

Description

This invention relates to a process for preparing crosslinked copolymers in the form of spheroidal beads having high crush strength and high resistance to osmotic shock.

Polymeric ion exchange resins in the form of spheroidal beads are used in many applications as chelating resins and as anion or cation exchangers. In many of these applications, the resins are subjected to stresses which cause substantial breakage in the beads. Said stresses may be mechanical, i.e., due to crushing or collisions between beads or the beads and their containers, or osmotic, such as when the beads are subjected to sudden or repeated changes in electrolyte concentration. The breakage of the ion exchange beads causes substantial losses in the efficiency of the ion exchange column and large costs in replacing the broken resins.

Gel-type (microporous) resins have especially poor osmotic properties and their use in applications where they are subject to sudden or repeated changes in their environment is greatly limited. As a result, macroporous resins are generally employed when good osmotic properties are essential. However, said macroporous resins have very poor mechanical properties and substantially lower ion exchange capacity than gel-type resins.

Various types of polymer beads and preparation process thereof are known in the art. US-A-4,152,496 discloses polymer beads of macroreticular copolymers having their macropores partially filled with a guest polymer.

GB-A-728 508 discloses the process for a preparation of ion exchange resins by first preparing seed beads and then causing them to imbibe a quantity of monomer which is later polymerized.

GB-A-1 418 560 on the other hand teaches preparation of foamable styrenic particles of uniform size. In view of the deficiencies of known ion exchange resins, it would be desirable to provide a gel type ion exchange resin having good osmotic and mechanical properties and high ion exchange capacity.

This object is attained by a process for preparing crosslinked copolymer beads the process comprising the imbibition of a monomer by polymer particles, the process being characterized by the following steps:

(a) forming a suspension of particles of a crosslinked polymer in a continuous aqueous phase, then
(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 40 to 95 weight percent of said monomers are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

This object is also attained by a process for preparing crosslinked copolymer beads comprising:

(a) forming a suspension of particles of a crosslinked or noncrosslinked polymer in a continuous aqueous phase, then

(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 20 to 95 weight percent of said monomer are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

The process of the present invention provides crosslinked spheroidal gel-type copolymer beads having a core/shell morphology, wherein said beads, when fully aminated to form an anion exchange resin, exhibit a crush strength of at least 700 g/bead and resistance to osmotic shock such that when the beads are contacted with 10 cycles of alternating 8 molar HCl and 8 M NaOH, no more than 15 percent by number of the beads are broken.

The ion exchange resins prepared by the method of this invention exhibit increased crush strengths and/or resistance to osmotic shock as compared to conventional gel-type ion exchange resins, while

retaining the high ion exchange capacity of conventional gel-type ion exchange resins.

The copolymer beads can be functionalized to form strong acid, weak acid, strong base, weak base or chelating type ion exchange resins, all of which will exhibit improved mechanical properties. For the purposes of this invention, the term ion exchange resin includes chelating resins as well as anion and cation exchange resins. Representative anionic, cationic or chelating groups are described hereinafter. Said resins retain other desired characteristics of gel-type resins, i.e., high capacity and good ion selectivity.

The term "core/shell morphology" as employed herein, means that the polymeric structure of the copolymer beads changes from the inside to the outside of the bead. Said changes in polymeric structure may be somewhat gradual from the inside to the outside of the bead, yielding a bead having a gradient of polymeric structure along any radius thereof. Alternatively, said changes in polymeric structure may be relatively abrupt as one moves along a radius of the bead outward from the center, yielding a bead having a relatively distinct core having one polymeric structure and a relatively distinct shell having another polymeric structure. The rate of said changes in the polymeric structure of the bead is not particularly critical as long as the bead exhibits the aforementioned crush strength and resistance to osmotic shock. Accordingly, as used herein, the terms "core" and "shell" refer to the polymeric structure of the inside and the outside of the bead, respectively, and the use of said terms should not be construed as meaning that the beads of this invention will exhibit a distinct interface between the polymers of the inside and the outside of the bead.

While it is not intended to limit the invention to any theory, it is believed that the difference in polymeric structure in the core and the shell is due to (a) differences in primary molecular weight between the polymers in the core and the shell, it being believed that the shell polymers will have a higher average primary molecular weight than the core polymers, (b) differences in the amount of crosslinking in the core and shell polymers, (c) interpenetration of the polymers of the shell and the core, or (d) differences in the amount of strain on the polymers of the core and the shell or combinations of (a), (b), (c) or (d). It is believed that the excellent mechanical or osmotic properties of the copolymer beads are due, at least in part, to one or more of the foregoing differences in structure between the shell polymers and the core polymers. In addition to the foregoing, the shell may comprise a polymer of different monomers than the polymers of the core, or the core may have a different porosity than the shell.

It is understood that in describing "core polymers" and "shell polymers" there is usually, if not always a significant amount of interpenetration of the polymers residing in the core and shell of the copolymer beads. Thus, the "core polymers" will extend somewhat into the shell of the bead, and vice versa. The terms "core polymers" and "shell polymers" and like terminology are employed herein to describe the polymeric material in the named portion of the bead in a general way without attempting to identify any particular polymers as "shell" or "core" polymers.

The aforementioned core/shell morphology of the copolymer beads is detectable using various known techniques for determining the structure of polymeric materials. In general, one or more of the following analytical techniques, among others, can be suitably employed to determine the core/shell morphology of the copolymer beads of the invention: dynamic thermal analysis, differential thermal analysis, osmium staining techniques, measurement of the respective refractive indices of the core and shell of the copolymer beads, conventional transmission electron microscopy, analytical transmission electron microscopy, scan transmission electron microscopy, and other suitable techniques. In addition, the beads often exhibit symmetrical strain patterns which are detectable by examination of the beads under polarized light. Often, the core/shell morphology of the copolymer beads is discernible simply from a visual inspection of the beads at no or low magnification, wherein the core is seen as an area of different color or as a darker or lighter area than the shell.

