxystyrene
8 polymers.

9 Corson, et al., Preparation of Vinylphenols and
10 Isopropenylphenols, 23 J. Org. Chem. 544-549 (1958)
11 (hereinafter referred to as "Corson, et al."), discloses a
12 process for making 4-hydroxystyrene from phenol. According
13 to that process, phenol is acylated to
14 4-hydroxyacetophenone which is then acetylated to
15 4-acetoxyacetophenone. The latter compound is hydrogenated
16 to 4-acetoxyphenyl- methylcarbinol which is, then,
17 dehydrated to 4-acetoxystyrene. The 4-acetoxystyrene is
18 saponified to 4-hydroxystyrene using potassium hydroxide.

19 Packham, Chelating Polymers Derived from Poly-4-
20 hydroxystyrene, 1964 J. of the Chemical Society 2617-2624,
21 describes the hydrolysis of cross-linked poly
22 (4-hydroxystyrene) by refluxing the polymer in alkaline
23 aqueous dioxan. Arshady, et al., Phenolic Resins for
24 Solid-Phase Peptide Synthesis: Copolymerization of Styrene
25 and p-Acetoxystyrene, 12 J. of Polymer Science 2017-2025
26 (1974), describes the hydrolysis of copolymers of styrene

1 and p-acetoxystyrene to the vinylphenol polymer using
2 hydrazine hydrate in dioxane.

3 Chen, et al., A Morphological Analogue of
4 Japanese Lacquer. Grafting of p-Hydroxystyrene onto
5 Pullulan by Ammonium Persulfate Initiation in
6 Dimethylsulfoxide, 23 J. Polymer Science: Polymer Chem.
7 Ed. 1283-1291 (1985) describes the hydrolysis of
8 p-acetoxystyrene grafted pullulan to p-hydroxystyrene
9 pullulan with hydrazine hydrate. Nakamura, et al, Effect
10 of Substituent Groups on Hydrogen Bonding of
11 Polyhydroxystyrene Derivatives, 15 Polymer J. 361-366
12 (1983), describes the hydrolysis of poly(p-acetoxystyrene)
13 dissolved in acetone to poly(p-hydroxystyrene) with
14 hydrochloric acid.

15 U.S. Patent No. 2,276,138 discloses the ester
16 interchange reaction of poly (4-acetoxystyrene) in methanol
17 using sodium methylate. About 84 percent of the acetate
18 groups are removed by the interchange reaction.

19 U.S. Patent No. 3,547,858 discloses a process for
20 the production of polymers containing hydroxyl groups which
21 comprises subjecting a polymer of an ester of an
22 unsaturated alcohol to the action of a hydrolyzing agent
23 while the polymer is in the molten state. In the
24 hydrolysis reaction, the ester groups are replaced by
25 hydroxyl groups. Water and, preferably, a lower alkyl
26 alcohol can be used as a hydrolyzing agent.

1 U.S. Patent No. 4,544,704 discloses the
2 hydrolysis of a copolymer of styrene and
3 p-isopropenylphenylacetate with aqueous sodium hydroxide in
4 methanol and toluene using a small amount of
5 benzyltrimethylammonium chloride as a phase transfer agent.

6 U.S. Patent No. 4,678,843 discloses a process for
7 hydrolyzing polymers of 4-acetoxystyrene to polymers of
8 p-vinylphenol. Ammonia is the hydrolysis catalyst. The
9 4-acetoxystyrene polymer is dissolved in a solvent which is
10 miscible with water. Ammonia gas or ammonium hydroxide is
11 added to the solution and the hydrolysis reaction is
12 carried out at a temperature of about 50°C to about 150°C
13 for a time sufficient to hydrolyze the acetoxy groups to
14 phenol groups. At the end of the hydrolysis reaction, wet
15 carbon dioxide gas is introduced into the reaction solution
16 as a sparge below the solution surface to remove the
17 ammonium salt. The 4-hydroxystyrene polymer is recovered
18 for use as an organic solvent solution and can be recovered
19 as a solid by removal of all solvents by vacuum
20 distillation or by precipitating the polymer from the
21 solution.

