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3,032,518

PROCESS FOR POLYMERIZING VINYL MONOMERS IN THE PRESENCE OF POLYMERIC REDUCING AGENT AND MIXTURE OF GASES

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No Drawing. Filed Jan. 14, 1959, Ser. No. 786,696
19 Claims. (Cl. 260—17.4)

This invention relates to a process for the polymerization of certain alkyl esters of an acrylic acid in an aqueous medium at relatively low pH values in the presence of a polymeric reducing agent containing an alcoholic hydroxy group and utilizing either a ceric salt or a cobaltic salt in which the process is carried out in the presence of a mixture of inert gas and oxygen wherein said mixture contains from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized. More particularly, this invention relates to a process for polymerizing a polymerizable monomer such as butyl acrylate in the presence of a polymeric reducing agent such as a cellulosic material and as an oxidizing agent a salt such as ceric nitrate in the presence of a mixture of an inert gas such as nitrogen admixed with oxygen wherein the percent by volume of the oxygen based on the total volume of gases utilized may be varied between about 0.75% and 2.1%.

One of the objects of the present invention is to polymerize certain alkyl esters of an acrylic acid in the presence of certain polymeric reducing agents and as an oxidizing agent a cobaltic salt or a ceric salt utilizing in the sphere of polymerization a mixture of an inert gas and oxygen wherein the mixture contains from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized. This object and other objects of the present invention will be discussed in greater detail hereinbelow.

In the practice of the process of the present invention, a part of the essence of the invention resides in the utilization of a mixture of an inert gas and oxygen wherein said mixture contains from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized. Among the inert gases which may be used in the practice of the process of the present invention are nitrogen, carbon monoxide, argon, Freon, helium and the like. Air per se may be utilized, provided that it is enriched with an inert gas such as any one of those recited hereinabove in order that the balance of the percentage of oxygen by volume present in the mixture gases is maintained within the critical ratio recited hereinabove.

The process of the present invention is carried out in an aqueous medium at a pH not greater than about 3.5 and preferably at a pH between about 1 and 2. The adjustment of the pH of the system can be accomplished by utilizing an acidic material and preferably one which bears a relationship to the particular ceric salt or cobaltic salt being utilized. For instance, if one utilizes as the ceric salt, ceric sulfate, one may use as the acidic material sulfuric acid whereas if one were to utilize cobaltic nitrate as the oxidizing material, one could utilize, as the acidic material, nitric acid. It is not imperative that this correlation between acidic material and oxidizing salt be maintained, but the process is carried out with greater facility when this correlation is observed. Among the ceric salts which one may use in the practice of the process of the present invention are ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, ceric iodate, ceric salts of organic acids, e.g., cerium naphthenate and cerium linoleate, and the like. Ceric compounds which are

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capable of forming ceric salts in situ under the acidic conditions of the polymerization reaction such as ceric oxide and ceric hydroxide, and the like, may be used. Among the cobaltic salts which may be used in the practice of the process of the present invention are cobaltic nitrate, cobaltic sulfate, cobaltic perchlorate, cobaltic ammonium nitrate, cobaltic ammonium sulfate, cobaltic pyrophosphate, cobaltic ammonium pyrophosphate, and the like. Cobaltic compounds which are capable of forming cobaltic salts in situ under the acidic conditions of the polymerization reaction such as cobaltic hydroxide, and the like, may be used. These cobaltic salts and/or these ceric salts may be used either singly or in combination with one another. The amount of cobaltic compound and/or ceric compound which is used in the practice of the process of the present invention may be varied over fairly wide limits. For example, one may utilize from about 10^{-6} to 10^{-1} mol of cobaltic ion and/or ceric ion per mol of polymerizable monomer. Preferably, one would use between about 10^{-3} to 10^{-2} mol of cobaltic ion and/or ceric ion per mol of polymerizable monomer.

Among the alkyl esters of an acrylic acid which may be used in the practice of the process of the present invention are the methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, and octyl esters of acrylic acid, methacrylic acid, and the like. More particularly, one may utilize methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tertiary-butyl acrylate, amyl acrylate, octyl acrylate, ethylhexyl acrylate, methyl methacrylate, propyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, and the like. Although these alkyl esters may be utilized in which the alkyl group contains between 1 and 8 carbon atoms, it is generally preferred that said alkyl group contain between 2 and 4 carbon atoms.

A further part of the essence of the present invention resides in the utilization of a polymeric reducing agent which contains at least one alcoholic hydroxy group. Reducing agents which contain a great plurality of alcoholic hydroxy groups may additionally be utilized, and in fact, are preferred. Illustrative of this class of polymeric reducing agents are polyvinyl alcohol, partial esters of polyvinyl alcohol, as for example, formylated polyvinyl alcohol, acetylated polyvinyl alcohol, sulfated polyvinyl alcohol, nitrated polyvinyl alcohol, and the like; partial ethers of polyvinyl alcohol such as cyanoethylated polyvinyl alcohol; cellulosic materials including cotton, cellulosic papers, viscose, regenerated cellulose materials such as cellophane, cuprammonium rayon, partial esters of cellulose such as cellulose acetate, cellulose propionate, cellulose nitrate, and the like; partial ethers of cellulose such as methyl cellulose, ethyl cellulose, hydroxy ethyl cellulose, cyanoethylated cellulose, and the like; starch, partial ethers of starch as for example cyanoethylated starch; partial esters of starch, as for example acetylated starch, and the like. The amount of polymeric reducing agent of the class described which may be utilized in the practice of the process of the present invention may be varied between about 1% and 1000% by weight based upon the weight of the monomeric material and preferably from between about 10% and 300% by weight based on the total weight of the polymerizable monomer.