When functionalized to form an ion exchange resin, the core/shell morphology of these beads can often be seen by immersing a dry bead into water and determining the rate at which the bead becomes hydrated. Typically, the penetration of the shell portion of these beads by water is more rapid than the penetration of the core.

The beads prepared by the method of this invention preferably have a shell containing an average proportion of crosslinking monomers which is less than or equal to the average proportion of crosslinking monomers in the core. Beads of this type will have a shell which is softer (i.e., less friable and more elastic) than the core of the bead, thus allowing the bead to retain its shape and integrity yet permitting the bead to distribute energy throughout its structure when subjected to external stresses and pressures. By distributing the energy throughout its structure, it is believed that the crush strength and resistance to osmotic shock of said heterogeneous beads is greatly enhanced.

Alternatively, or in addition to the difference in the crosslink densities of the core and the shell, the polymers in the shell advantageously have a higher molecular weight than the polymers of the core. It is believed that said higher molecular weight of the shell polymers imparts mechanical strength to the bead and increases its resistance to osmotic shock.

The copolymer beads prepared by the method of this invention generally exhibit an effective crosslink density which is higher than the average proportion of the crosslinking monomers actually employed in the preparation of the core and the shell. The effective crosslink density is determined from the percent volume increase after swelling the beads with toluene by using a graph such as depicted on page 879 of the *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edition, published in 1966 by John Wiley and Sons,

Vol. 11, R. M. Wheaton and A. H. Seamster, "Ion Exchange". In general, the beads will exhibit an effective crosslink density of 1.5 to 5 times that predicted from the average proportion of cross-linking monomers employed in the polymerization of the core and shell. While the cause of this high effective crosslink density is not precisely known and it is not intended to limit the invention to any theory, it is believed that this effect is due to (a) entanglement of the macromolecules of the shell with the polymers of the core, (b) complete stretching of polymer chains in the core due to the imbibition of monomers which are subsequently polymerized therein, (c) high molecular weight of the shell polymers due to the polymerization thereof at high conversion as described hereinafter, or (d) a combination thereof.

The crush strength of the copolymer beads is excellent whether employed as an anion or cation exchange resin or as a chelating resin. However, the mechanical and osmotic properties of the resin vary somewhat according to the type and amount of active ion exchange groups contained thereon. Since the crush strength of a copolymer bead is generally lowest when fully aminated to form an anion exchange resin, the crush strengths of said fully aminated beads are used herein for the purposes of comparing the crush strengths of copolymer beads. By "fully aminated" is meant that at least 75, preferably at least 90, more preferably at least 95 percent of the repeating units in the bead to which amine groups can be attached bear amine groups. The degree of amination is often indicated from the ion exchange capacity of the aminated resin. Fully aminated gel-type ion exchange resins generally exhibit a dry weight capacity of at least 4.0 meq/g, usually at least 4.2 meq/g, although it is noted that capacity can also be influenced by other factors, such as the degree of crosslinking, the particular polymers present in the resin and the porosity of the resin.

"Crush strength", as that term is used herein, refers to the mechanical load required to break individual beads, given as a number average of about 30 testings. The crush strength of gel-type beads of this invention which have been fully aminated to form anion exchange resins is at least about 700 g/bead preferably at least 1000 g/bead, more preferably at least 1200 g/bead. By contrast, most previously known gel-type copolymer beads, when fully aminated to form anion ion exchange resins, exhibit crush strengths of less than 500 g/bead. When sulfonated to form strong acid-type cation exchange resins, the copolymer beads of this invention generally exhibit crush strengths of at least 1200 g/bead and usually over 1500 g/bead. Frequently, strong acid cation exchange beads of this invention will exhibit crush strengths of 2000 g/bead or more. By contrast, most previously known strong acid, gel-type ion exchange resins exhibit crush strengths of less than 1000 g/bead, usually less than 800 g/bead.

The functionalized beads (i.e., those to which active ion exchange sites have been attached) also exhibit excellent resistance to osmotic shock. Resistance to osmotic shock for the purposes of this invention is measured by subjecting a quantity of the functionalized beads to 10 cycles of alternate treatments with 8 M HCl and 8 M NaOH, wherein each treatment is separated by backwashings with deionized water. One full cycle of said treatment comprises (a) immersing a quantity of beads into 8 M HCl for one minute, (b) washing with deionized water until the wash water is neutral, (c) immersing the beads in 8 M NaOH for one minute and (d) washing the beads with deionized water until the wash water is neutral. All references to alternating treatments with 8 M HCl and 8 M NaOH contained herein refer to repeating cycles of this test. The resistance to osmotic shock of the beads is measured by the number of beads which remain unbroken after 10 cycles of the test. Typically, at least 85 percent of the functionalized beads of this invention will remain unbroken after 10 cycles of the osmotic shock test. Preferably, at least 90 percent, more preferably at least 95 percent, of the functionalized beads will remain unbroken after 10 cycles of the osmotic shock test.

Ion exchange resins comprising copolymer beads having a core/shell morphology as described hereinbefore to which active ion exchange sites are attached will generally exhibit crush strengths of at least 1000 g/bead and less than 15 percent breakage when tested for resistance to osmotic shock as described hereinbefore. Preferably, said ion exchange resin has a crush strength of at least 1200 g/bead and exhibits less than 10 percent breakage when subjected to the aforementioned osmotic shock test. Cation exchange resins comprising copolymer beads having the core/shell morphology as described hereinbefore which have been sulfonated will often have crush strengths of over 1500 g/bead and exhibit less than 5 percent breakage on the aforementioned osmotic shock test.