22 U.S. Patent No. 4,689,371 discloses the
23 production of poly-(4-vinylphenol) by hydrolyzing polymers
24 of 4-acetoxystyrene by methanolysis with quaternary
25 ammonium hydroxides as the catalyst. The 4-acetoxystyrene
26 polymer is dissolved in a solvent which is miscible with
27 water. Ammonium hydroxide is added and the reaction is

1 carried out at a temperature of about 50°C to about 80°C
2 for a time sufficient to hydrolyze the acetoxy group. The
3 reaction product is heated to a temperature of about 50°C
4 to about 150°C to distill off methyl acetate and the
5 decomposition products of the quaternary ammonium
6 hydroxide. The 4-vinylphenol polymer can be used per se as
7 a solution or it can be recovered as a solid by removal of
8 all solvents by vacuum distillation or by precipitating the
9 polymer from the solution.

10 U.S. Patent No. 4,822,862 discloses the
11 production of homopolymers and copolymers of p-vinylphenol
12 by hydrolyzing homopolymers or copolymers of
13 4-acetoxystyrene with a base such as an alkali metal
14 hydroxide, an ammonium hydroxide, a quaternary ammonium
15 hydroxide or a water soluble amine. The hydrolysis
16 reaction occurs in an emulsion containing the polymers of
17 4-acetoxystyrene in water, without isolating the polymer.
18 The vinylphenol polymer is recovered from the emulsion by
19 acidifying the reaction mass and by filtering, washing and
20 drying the solid polymer or by coagulating the emulsion
21 with alum and, after acidification, recovering, washing and
22 drying the solid polymer.

23 U.S. Patent No. 4,857,601 discloses the selective
24 hydrolysis of copolymers of p-acetoxystyrene and dialkyl
25 muconates or alkyl sorbates to copolymers of p-vinylphenol
26 and dialkyl muconates or alkyl sorbates using acid or base
27 catalysts in an alcohol or water. The reactant copolymer

1 is slurried in an alcohol or aqueous base. The product is
2 dissolved in the alcohol or aqueous base and is recovered
3 as a solution.

4 U.S. Patent No. 4,868,256 discloses the
5 hydrolysis of polymers of 3,5-dibromo-4-acetoxystyrene to
6 polymers of 3,5-dibromo-4-acetoxystyrene with a base or an
7 acid such as tetramethyl ammonium hydroxide, aqueous NH_3 ,
8 NaOH , KOH , HCl , and H_2SO_4 .

9 U.S. Patent No. 4,877,843 discloses the selective
10 hydrolysis of copolymers of 4-acetoxystyrene and allyl
11 esters of unsaturated acids slurried in an alcohol or water
12 to copolymers of p-vinylphenol and allyl esters of
13 unsaturated acids with an acid or a base. If the reaction
14 is an alcoholysis reaction in alcohol, the polymer can be
15 recovered by precipitating and coagulating the polymer in
16 water. If the hydrolysis reaction is carried out in
17 aqueous base, the polymer can be recovered from solution by
18 precipitation with acid. The alcohols used are the one to
19 four carbon alcohols. The acids used are mineral acids and
20 organic acids with dissociation constants in aqueous
21 solution of less than 2. The bases used are alkali metal
22 hydroxides and alkoxides and quaternary ammonium
23 hydroxides.

24 U.S. Patent No. 4,898,916 discloses the
25 production of polymers of 4-vinylphenol by the acid
26 catalyzed transesterification of polymers of
27 4-acetoxystyrene in an alcohol. Polymers of

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1 4-acetoxystyrene are slurried in an alcohol and are
2 hydrolyzed to polymers of 4-vinylphenol in the presence of
3 a mineral or organic acid as well as Lewis acids which have
4 dissociation constants in aqueous solution of less than 2.
5 The alcohols used are one to four carbon alcohols. The
6 4-vinylphenol polymer product is recovered as a solution in
7 the alcohol to be used as such or it can be further
8 recovered as a solid from such solutions by utilizing well
9 known techniques.