In carrying out the process of the present invention, atmospheric pressures are preferably utilized although each of sub-atmospheric and super-atmospheric pressures could be adopted. The temperature at which the process of the present invention may be carried out can be varied between about 0° C. and 50° C. regardless of whether a ceric salt or a cobaltic salt is chosen. For optimum results in the use of the ceric salts, temperatures between about 20 and 30° C. may be utilized whereas with the

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cobaltic salts, temperatures between about 0 and 10° C. should be used.

In order that the concept of the present invention may be more completely appreciated, the following examples are set forth primarily for the purpose of illustration in which all parts by weight unless otherwise indicated. Any specific recitation of quantities or conditions should not be interpreted as a limitation on the case except as is indicated in the appended claims.

Example 1

Into a suitable blending apparatus, there was introduced 500 parts of distilled water, 125 parts of n-butyl acrylate and 1.425 parts of Arquad 18 (an emulsifier, the active ingredient of which is octadecyl trimethyl ammonium chloride at 35% solids in water). The n-butyl acrylate used had been previously washed with 5% sodium hydroxide and distilled water in order to remove any possible traces of polymerization inhibitor present. After a thorough blending of the water, the monomer and the emulsifier has been accomplished, the aqueous emulsion was diluted with 1750 additional parts of distilled water. The resulting emulsion was then introduced into a suitable reaction vessel equipped with a purging tube for passing the mixture of the inert gas and the oxygen through the liquid. A piece of cellulosic paper weighing 10.9 parts was rolled and immersed in the emulsion. The system was then flushed or purged for 30 minutes with a mixture of air and carbon dioxide at a gas rate of 190 cc. per minute per liter of liquid wherein the gaseous mixture had an effective oxygen concentration of 1%. 125 parts of a 0.1 mol solution of ceric ammonium nitrate in 1 mol nitric acid was then added to the reaction vessel through a dropping funnel. When the ceric salt addition had been completed, the reaction was allowed to continue for two additional hours while continuously purging at the gas rate and oxygen concentration indicated hereinabove. Thereafter, the product was removed, washed thoroughly with water and dried to a constant weight in a force draft oven at 220° F. The pickup of monomer based on the initial weight of the paper amounted to 268%. No homopolymer coagulant or latex was obtained. The temperature of the system during reaction had been maintained at 24° C. $\pm 1^\circ$ C. The conversion of monomer to polymer in this reaction was calculated at 26.34%.

Example 2

Example 1 was repeated in every detail except that the reaction time after the ceric salt addition had been completed was only 40 minutes. The conversion of monomer to polymer was 5% and the percent of pickup of the polymer on the cellulosic paper was 51%.

Example 3

Example 1 was repeated in every detail except that the reaction was permitted to continue for one hour after the ceric salt addition had been completed. The conversion of monomer to polymer was 6.77% and the pickup of polymer by the cellulosic paper amounted to 69%.

Example 4

Example 1 was repeated in every detail except that the reaction time after the ceric salt addition had been completed was three hours. The conversion of monomer to polymer was 48.09% and the pickup of polymer by the cellulosic paper was 489%.

Example 5

The following are comparative examples intended to illustrate the effectiveness of the use of at least a small amount of oxygen admixed into the inert gas.

Example 1 was repeated in every detail except that the effective oxygen concentration in the carbon dioxide was 0. The percent of conversion of monomer to polymer was 25.59% and the pickup of polymer grafted onto the cellulosic paper was 261%. However, the conversion

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of monomer to homopolymer was 62.54%, representing a waste of the monomeric material which did not become grafted onto the paper. As a further illustration, Example 1 was repeated again in every detail except that the effective oxygen concentration was 0.26%. The conversion of monomer to polymer grafted onto the paper was 27.95% while the pickup weight on the paper was 284.5% while the conversion of monomer to homopolymer was 58.78%. Example 1 was again repeated in every detail except that the concentration of effective oxygen was held at 0.51%. The percent of graft polymer produced was 28.54% whereas the graft polymer pickup on the cellulosic paper was 290.6% but the conversion of monomer to homopolymer was 53.6%.

Example 6

This example is illustrative of the present invention and should be compared with the findings set forth in the various experimental runs recited in the preceeding comparative example.

Example 1 was repeated in every detail except that the concentration of oxygen in the inert gas mixture was 0.76%. The percent of graft polymer produced was 39.52% while the pickup weight of polymer on the cellulosic paper was 401%. The conversion of monomer to homopolymer, however, was 0%.