In addition, the ion exchange resins comprising copolymer beads having a core/shell morphology as described hereinbefore, when fully aminated or sulfonated, will exhibit ion exchange capacity comparable to those of conventional gel-type resins. It is noted, however, that ion exchange resins having somewhat lower ion exchange capacity can be prepared from the copolymer beads by intentionally underfunctionalizing the beads. However, the dry weight capacity of the anion exchange resins of this invention will generally be at least about 2.5, preferably at least 3.5, more preferably at least 4.0 meq/g. Cation exchange resins will generally exhibit a dry weight capacity of at least 2.5, preferably at least 4.5, more preferably at least 5.0 meq/g.

The copolymer beads can be prepared in any suitable size but advantageously have an average diameter in the range from about 50 to 7000 micrometers (μm), more preferably from about 200 to 2000 micrometers. Said beads are of the so-called "gel" or "microporous" type. In addition, the core of the beads may contain polymeric material which is water-soluble when ion exchange sites are attached thereto, all or a portion of which material may be extracted to form pores or channels in the beads. The preparation of such gel and extractable seed beads is described more fully hereinafter.

The copolymer beads are advantageously prepared by forming a suspension of swelled polymer particles and contacting said polymer particles with a monomer feed comprising at least one monomer under conditions such that free radicals catalyze the polymerization of said monomer to form copolymer beads having a core/shell morphology. Said polymerization is carried out as a suspension polymerization wherein the polymeric particles and the monomers to be polymerized are suspended in a suitable suspending medium which is generally an aqueous solution containing a suspension stabilizer.

The preparation of the polymer particles can be accomplished by any convenient procedure.

Said "second stage" polymer particles are advantageously prepared by suspending a plurality of seed particles in a continuous phase, swelling said seed particles with an initial monomer charge comprising mono- and polyethylenically unsaturated monomers and a free radical initiator and polymerizing the monomers within said seed particle until the conversion thereof to polymer is at least 20, preferably 40 to 95 weight percent of said monomer.

The seed polymer particles are advantageously prepared by the suspension polymerization of a monoethylenically unsaturated monomer and a polyethylenically unsaturated monomer to form a crosslinked polymer. The amount of polyethylenically unsaturated monomer employed is chosen such that the seed particle is sufficiently crosslinked to render it insoluble in the monomer feed but less than an amount which renders the seed unable to imbibe the monomers of the monomer feed. Generally, said seed particle is prepared using from about 0.05 to about 12.5 weight percent of crosslinking monomer. The polymerization is carried out using free radical initiators under conditions such that a plurality of crosslinked polymer particles is prepared. The polymerization is continued until the conversion of the monomers to polymer is at least 20, preferably at least 50, more preferably about 50 to 80 percent. According to this process, crosslinked polymer particles are prepared containing therein a quantity of unreacted monomers and a plurality of free radicals.

In the preparation of the seed polymer particles, a suspension is formed comprising polymeric seed particles in a continuous phase. Said seed particles advantageously comprise a crosslinked addition polymer but may be a crosslinked condensation polymer such as phenol/formaldehyde polymer. Said seed particles are crosslinked in an amount which renders them insoluble in the type and amount of monomers employed in later stages of the process but less than an amount which renders them unable to imbibe free radical initiators and monomers. In general, said seed particles are prepared using from about 0.05 to about 12.5, preferably from about 0.2 to 2.0, weight percent of a crosslinking monomer. Into the suspension containing the crosslinked seed particles is added a free radical initiator which is essentially insoluble in the continuous phase and which is imbibed by the seed particle. When the polymer particles are formed in this manner, the seed particle has imbibed said free radical initiator.

According to the invention, a polymer particle is employed which is advantageously prepared by suspending a plurality of polymeric seed particles in an appropriate suspending medium, imbibing into said particles a free radical-containing initial monomer charge and polymerizing the monomers in the initial monomer charge until the conversion thereof into polymer is at least 20 to 95 percent, preferably at least 40 percent. These particles will then comprise two polymeric networks. In this process, the seed is advantageously an addition polymer but may be a condensation polymer such as a phenol/formaldehyde polymer. Said seed polymer may be crosslinked or noncrosslinked, provided that said seed particle is insoluble in the type and amount of monomers employed in the initial monomer charge. Within the aforementioned broad limits, the amount of crosslinking in the seed particle is chosen such that the seed can imbibe the desired amount of monomers in the initial monomer charge. In general, increased amounts of crosslinking will decrease the amount of the initial monomer charge which can be imbibed by the seed particles. Advantageously, the seed particles are prepared using less than about 10 weight percent of a crosslinking monomer, preferably from 0.1 to 1.0 weight percent of a crosslinking monomer.

The initial monomer charge employed in the preparation of the polymer particles contains both mono- and polyethylenically unsaturated monomers which, when polymerized, form a crosslinked polymer. The amount of crosslinking monomer employed herein is generally sufficient to render the beads, when functionalized, insoluble in water and to impart physical integrity and mechanical strength to the beads. In general, the initial monomer charge will comprise from 0.5 to 25, preferably from 1 to 12, weight percent of a crosslinking monomer. In addition, said initial monomer charge will advantageously comprise from 0.005 to 2 weight percent of a free radical initiator.

To reduce the formation amount of offsize particles or "fines", the relative proportions of seed particles and initial monomer charge are chosen such that at least 75 weight percent, preferably essentially all of the initial monomer charge is imbibed into the seed particles. Said proportions will, of course, vary with the size of the seed particle and the degree of crosslinking in the seed particle. For example, a seed particle of relatively small size will generally imbibe proportionately less monomer than larger particles of similar crosslink density. Similarly, high crosslink density in the seed particle limits the particles' ability to imbibe monomers. In general, the seed particles will generally imbibe from 0.5 to 19, preferably from 1.5 to 9, times their weight of the initial monomer charge. The swelled polymer particle advantageously comprises from 5 to 90, preferably from about 10 to about 70, more preferably from about 25 to about 50, weight percent of the weight of the product copolymer bead.