10 U.S. Patent No. 4,912,173 describes the
11 hydrolysis of polymers of 4-acetoxystyrene suspended in
12 water in finely divided particulate form to polymers of
13 4-hydroxystyrene using aqueous nitrogen bases. The
14 nitrogen bases used are ammonia, primary, secondary or
15 tertiary water soluble amines and water soluble quaternary
16 ammonium hydroxides. When ammonium hydroxide is used as
17 the base, the suspended polymer product remains in
18 suspension and the water is removed by filtration,
19 decantation or centrifugation. After washing and drying
20 the polymer is ready for use. When other bases are used,
21 the particles are sometimes softened or solubilized.
22 Agglomerated polymers can be recovered by removing the
23 water, washing and drying, as described above. Solubilized
24 polymers are recovered after precipitation with acid.

25 U.S. Patent No. 4,962,147 discloses the
26 hydrolysis of poly(4-acetoxystyrene), in suspension in its
27 polymerization medium, to poly(4-hydroxystyrene) with

1 ammonia. Ammonia is preferably used as ammonium hydroxide.
2 It can also be used in gaseous form which is preferably
3 introduced below the surface of the aqueous reaction
4 medium. During the hydrolysis reaction, the suspended
5 polymer remains in suspension in solid finely divided form.

6 U.S. Patent No. 4,965,400 discloses the
7 hydrolysis of 3,5-disubstituted-4-acetoxystyrene to form
8 substituted 4-hydroxystyrene analogs. The hydrolysis
9 agents are NH_3 , NaOH , KOH , tetramethylammonium hydroxide,
10 HCl or H_2SO_4 .

11 In most of the above referenced processes, the
12 reaction was carried out with the reactants being in
13 solution or the 4-hydroxystyrene polymer product was
14 recovered as a solution. As a result, a large reactor
15 volume was required to accommodate the reaction.
16 Furthermore, in order to recover the product as a solid
17 from the solution, certain steps had to be used such as
18 precipitation with a nonsolvent, acidification of the salt
19 form of the polymer, spray drying or the like. Such steps
20 were time-consuming and uneconomical because they required
21 additives and/or energy.

22 According to the present invention, the
23 hydrolysis reaction is carried out in suspension and the
24 polymer product thereof is in suspension. The solid
25 product is intact and is easily and economically recovered
26 by well known techniques such as filtration.

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1 Another disadvantage of prior processes was that,
2 oftentimes, a satisfactory degree of hydrolysis of
3 copolymers of 4-acetoxystyrene to copolymers of
4 4-hydroxystyrene could not be achieved when the amount of
5 4-acetoxystyrene in the reactant polymer was less than
6 about fifty (50) weight percent of the total weight
7 attributed to 4-acetoxystyrene and the copolymer
8 polymerizable therewith. According to the present
9 invention, copolymers of 4-acetoxystyrene are hydrolyzed to
10 a satisfactory degree with hydroxylamine regardless of the
11 amount of 4-acetoxystyrene present therein.

12 These and other advantages of the present
13 invention will become apparent from the following
14 description.

15 Summary of the Invention

16 Homopolymers or copolymers of 4-acetoxystyrene
17 are hydrolyzed with hydroxylamine to produce homopolymers
18 or copolymers of 4-hydroxystyrene. The hydroxylamine is
19 available to the reaction as a free base or from an acid
20 salt of hydroxylamine which is neutralized with a base to
21 provide the hydroxylamine.

22 The reaction is carried out with the reactants
23 and the products being in suspension. The products are
24 solid intact particles which are easily and economically
25 recoverable by filtration or similar techniques.

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In the case of homopolymers, the reactants are hydrolyzed to a high degree, with the hydrolysis in most cases being more than 99.5 percent. In the case of copolymers, the reactants are hydrolyzed to a satisfactory degree, even in cases wherein the amount of 4-acetoxystyrene present in the reactant copolymer is substantially less than fifty (50) percent of the total weight attributed to 4-acetoxystyrene and the copolymer polymerizable therewith.

According to one aspect of the present invention, there is provided a process for producing a copolymer of 4-hydroxystyrene, comprising the step of reacting a copolymer of 4-acetoxystyrene in suspension with hydroxylamine.

According to another aspect of the present invention, there is provided a method of preparing a copolymer of 4-hydroxystyrene in suspension, comprising the step of hydrolyzing a 4-acetoxystyrene copolymer in suspension with hydroxylamine.