Example 7

Example 1 was repeated again in every detail except that the concentration of effective oxygen in the inert gaseous mixture was 1.4%. The percent of graft polymer converted from monomer onto the cellulosic paper was 7.27% whereas the pickup of polymer grafted onto the cellulosic paper was 73.9%. The conversion of monomer to homopolymer was 0%.

Example 8

Example 1 was repeated again in every detail except that the concentration of effective oxygen was held at 2.1%. The percent of polymer grafted onto the cellulosic paper was 2.87% while the polymer pickup on the paper was 29.2% but the conversion of monomer to homopolymer was 0%.

Example 9

This is another comparative example, not illustrative of the present invention inasmuch as Example 1 was repeated in every detail except that the effective oxygen concentration was held at 2.7%. The percent of polymer grafted onto the paper was 0.65% while the polymer pickup by the paper was 6.6% and the conversion of monomer to homopolymer was 0%.

Example 10

Example 1 was repeated in every essential detail with the following exceptions. In the place of the 125 parts of the n-butyl acrylate there was utilized 125 parts of methyl methacrylate and the cellulosic paper weighed 10.72 parts instead of 10.9 parts. The gas rate was 172 milliliters per minute per liter of liquid with an effective oxygen concentration of 1.4% by volume. The reaction time after the ceric salt addition was one hour and the monomer grafted onto the polymer displayed a pickup weight of 153%.

Example 11

Into a suitable reaction vessel equipped as in Example 1, there was introduced an aqueous solution of 125 parts of methyl acrylate dissolved in 2250 parts of distilled water whereupon a piece of cellulosic filter paper weighing 11.75 parts was rolled up and placed into the solution. A mixture of carbon dioxide and air was used to flush or purge the system for 30 minutes using a gas rate of 176 milliliters per minute per liter of liquid with an effective oxygen concentration of 1.8% by volume. 125 parts of 0.1 mol ceric ammonium nitrate in 1 mol nitric acid was introduced into the reaction system as in

Example 1. Upon the completion of the addition, the reaction was allowed to continue for one and one-third hours. The monomer pickup grafted onto the paper base amounted to 418%.

Example 12

Into the suitable reaction vessel equipped as in Example 1, there was introduced an emulsion of 125 parts of a mixture of n-butyl acrylate/acrylonitrile monomers, 80/20, respectively, emulsified in 2250 parts of distilled water using 1.425 parts of Arquad 18. While holding the charge at $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$, there was introduced a mixture of carbon dioxide and oxygen through the purging tube at a gas rate of 170 milliliters per minute per liter of liquid with an effective oxygen concentration of 1.2% by volume. A piece of cellulosic filter paper weighing 9.61 parts was rolled up and introduced into the emulsion. 125 parts of 0.1 mol ceric ammonium nitrate in 1 mol of nitric acid was added through a dropping funnel as in Example 1. After the addition of the ceric salt solution, the reaction was allowed to continue for three hours. The monomer pickup grafted onto the cellulosic base amounted to 322% based on the weight of the paper.

The process of the present invention may be carried out in aqueous solution or in aqueous emulsion. It can be seen from certain of the examples set forth hereinabove that the use of an emulsifier was either desirable or necessary. There is nothing critical about the choice of emulsifier and one skilled in the art will readily be able to select any one of a plurality of commercially available emulsifiers for the purpose when and as necessary. Further delineation of detail about the emulsifiers and quantities thereof to be utilized is considered to be unnecessary.

I claim:

1. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

2. A process comprising polymerizing, in an aqueous emulsion medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

3. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent comprising a ceric salt and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

4. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a polymeric reducing agent containing an alcoholic

hydroxy group, utilizing an oxidizing agent comprising a cobaltic salt and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

5. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, butyl acrylate in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

6. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, ethyl acrylate in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

7. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, methyl methacrylate in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

8. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a cellulosic material, utilizing an oxidizing agent from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

9. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of cotton, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

10. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of paper, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

11. A process comprising polymerizing, in the aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a regenerated cellulosic film, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of poly-

merization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

12. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 1 and 8 carbon atoms in the presence of a polyvinyl alcohol, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

13. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, butyl acrylate in the presence of a cellulosic material, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

14. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, ethyl acrylate in the presence of a cellulosic material, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

15. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, methyl methacrylate in the presence of a cellulosic material, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

16. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, butyl acrylate in the presence of paper, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by vol-

ume of oxygen based on the total volume of gases utilized.

17. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, ethyl acrylate in the presence of paper, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

18. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, methyl methacrylate in the presence of paper, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

19. A process comprising polymerizing, in an aqueous medium, at a pH not greater than 3.5, an alkyl ester of an acrylic acid selected from the group consisting of acrylic and methacrylic acids wherein said alkyl group contains between 2 and 4 carbon atoms in the presence of a polymeric reducing agent containing an alcoholic hydroxy group, utilizing an oxidizing agent selected from the group consisting of ceric salts and cobaltic salts and maintaining in the sphere of polymerization a mixture of an inert gas and oxygen, said mixture containing from about 0.75% and 2.1% by volume of oxygen based on the total volume of gases utilized.

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