The prepared polymer particle is suspended in an appropriate suspending medium. In general, said suspending medium is a liquid in which both the polymer particle and the monomers to be contacted

therewith are insoluble. Said suspending medium is typically an aqueous solution containing from 0.1 to 1.5 weight percent of a suspension stabilizer, but for the polymerization of water-soluble monomers, may be an organic compound. Suitable suspension stabilizers include gelatin, polyvinyl alcohol, sodium methacrylate, carboxymethylmethylcellulose, as well as surfactants such as sodium lauryl sulfate, sulfonated polystyrenes and the like. In addition, the suspension may suitably contain polymerization inhibitors, dispersants, and other materials known to be advantageously employed in the suspension polymerization of ethylenically unsaturated monomers.

The suspension is then contacted with a monomer feed comprising at least one ethylenically unsaturated monomer under conditions such that the free radicals contained in the polymer particles catalyze the polymerization of said monomer feed. Copolymer beads prepared according to this process usually exhibit a core/shell morphology. Generally, the crosslinked polymer particles will reside mainly in the core of the polymer beads prepared by this process, while the polymers formed from the monomer feed will generally reside in the shell of the copolymer bead. However, it is believed that interpenetration occurs between the polymers of the core and those derived from the monomer feed. Accordingly, the interface between the core and shell may be gradual rather than sharp.

Advantageously, the suspension is heated to a temperature sufficient to initiate the free radical polymerization of ethylenically unsaturated monomers. To the heated suspension is then added a monomer feed under conditions such that essentially all polymerization of said monomers is initiated by the free radicals contained in the polymer particles. Preferably, the ratio of the weight of polymer to the combined weight of polymer and monomer present at any time during the addition of the monomer feed (instantaneous conversion) is at least about 20, more preferably at least 50 percent.

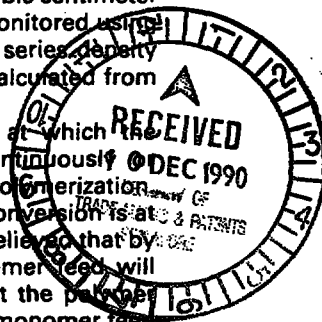
Instantaneous conversion may be measured in various ways, with the particular means of monitoring the reaction left to the practitioner as a matter of choice. The reaction may be monitored chemically, such as by taking periodic infrared spectra of the reaction mixture as the reaction proceeds to monitor the conversion of the carbon-carbon double bonds of the monomer to polymer. The difference in density between the unreacted monomers and the polymers can also form a basis for monitoring the mixture. For example, a reaction mixture containing about 1.35 g of styrene monomer per gram of water will have a density of about 0.936 g per cubic centimeter before polymerization and about 1.04 g per cubic centimeter after polymerization (at about 96 percent conversion). Said differences in density can be monitored using gravimetric techniques or preferably by the use of a nuclear densitometer such as an SG series density gauge sold by Texas Nuclear. More simply, the instantaneous conversion can be readily calculated from the heat of polymerization.

The instantaneous conversion is advantageously controlled by adjusting the rate at which the monomer feed is added to the suspension. Said monomer feed may be added continuously or intermittently to the suspension at constant or various rates during the course of the polymerization. Advantageously, the rate of addition of the monomer feed is such that the instantaneous conversion is at least 20, preferably at least 50 percent at all times during the polymerization reaction. It is believed that by maintaining the instantaneous conversion at higher levels, the monomers in the monomer feed will polymerize to form higher molecular weight polymers which are highly entangled about the polymer particles. It is believed that the primary molecular weight of the polymers formed from the monomer feed according to this semi-continuous process are higher than that of polymers prepared according to conventional suspension polymerization processes by as much as a factor of 10, or more.

The monomer feed may contain a proportion of a polyethylenically unsaturated monomer or may consist entirely of monoethylenically unsaturated monomers. It is noted here that the monomers in the monomer feed may vary with time, in the proportion of crosslinking monomer contained therein or in the type of monomers employed or both. Advantageously, the monomer feed will, on the average, contain a proportion of crosslinking monomers no greater than the average proportion of crosslinking monomer in the polymeric particles. More advantageously, a lower proportion of the crosslinking monomer is employed in the monomer feed, yielding a heterogeneous copolymer bead having a higher proportion of crosslinking in the core and a lower proportion of crosslinking in the shell.

In order to ensure that the polymerization of the monomers in the monomer feed is essentially completely catalyzed by the free radicals contained in the polymeric particles, the monomer feed advantageously contains essentially no initiators. In addition, the continuous phase is also essentially free of initiators. One or more free radical inhibitors which are soluble in the continuous phase are advantageously employed to inhibit the formation of free radicals in said continuous phase. Accordingly, while it is not intended that this invention be bound by any theory, it is believed that the generation of free radicals will occur almost exclusively within the free radical polymer matrix. Therefore, it is believed that this formation of free radicals inside the free radical matrix will tend to cause the monomers of the monomer feed to form high molecular weight chains which are highly entangled about the polymeric structure of the free radical matrix.

After all the monomer feed is added to the reaction mixture, the reaction mixture is maintained at the polymerization temperature until the polymerization reaction is essentially complete. Advantageously, the polymerization temperature is increased about 20°–30°C during the final stages of the polymerization reaction to "finish off" the reaction. The resulting polymer beads are recovered via conventional means such as filtration and advantageously dewatered and dried.