According to a further aspect of the present invention, there is provided a method of preparing a copolymer of 4-hydroxystyrene, comprising the step of interacting a solid polymer of 4-acetoxystyrene in suspension with hydroxylamine.

Detailed Description of the Invention

According to the present invention, a process for the production of polymers of 4-hydroxystyrene is disclosed by hydrolyzing polymers of 4-acetoxystyrene with hydroxylamine. In the process, the acetoxy groups of the 4-acetoxystyrene parts of the polymer are replaced with hydroxy groups to produce the 4-hydroxystyrene polymer. The

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process is used to convert homopolymers of 4-acetoxystyrene to homopolymers of 4-hydroxystyrene and copolymers of 4-acetoxystyrene to copolymers of 4-hydroxystyrene. The term polymer, as used herein, refers to a homopolymer or a
5 copolymer.

The reactant polymers of 4-acetoxystyrene are in suspension in the form of beads and are hydrolyzed by the hydroxylamine to produce polymers of 4-hydroxystyrene in suspension in the form of suspended intact solid
10 particulates whereby the use of solvents and the

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1 difficulties associated therewith are eliminated. The
2 solid polymer products are separated from the remaining
3 compounds of the reaction mass by filtration, decantation
4 or centrifugation and, after washing and drying, they are
5 ready for use. When a sufficient amount of hydroxylamine
6 is used, more than 98.0 percent and, in most cases, more
7 than 99.5 percent of the polymers of 4-acetoxystyrene are
8 hydrolyzed to the corresponding polymers of
9 4-hydroxystyrene.

10 The monomer 4-acetoxystyrene is a well known
11 compound which can be produced by the method described in
12 Corson et al, or by any
13 other method known to those skilled in the art. The
14 monomer readily polymerizes in solution, suspension,
15 emulsion or bulk using well known free radical catalysts
16 such as, for example, the peroxide and azo compounds. Such
17 polymerization can take place in the absence of comonomers
18 whereby the resultant product is a homopolymer or in the
19 presence of comonomers whereby the resultant product is a
20 copolymer. Examples of processes used for the production
21 of homopolymers or copolymers of 4-acetoxystyrene are the
22 processes disclosed in U.S. Patent Nos. 4,822,862,
23 4,912,173 and 4,962,147.

24 Other well known processes can also be used.

25 In the case of copolymerization, the most
26 commonly used comonomer is styrene. Other comonomers
27 include vinyltoluene; alpha-methylstyrene; ortho-, meta-,

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1 and para- chloro - and bromostyrene; the diene monomers
2 such as butadiene; the acrylate and methacrylate ester
3 monomers such as methyl acrylate, methyl methacrylate,
4 ethyl acrylate, butyl acrylate, butyl methacrylate and
5 2-ethylhexyl acrylate; acrylonitrile; methacrylonitrile;
6 the polymerizable acids such as acrylic acid, methacrylic
7 acid, maleic acid, fumaric acid and the like; and the
8 allyl ester comonomers described in U.S. Patent No.
9 4,877,843. It should be noted that, although copolymers of
10 4-acetoxystyrene and maleic anhydride are hydrolyzable by
11 hydroxylamine, such hydrolysis is not desirable for the
12 production of copolymers of 4-hydroxystyrene and maleic
13 anhydride because the hydroxylamine opens the rings of the
14 maleic anhydride.

15 Useful copolymers of 4-acetoxystyrene contain
16 about one (1) to about 99 parts by weight of
17 4-acetoxystyrene to about 99 to about one (1) part of
18 comonomer polymerizable therewith. Alternatively stated,
19 in useful copolymers, the amount of 4-acetoxystyrene is in
20 the range of about one (1) to about 99 weight percent of
21 the total weight attributed to 4-acetoxystyrene and the
22 comonomer polymerizable therewith. Preferred copolymers
23 contain about 25 to about 75 parts by weight of
24 4-acetoxystyrene to about 75 to about 25 parts by weight of
25 comonomer.