The monomers employed in the preparation of the free radical matrix (i.e., those employed in the formation of the seed particle and initial monomer charge, if any) and the monomer feed are advantageously suspension polymerizable ethylenically unsaturated monomers. Such suspension polymerizable monomers are well known in the art and reference is made to *Polymer Processes*, edited by Calvin E. Schildknecht, published in 1956 by Interscience Publishers, Inc., New York, Chapter III, "Polymerization in Suspension" by E. Trommsdorff and C. E. Schildknecht, pp. 69—109 for purposes of illustration. In Table II on pp. 78—81 of Schildknecht are listed diverse kinds of monomers which can be employed in the practice of this invention. Of such suspension polymerizable monomers, of particular interest herein are the water-insoluble monomers including the monovinylidene aromatic such as styrene, vinyl naphthalene, alkyl substituted styrenes (particularly monoalkyl substituted styrenes such as vinyltoluene and ethyl vinylbenzene) and halo-substituted styrenes such as bromo- or chlorostyrene, the polyvinylidene aromatic such as divinylbenzene, divinyltoluene, divinyl xylene, divinyl naphthalene, trivinylbenzene, divinyl diphenyl ether, divinyl diphenyl sulfone and the like; esters of α,β -ethylenically unsaturated carboxylic acids, particularly acrylic or methacrylic acid, such as methyl methacrylate, ethyl acrylate, diverse alkylene diacrylates and alkylene dimethacrylates, and mixtures of one or more of said monomers. Of said monomers, the monovinylidene aromatics, particularly styrene or a mixture of styrene with a monoalkyl substituted styrene; the polyvinylidene aromatics, particularly divinylbenzene; esters of α,β -ethylenically unsaturated carboxylic acids, particularly methyl methacrylate or mixtures containing methylmethacrylate, particularly a mixture of styrene and divinylbenzene or styrene, divinylbenzene and methyl methacrylate are preferably employed herein.

Also included within the polymerizable monomers useful herein are those monomers which form a solution with a liquid, generally water, wherein the resulting solution is sufficiently insoluble in one or more other liquids, generally a water-immiscible oil or the like, such that the monomer solution forms droplets upon its dispersion in said other liquid. Representative of such monomers are water-soluble monomers which can be polymerized using conventional water-in-oil suspension (i.e., inverse suspension) polymerization techniques such as described by US—A—2,982,749 including ethylenically unsaturated carboxamides such as acrylamide, methacrylamide; aminoalkyl esters of unsaturated carboxylic acids and anhydrides; ethylenically unsaturated carboxylic acids, e.g., acrylic or methacrylic acid, and the like. Preferred of such monomers for use herein are the ethylenically unsaturated carboxamides, particularly acrylamide, and the ethylenically unsaturated carboxylic acids, particularly acrylic or methacrylic acid.

In addition to the aforementioned ethylenically unsaturated monomers, the seed particles employed in the preparation of the polymer particles can also comprise a crosslinked condensation polymer such as phenol/formaldehyde resin. In general, said condensation polymers must be able to imbibe the free radical initiators and the monomers of the initial monomer charge, if any, and the monomer feed.

The monomer feed may contain different monomers than those used to prepare the polymer particle. For example, the monomer feed may comprise styrene, divinylbenzene and methylmethacrylate and the polymer particle may comprise primarily styrene/divinylbenzene polymers. When the polymer particle is prepared by imbibing a catalyst containing initial monomer charge into a seed particle, the seed particle may contain different monomers than the initial monomer charge. Similarly, the composition of the polymers of the polymeric shell may be varied from the inside to the outside of the shell by changing the composition of the monomer feed during the course of the polymerization thereof. The monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the produced polymer beads.

Because the polymers contained in the polymer beads can be widely varied, the beads can be readily tailored for specific end-uses.

Beads having an extractable seed are advantageously prepared using a lightly crosslinked or noncrosslinked seed particle which is insoluble in the amount and type of monomers used in the preparation of the polymeric particles and the initial monomer charge, but when active ion exchange sites are attached thereto, become water-soluble and are extractable from the bead when immersed in water. Beads prepared having such extractable seeds will contain small voids when all or a portion of the seed is removed therefrom.

Copolymer beads having relatively uniform size are prepared according to the process of this invention by using uniform size seed particles. Uniform size seed particles are prepared by screening the seed particles or by preparing the seed particles using a process which produces polymer particles of uniform size, such as those taught in published European Patent Application Nos. 0005619 and 0051210. Advantageously, at least 80 percent of the seed particles employed to prepare the copolymer beads of this invention are greater than 0.5 and no more than 1.5 times the weight average particle size of the seed particles.

The size of the copolymer beads is advantageously in the range from about 50 to 2000 micrometers (μm), preferably from about 200 to 1200 μm . Control of the size of the beads is achieved primarily by controlling the size and crosslinking in the seed particles employed, if any, and the amount of monomers employed in the monomer feed. The seed particles can range in size from very small particles, i.e. about 10 μm , to larger particles having a diameter of 750 μm or more. Preferably the size of the seed particle is in the range from 100 to 750 μm in diameter.

The polymer beads are converted to anion or cation exchange beads using techniques well-known in

the art for converting crosslinked addition polymers of a mono- and polyethylenically unsaturated monomer to such resins. In the preparation of weak base and chelating resins from poly(vinylaromatic) copolymer beads such as crosslinked polystyrene beads, the beads are advantageously haloalkylated, preferably halomethylated, most preferably chloromethylated, and the ion active exchange groups subsequently attached to the haloalkylated copolymer. Methods for haloalkylating the crosslinked addition copolymers and the haloalkylating agents included in such methods are also well known in the art. Illustrative of such are US—A—(5) 2,642,417; 2,960,480; 2,597,492; 2,597,493; 3,311,602 and ion exchange by F. Helfferich, published in 1962 by McGraw-Hill Book Company, N.Y. Typically, the haloalkylation reaction consists of swelling the crosslinked addition copolymer with a haloalkylating agent, preferably bromomethylmethyl ether, chloromethylmethyl ether or a mixture of formaldehyde and hydrochloric acid, most preferably chloromethylmethyl ether and then reacting the copolymer and haloalkylating agent in the presence of a Friedel-Craft catalyst such as zinc chloride, iron chloride and aluminum chloride.