26 In the prior hydrolysis processes, copolymers
27 containing an amount of 4-acetoxystyrene of about fifty

1 (50) or more weight percent of the total weight attributed
2 to 4-acetoxystyrene and the comonomer polymerizable
3 therewith were hydrolyzed to a satisfactory degree.
4 Copolymers, however, containing a lesser amount of
5 4-acetoxystyrene were difficult to hydrolyze to a
6 satisfactory degree because the comonomer inhibited the
7 hydrolysis of the 4-acetoxystyrene parts of the polymer.
8 According to the present invention, 4-acetoxystyrene
9 copolymers containing an amount of 4-acetoxystyrene as low
10 as one (1) weight percent of the total weight attributed to
11 4-acetoxystyrene and the comonomer polymerizable therewith
12 are hydrolyzed to a degree wherein more than 98.0 percent
13 of the 4-acetoxystyrene parts of the copolymer are
14 hydrolyzed to 4-hydroxystyrene parts. The hydrolyzing
15 agent of the present invention is hydroxylamine.
16 Hydroxylamine is available to the reaction as a free base
17 or from an acid salt thereof such as hydroxylamine
18 hydrochloride or hydroxylamine sulfate which is neutralized
19 with aqueous ammonia or with any other base which does not
20 interfere with the hydrolysis of the polymer reactant with
21 the hydroxylamine. The stoichiometric amount of
22 hydroxylamine required is one (1) mole of hydroxylamine per
23 mole of 4-acetoxystyrene monomer present in the reaction.
24 An excess amount of about one hundred ten (110) to about
25 four hundred (400) mole percent is used, however, to ensure
26 satisfactory completion of the hydrolysis of the
27 4-acetoxystyrene parts. The hydroxylamine diffuses into

1 the solid reactant polymers of 4-acetoxystyrene and
2 interacts with the acetoxy parts thereof to convert them to
3 hydroxy parts.

4 In carrying out the hydrolysis reaction,
5 homopolymers or copolymers of 4-acetoxystyrene are
6 suspended as solid particles in water. The size of the
7 particles is in the range of about 0.01 to about 2.0
8 millimeters. A suspension agent which is inert to the
9 reaction may be used to assist the suspension. An example
10 of such agent is a polyacrylic acid solution having a
11 molecular weight of about 190,000, previously being known
12 by the trademark Acrysol A3, but presently being known by
13 the trademark Acumer 1530, manufactured by Rohm and Haas
14 Company and described in Rohm and Haas Company Technical
15 Bulletin FC-103, dated 1990 (hereinafter referred to as
16 "Acrysol A3"). The use of a suspension agent, however, is
17 not necessary. When hydroxylamine is used as a free base,
18 hydroxylamine which is preferably in an aqueous solution is
19 added to the suspension. When the hydroxylamine is
20 available to the reaction from a salt of the hydroxylamine,
21 that salt and the base for neutralizing such salt to obtain
22 the hydroxylamine are added to the suspension. The
23 reactants are continuously stirred by well known stirring
24 means to maintain the homogeneity of the suspension and are
25 heated to a temperature of about 50°C to about 95°C until
26 the desired amount of hydrolysis is obtained.

1 Depending on the degree of heating and the nature
2 of the reactants, the hydrolysis takes place in about one
3 (1) to about six (6) hours with more than 98.0 percent and,
4 in most cases, more than 99.5 percent of the
5 4-acetoxystyrene parts of the polymer being converted to
6 4-hydroxystyrene.

7 The reaction is carried out in a batch mode under
8 atmospheric or slightly above atmospheric conditions. In
9 order to obtain a polymer product with a desirable color,
10 the reaction is carried out under an oxygen-free
11 environment. Accordingly, nitrogen is provided to the
12 reaction mass to maintain such environment. It should be
13 understood, however, that an oxygen-free environment is
14 necessary only for the purpose of obtaining a desirable
15 polymer color and that the hydrolysis reaction described
16 herein can proceed, even in the presence of oxygen. In the
17 latter case, the polymers have a dark, undesirable color.

18 The 4-hydroxystyrene polymer products are white
19 solid particles which are intact and which do not dissolve
20 in the reaction mass. The solid particles are easily
21 separated from the reaction mass by filtration,
22 centrifugation or decantation. The separated particles are
23 washed and dried and are ready for use.

24 The following examples further illustrate the
25 invention but are not to be construed as limitations on the
26 scope of the invention contemplated herein.