Generally, ion exchange beads are prepared from the haloalkylated bead by contacting said bead with a compound reactive with the halogen of the haloalkyl group and which, upon reaction, forms an active ion exchange group. Such compounds and methods for preparing ion exchange resins therefrom, i.e., weak base resins and strong base resins, are well known in the art and US Patents 2,632,000; 2,642,417; 2,632,001; 2,992,544 and F. Helfferich are illustrative thereof. Typically, a weak base resin is prepared by contacting the haloalkylated copolymer with ammonia, a primary amine or a secondary amine. Representative primary and secondary amines include the methyl amine, ethyl amine, butyl amine, cyclohexyl amine, dimethyl amine, diethyl amine and the like. Strong base ion exchange resins are prepared using tertiary amines such as trimethyl amine, triethyl amine, tributyl amine, dimethylisopropanol amine, ethylmethylpropyl amine or the like as aminating agents.

Amination generally comprises heating with reflux a mixture of the haloalkylated copolymer beads and at least a stoichiometric amount of the aminating agent, i.e., ammonia or the amine, to a temperature sufficient to react the aminating agent with the halogen atom attached to the carbon atom α to the aromatic nucleus of the polymer. A swelling agent such as water, ethanol, methanol, methylene chloride, ethylene dichloride, dimethoxymethylene or combinations thereof is optionally, but advantageously employed. Conventionally, amination is carried out at conditions such that anion exchange sites are uniformly dispersed throughout the entire bead. Such complete amination is generally obtained within 2 to 24 hours at reaction temperatures between 25° and about 150°C.

Methods for converting copolymer beads other than poly(vinylaromatic) beads to anion exchange resins are illustrated in Helfferich, pp. 48—58. In addition, methods for attaching other types of anion exchange groups, such as phosphonium groups, to copolymer beads are described therein.

Generally, chelate resin beads are prepared from the haloalkylated polymer by attaching thereto the chelate active groups, e.g. carboxyl groups. Illustrative of the well-known methods for preparing chelate resins is US—A—2,888,441 wherein the haloalkylated polymer is aminated by techniques hereinbefore described and the aminated copolymer subsequently reacted with suitable carboxyl containing compound such as chloroacetic acid. Alternatively, the haloalkylated polymer can be directly reacted with (1) a suitable amino acid, such as diamino acetic acid or glycine, or (2) an amino pyridine such as 2-picolyamine and N-methyl-2-picolyamine to form a chelate resin.

Cation exchange resin beads can be prepared using techniques well known in the art for converting the crosslinked addition copolymer of mono- and polyethylenically unsaturated monomers to a cation exchange resin. Illustrative of such methods of preparing cation exchange resin are US Patents 2,500,149; 2,631,127; 2,764,564 and F. Helfferich. In general, the cation exchange resins useful herein are strong acid resins which are prepared by sulfonating the copolymer beads. While the sulfonation may be conducted neat, generally, the bead is swollen using a suitable swelling agent and the swollen bead reacted with the sulfonating agent such as sulfuric or chlorosulfonic acid or sulfur trioxide. Preferably, an excess amount of the sulfonating agent, for example, from 2 to 7 times the weight of the copolymer bead, is employed. The sulfonation is conducted at a temperature from 0° to 150°C.

Because of the improved strength of the resins of this invention, they can be employed under harsher conditions than previous gel-type resins. For example, the gel-type ion exchange resins can be advantageously employed in condensate polishing operations which now employ macroporous resins, or in mining operations, wherein high capacity resins with good mechanical and osmotic properties are needed, as well as in other uses for which conventional ion exchange resins are now employed.

The following examples are intended to illustrate the invention and are not intended to limit the scope thereof in any way. All parts and percentages are by weight based on the weight of the organic and water phases unless otherwise noted.

EP 0 101 943 B1

Example 1

Into a 3 liter, stainless steel reactor equipped with an agitator, 35 parts by weight of 0.3 percent crosslinked styrene/divinylbenzene copolymer seed having a particle size of 150–300 μm and sufficient water to suspend the seed particles were added. Further added, with agitation, was an initial monomer charge comprising 1.9 parts divinylbenzene (DVB), 63 parts styrene, 0.036 part t-butylperoctoate (TBPO) (based on the total weight of all monomers employed), 0.025 part t-butylperbenzoate (TBPB) (based on the total weight of all monomers employed), 0.15 part carboxymethyl methylcellulose (CMMC) and 0.15 part sodium dichromate. Water was then added in an amount such that the weight phase ratio was 1.0 after the addition of the monomer feed. The reaction mixture was then heated to 70°C and maintained at 70°C for 3 hours, at which time a monomer feed of 98.5 percent of styrene and 1.5 percent of DVB was begun. The monomer feed was fed at a constant rate into the reactor over a 10-hour period until said monomer feed comprised 71.4 percent by weight of the combined weight of the initial charge and the monomer feed. The reaction mixture was heated at 90°C for an additional 1.5 hours and then raised to 100°C for approximately 1.5 hours.

A portion of the copolymer beads thus obtained were dried and a 20 ml portion was measured into a column. The beads were then immersed in toluene and the change in volume of the beads measured. From the change in volume, the effective crosslink density was determined using a graph such as depicted on page 879 of the *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd. Ed., published in 1966 by John Wiley and Sons, Vol. II, R. M. Wheaton and A.H. Seamster, "Ion Exchange". The effective crosslink density (toluene swell crosslink percent) is shown in Table I following.

A 100 g portion of the copolymer beads were chloromethylated by reacting the beads with an excess of chloromethylmethyl ester in the presence of ferric chloride. The chloromethylated beads were then reacted with trimethylamine to form a strong base anion exchange resin bearing a plurality of quaternary ammonium ions. The anion exchange resin was then tested for percent original spheres, crush strength, resin size, osmotic shock resistance, dry weight capacity, and water retention capacity. The results are as given in Table I.

The crush strength of the anion exchange resin of this and the following examples was determined by testing about 30 beads using a Chatillon Scale, Model DPP-1KG. The force, in grams, required to fracture each individual bead is recorded, with the crush strength reported as the average of about 30 such testings.

The number percent of the resin beads having flawless spheres (percent original spheres) was evaluated placing a small amount of the resin in a petri dish. A microscope having a camera mounted thereon was adjusted until about 200 resin beads fell within the vision field of the camera. A photograph was then taken. From the photograph, the total number of beads were counted, the total number of broken or cracked counted, and the number percent of spherical beads calculated.

The size of the resin beads, when swollen with water, was determined by screen analysis.

The resistance to osmotic shock of the resin beads was tested using the procedure described hereinbefore wherein the beads are contacted with 10 cycles of alternating 8 M HCl and 8 M NaOH, with the results reported as the number percent of beads which remain unbroken after 10 cycles of the test.

The dry weight capacity of the resin was determined by drying a sample of the resin in the chloride form under an infrared lamp on a moisture balance until a constant weight was obtained. The dried resin was then cooled to room temperature in a closed vessel. About 0.5 gram of the dried resin was weighed into a suitable flask. The resin was then heated to 70°–80°C with 100 ml of distilled water, 4 ml of sulfuric acid and 5 g Na_2SO_4 for 5 minutes. The mixture was cooled and titrated with 0.1 N AgNO_3 to an endpoint as indicated using a chloride sensitive electrode. The dry weight capacity was then reported as meq/g of resin.

Example 2

The procedure of Example 1 was again repeated with 285 μm seed particles and 0.3 part CMMC. After the reactor was loaded with the seed particles and initial monomer charge, the suspension was heated to 80°C for 2.5 hours. The monomer was 100 percent styrene, fed over a 6 hour period commencing 2.5 hours after the resin mixture reached 80°C. The reaction mixture was heated for 3 additional hours at 80°C after all the monomer feed was added, and then finished off at 100°C for 2 hours. The beads thus prepared were chloromethylated and aminated in the manner described in Example 1 and the properties of the aminated beads are as reported in Table I.

Example 3

The procedure of Example 1 was again repeated using a 0.3 weight percent crosslinked seed having an average particle size of 206 μm . The sodium dichromate used in this example was increased to 0.3 part. The reaction mixture was heated to 80°C for 3.5 hours, at which time the monomer feed comprising 98.5 percent styrene and 1.5 percent DVB are added over a 6 hour period. Following the addition of the monomer feed, the reaction mixture was held at 80°C for 3 more hours and then finished off at 100°C for 2 hours. The beads thus obtained were chloromethylated and aminated as in Example 1 and the properties thereof are described in Table I.

Example 4

The procedure of Example 3 was repeated, this time using 35 parts of 0.3 percent crosslinked seed particle with a particle size between 250 and 300 μm , 6.5 parts DVB and 58.4 parts styrene in the initial charge to the reaction vessel. The monomer feed was begun 2.5 hours after the reaction mixture reached

EP 0 101 943 B1

80°C, and comprised 3.5 percent DVB and 96.5 percent styrene. The beads were chloromethylated and aminated as described in the previous examples. The properties of the beads are described in Table I.

Example 5

5 The general procedure of Example 3 was repeated, this time using 35 parts of 0.3 percent crosslinked seed particles having diameters between 350 and 500 μm , 1.5 parts DVB and 63.4 parts styrene. The reaction mixture was heated to 80°C for 3 hours and a monomer feed comprising 99 percent styrene and 1 percent DVB was added over a 6 hour period. The reaction was then heated at 80°C for an additional 3 hours and finished off at 100°C for 2 hours. The beads thus obtained were chloromethylated and aminated as described in the previous examples. The properties of the beads are described in Table I.

Example 6

15 The procedure of Example 3 was again repeated, using 40 parts of 0.25 percent crosslinked seed particles with diameters between 150 and 212 μm , 4.2 parts DVB and 55.7 parts styrene. The monomer feed comprised 2.5 percent DVB and 97.5 percent styrene, and was begun 2.5 hours after the initial charge to the reaction vessel was heated at 80°C. The monomer feed was added over a 6 hour period, after which the reaction vessel was maintained at 80°C for 4 hours and finished off at 110°C for 2 hours. The beads thus obtained were chloromethylated and aminated as described in Example 1. The properties of the anion exchange resin thus obtained are described in Table I.

TABLE I

Example No.	Ave. ¹ DVB %	Toluene ² Swell Crosslink %	Crush ³ Strength, grams	% Orig. ⁴ Spheres	Resin Size, μ	% Spheres ⁵ 10 Cycles Osmotic Shock Test	Dry ⁶ Weight Capacity (meq/g)	Water ⁷ Retention Capacity %
1	1.64	4.0	1470	98	600—1000	80	4.28	57.2
2	0.57	4.5	1220	100	850	88	4.44	54.7
3	1.64	4.25	1700	98	600—850	95	4.40	55.4
	4.39	6.65	1300	98	800	97	4.13	42.2
	1.16	3.0	3900*	99	1700	55	4.41	56.6
	3.0	6.85	1400	96	500—710	95	4.07	46.4

¹ The weight of percent DVB employed in preparing the copolymer bead based on the total weight of all monomer employed and the seed particle. The weight percent of DVB employed in the seed particle, the initial monomer charge and the monomer feed are given in each particular example.