1 Example 1

2 A two hundred fifty (250) milliliter round bottom
3 flask was fitted with a chilled water reflux condenser, a
4 thermowell with a thermocouple, a nitrogen purge fitting,
5 an overhead stirrer and an external heating mantel. One
6 hundred (100) grams of deionized water, four (4) grams of
7 a 25 weight percent aqueous polyacrylic acid solution (the
8 suspension agent previously referred to as Acrysol A3),
9 twenty (20) grams (0.12 moles) of a homopolymer of
10 4-acetoxystyrene having a weight average molecular weight
11 of 8750, and an aqueous solution of hydroxylamine
12 containing 9.46 grams of water and 9.46 grams (0.29 moles)
13 of hydroxylamine free base were added to the flask.

14 The reaction mixture was stirred to suspend the
15 4-acetoxystyrene polymer and heated to 83°C over a period
16 of two (2) hours and 45 minutes. At the end of that
17 period, a sample of the suspended polymer beads was taken
18 and analyzed by Fourier Transform Infrared Analysis (herein
19 referred to as "FTIR"). The analysis showed that the
20 sample was completely hydrolyzed to 4-hydroxystyrene
21 polymer.

22 The reaction mixture was cooled and the suspended
23 solid particles of the product were removed from the
24 reaction mass by filtration. Then, they were washed with
25 deionized water and dried overnight in a vacuum oven at
26 70°C.

1 Example 2

2 A two hundred fifty (250) milliliter round bottom
3 flask was fitted with a chilled water reflux condenser, a
4 thermowell with a thermocouple, a nitrogen purge fitting,
5 a magnetic stirrer and an external heating mantel. One
6 hundred (100) grams of deionized water, four (4) grams of
7 a 25 weight percent aqueous polyacrylic acid solution (the
8 suspension agent previously referred to as Acrysol A3),
9 fifteen (15) grams (0.093 moles) of a homopolymer of
10 4-acetoxystyrene having a molecular weight of 16,000, and
11 20.4 grams of hydroxylamine hydrochloride were added to the
12 flask.

13 The reaction mixture was stirred to suspend the
14 4-acetoxystyrene polymer and heated to 85°C over a period
15 of three (3) hours. At the end of that period, a sample of
16 the suspended polymer beads was removed from the flask and
17 was placed in methanol. The sample did not dissolve in
18 methanol, an indication that the sample was substantially
19 unreacted 4-acetoxystyrene polymer. The reaction mixture
20 was then treated with a minimum amount of 28 percent by
21 weight aqueous ammonia to raise its pH to 10. One hour
22 later, a sample of the polymer beads was taken and was
23 placed in methanol wherein it dissolved. A sample was then
24 analyzed by FTIR. The analysis showed that the sample was
25 completely hydrolyzed to 4-hydroxystyrene polymer. The
26 reaction mixture was cooled and the suspended solid
27 particles of the product were removed from the reaction

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1 mass by filtration. Then, they were washed with deionized
2 water and dried overnight in a vacuum oven at 70°C.

3 Example 3

4 A five hundred (500) milliliter round bottom
5 flask was fitted with a chilled water reflux condenser, a
6 thermowell with a thermocouple, a nitrogen purge fitting,
7 an overhead stirrer and an external heating mantel. One
8 hundred (100) grams of deionized water, four (4) grams of
9 a 25 weight percent aqueous polyacrylic acid solution (the
10 suspension agent previously referred to as Acrysol A3),
11 twenty (20) grams of a 25/75 mole ratio of a copolymer of
12 4-acetoxystyrene/styrene having a weight average molecular
13 weight of 20,700, and 32.65 grams of hydroxylamine sulfate
14 were added to the flask. The reaction mixture was treated
15 with a minimum amount of 28 weight percent by weight
16 aqueous ammonia to raise its pH to 10.

17 The reaction mixture was stirred to suspend the
18 4-acetoxystyrene/styrene copolymer and heated to 85°C over
19 a period of three (3) hours. At the end of that period, a
20 sample of the suspended solid bead was placed in methanol
21 and did not dissolve. One (1) hour and ten (10) minutes
22 later, another sample was analyzed by FTIR and the analysis
23 showed that the hydrolysis was not complete. Two (2) hours
24 later (six (6) hours and ten (10) minutes from the start of
25 the procedure), another sample of the suspended polymer
26 beads was taken and analyzed by FTIR. The analysis showed

1 that the sample was completely hydrolyzed to
2 4-hydroxystyrene copolymer.

3 The reaction mixture was cooled and the suspended
4 solid particles of the product were removed from the
5 reaction mass by filtration. Then, they were washed with
6 deionized water and dried overnight in a vacuum oven at
7 70°C.

8 Example 4

9 A five hundred (500) milliliter round bottom
10 flask was fitted with a chilled water reflux condenser, a
11 thermowell with a thermocouple, a nitrogen purge fitting,
12 an overhead stirrer and an external heating mantel. One
13 hundred (100) grams of deionized water, four (4) grams of
14 a 25 weight percent aqueous polyacrylic acid solution (the
15 suspension agent previously referred to as Acrysol A3), 15
16 grams of a 10/90 mole ratio copolymer of
17 4-acetoxystyrene/styrene having a weight average molecular
18 weight of 19,800, and 8.16 grams of hydroxylamine sulfate
19 were added to the flask. The pH of the mixture was raised
20 to 10 with a minimum amount of 28 weight percent by weight
21 aqueous ammonia.

22 The reaction mixture was stirred to suspend the
23 4-acetoxystyrene/styrene copolymer and heated to 87°C over
24 a period of 5.5 hours. At the end of that period, a sample
25 of the suspended polymer beads was taken and analyzed by
26 FTIR. The analysis showed that the sample was hydrolyzed

1 more than fifty (50) percent to 4-hydroxystyrene/styrene
2 copolymer.

3 The reaction mixture was cooled and the suspended
4 solid particles of the product were removed from the
5 reaction mass by filtration. Then, they were washed with
6 deionized water and dried overnight in a vacuum oven at
7 70°C.

8 Example 5

9 A three hundred (300) milliliter round bottom
10 flask was fitted with a chilled water reflux condenser, a
11 thermowell with a thermocouple, a nitrogen purge fitting,
12 a magnetic stirrer and an external heating mantel.
13 Seventy-five (75) grams of deionized water, three (3) grams
14 of a 25 weight percent aqueous polyacrylic acid solution
15 (the suspension agent previously referred to as
16 Acrysol A3), 15 grams of a 10/90 mole ratio copolymer of
17 4-acetoxystyrene/styrene having a weight average molecular
18 weight of 19,700, and 8.19 grams of hydroxylamine
19 hydrochloride were added to the flask. The pH of the
20 mixture was raised to 10 as described in the prior examples
21 with aqueous ammonia.

22 The reaction mixture was stirred to suspend the
23 4-acetoxystyrene polymer and heated to 85°C over a period
24 of 5.5 hours. At the end of that period, a sample of the
25 suspended polymer beads was taken and analyzed by FTIR.
26 The analysis showed that the sample was hydrolyzed more

1 than ninety (90) percent to 4-hydroxystyrene/styrene
2 copolymer.

3 The reaction mixture was cooled and the suspended
4 solid particles of the product were removed from the
5 reaction mass by filtration. Then, they were washed with
6 deionized water and dried overnight in a vacuum oven at
7 70°C.

8 Example 6

9 A two hundred fifty (250) milliliter round bottom
10 flask was fitted with a chilled water reflux condenser, a
11 thermowell with a thermocouple, a nitrogen purge fitting,
12 an overhead stirrer and an external heating mantel. One
13 hundred (100) grams of deionized water, four (4) grams of
14 a 25 weight percent aqueous polyacrylic acid solution (the
15 suspension agent previously referred to as Acrysol A3), ten
16 (10) grams of a 25/75 mole ratio copolymer of
17 4-acetoxystyrene/styrene having a molecular weight of
18 20,700, and 6.15 grams of hydroxylamine hydrochloride were
19 added to the flask. The pH of the mixture was raised to 10
20 as described in the previous examples.

21 The reaction mixture was stirred to suspend the
22 4-acetoxystyrene/styrene copolymer and heated to 89°C over
23 a period of four (4) hours. At the end of that period, a
24 sample of the suspended polymer beads was taken and
25 analyzed by FTIR. The analysis showed that the sample was
26 completely hydrolyzed to 4-hydroxystyrene/styrene
27 copolymer.

1 The reaction mixture was cooled and the suspended
2 solid particles of the product were removed from the
3 reaction mass by filtration. Then they were washed with
4 deionized water and dried overnight in a vacuum oven at
5 70°C.-

6 Example 7

7 A two hundred fifty (250) milliliter round bottom
8 flask was fitted with a chilled water reflux condenser, a
9 thermowell with a thermocouple, a nitrogen purge fitting,
10 an overhead stirrer and an external heating mantel. Eighty
11 (80) grams of deionized water, 3.2 grams of a 25 weight
12 percent aqueous polyacrylic acid solution (the suspension
13 agent previously referred to as Acrysol A3), 15 grams of a
14 50/50 mole ratio copolymer of 4-acetoxystyrene/ethyl
15 acrylate having a weight average molecular weight of
16 34,400, and 55.61 grams of hydroxylamine hydrochloride were
17 added to the flask. The pH of the mixture was raised to 10
18 as described in the previous examples.

19 The reaction mixture was stirred to suspend the
20 4-acetoxystyrene/ethyl acrylate copolymer and heated to
21 43°C for one (1) hour, 50°C for one (1) hour and 61°C for
22 two (2) hours. At the end of that period, a sample of the
23 suspended polymer beads was taken and analyzed by FTIR.
24 The analysis showed that the sample was completely
25 hydrolyzed to 4-hydroxystyrene/ethyl acrylate polymer.

26 The reaction mixture was cooled and the suspended
27 solid particles of the product were removed from the

1 reaction mass by filtration. Then, they were washed with
2 deionized water and dried overnight in a vacuum oven at
3 70°C.

4 While the invention is described with respect to
5 specific embodiments, modifications thereof can be made by
6 one skilled in the art without departing from the spirit of
7 the invention. The details of said embodiments are not to
8 be construed as limitations except to the extent indicated
9 in the following claims.

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CLAIMS:

1. A process for producing a copolymer of 4-hydroxystyrene, comprising the step of reacting a copolymer of 4-acetoxystyrene in suspension with
5 hydroxylamine.
2. The process according to claim 1, wherein the hydroxylamine is in the form of a free base.
3. The process according to claim 1, further comprising the step of deriving the hydroxylamine from an
10 acid salt of the hydroxylamine prior to the reacting step.
4. The process according to any one of claims 1 to 3, wherein more than 99.5 percent of the 4-acetoxystyrene parts of the 4-acetoxystyrene copolymer are converted to 4-hydroxystyrene parts.
- 15 5. The process according to any one of claims 1 to 4, wherein the reacting step is carried out under a temperature of about 50°C to about 95°C.
6. The process according to any one of claims 1 to 5, wherein the copolymer of 4-acetoxystyrene is in its solid
20 state.
7. The process according to any one of claims 1 to 6, wherein the copolymer of 4-acetoxystyrene is suspended in an aqueous medium.
8. The process according to any one of claims 1 to 7,
25 wherein the copolymer of 4-acetoxystyrene is in the form of particles ranging from about 0.01 to about 2.0 millimeters in size.

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9. The process according to any one of claims 1 to 8, wherein the hydroxylamine is in an aqueous solution.

10. The process according to any one of claims 1 to 9, further comprising the step of forming the copolymer of
5 4-hydroxystyrene in its solid state as a result of the reacting step.

11. A method of preparing a copolymer of
4-hydroxystyrene in suspension, comprising the step of
hydrolyzing a 4-acetoxystyrene copolymer in suspension with
10 hydroxylamine.

12. A method of preparing a copolymer of
4-hydroxystyrene, comprising the step of interacting a solid
copolymer of 4-acetoxystyrene in suspension with
hydroxylamine.

15 13. The method according to claim 12, wherein the
copolymer of 4-hydroxystyrene is solid.

14. The process according to any one of claims 1 to
10, wherein the reacting step is carried out in the absence
of oxygen.

SMART & BIGGAR
OTTAWA, CANADA

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