² The effective crosslink density as determined by swelling the copolymer bead in toluene prior to the functionalization thereof and measuring the increase in volume of said beads.

³ The average force required to fracture the functionalized bead given as an average of about 30 testing. A small crush head is used for these testings, except that a large crush head is used for those values marked with an asterisk.

⁴ The number percent of functionalized beads which are flawless, i.e., are not broken or cracked.

⁵ The number percent of functionalized beads which withstand 10 cycles of alternating treatments with 8 M HCl and 8 M NaOH without breaking.

⁶ Dry weight capacity expressed as meq/g, determined according to the procedure described in Example 1.

⁷ Water retention capacity expressed as weight percent water based on the total weight of the functionalized resin and the water imbibed therein.

EP 0 101 943 B1

As can be seen from Table I, the copolymer beads of this invention exhibited a higher effective crosslink density as measured by toluene swell than actual crosslink density. The aminated resin beads of this invention exhibit excellent crush strength and little breakage upon being subjected to 10 cycles of alternating 8 M hydrochloric acid and 8 M hydroxide. In addition, the dry weight capacity these resins is generally high, indicating that the beads are fully aminated.

Example 7

Into a 1 gallon, stainless steel reactor equipped with an agitator, 35 parts by weight of 0.3 percent crosslinked styrene DVB copolymer seed particles having a particle size of about 285 μm were loaded. To the seed particles, 65 parts water, 3.25 parts DVB, 61.7 parts styrene, 0.036 weight percent TBPO (based on the total weight of monomers employed), 0.025 weight percent TBPB (based on the total weight of monomers employed), 0.3 part CMMC and 0.15 part sodium dichromate were added with agitation. Water was added until the weight phase ratio was 1.0. The reaction mixture was then heated until the temperature was 80°C and was held at 80°C for 2.5 hours, at which time a monomer feed consisting of 3.5 percent DVB and 96.5 percent styrene was begun. The monomer feed continued for 6 hours until the monomer feed constituted 71.4 percent of the combined weight of the initial charge, exclusive of water, and the monomer feed. The reaction was maintained at 80°C for 3 more hours and then finished off at 100°C for 5.5 hours. The toluene swell crosslink percent was determined according to the procedure of Example 1. A 100 g portion of the beads were converted to strong acid cation exchange resins by sulfonating the beads using a 98–100 weight percent sulfuric acid. The crush strength and percent of original spheres, resistance to osmotic shock and water retention capacity of the sulfonated resins were determined according to the methods described in Example 1, and the results are given in Table II. Dry weight capacity was determined by titrating with a standardized sodium hydroxide solution in the presence of sodium chloride.

Example 8

The procedure of Example 7 was repeated except that the monomer feed contained no DVB. The resin beads so prepared were sulfonated according to the manner of Example 7. The properties of the sulfonated resin are described in Table II.

Example 9

The procedure of Example 7 was repeated using 5.9 parts DVB and 59.0 parts styrene in the initial charge. The monomer feed comprising 95 percent styrene and 5 percent DVB was begun 2.5 hours after the reaction mixture reached 80°C and was fed over a 6 hour period. After the monomer feed ended, the reaction was maintained at 80°C for 3.5 hours and then finished off at 100°C for 2 hours. The beads thus obtained were sulfonated. The sulfonated beads have the properties described in Table II.

Example 10

The procedure of Example 9 was repeated using 7.8 parts DVB and 57.1 parts styrene in the initial monomer charge. After the monomer feed was completed, the reaction mixture was held at 80°C for 4 hours and finished off at 110°C for 2 hours. The beads thus obtained were sulfonated. The sulfonated beads have the properties described in Table II.

Example 11

Into a 75.7 l (20 gallon), glass-lined reactor equipped with an agitator, 35 parts by weight of 0.3 percent crosslinked styrene DVB copolymer seed particles having a particle size of about 280–300 μm were loaded. To the seed particles, 65 parts water, 4.2 parts DVB, 60.7 parts styrene, 0.036 weight percent TBPO (based on the total weight of monomers employed), 0.025 weight percent TBPB (based on the total weight of monomers employed), 0.4 part stabilizer and 0.3 part sodium dichromate were added with agitation. Water was added until the weight phase ratio, after the addition of the monomer feed, was 1.0. The reaction mixture was then heated until the temperature reached 78°C and was held at 78°C for 2.75 hours, at which time a monomer feed consisting of 2.5 percent DVB and 97.5 percent styrene was begun. The monomer feed continued for 6 hours until the monomer feed constituted 71.4 weight percent of the copolymer bead. The reaction was maintained at 78°C for 3.25 hours and then finished off at 100°C for 2 hours. The beads so obtained were sulfonated using 93 weight percent sulfuric acid. The sulfonated beads have properties described in Table II.

In order to further illustrate the resistance of these cation exchange resin beads to osmotic shock, a portion of the beads were immersed in a 93 percent sulfuric acid solution, removed and instantaneously washed with copious amounts of deionized water while draining the sulfuric acid. In this test, the resin beads are very rapidly hydrated. This test is generally even more severe than the cycling between 8 M HCl and 8 M NaOH described hereinbefore. Fewer than 5 percent of the resin beads of this example were broken when subjected to this test.

Example 12

The procedure of Example 11 was repeated using 1.9 parts DVB and 63.0 parts styrene in the initial charge. The monomer feed was 98.5 percent styrene and 1.5 percent DVB. The beads thus obtained were sulfonated as described in Example 8. The properties of the sulfonated beads are described in Table II.

The beads of this example were subjected to the instantaneous hydration test described in Example 11, with fewer than 5 percent of the resin beads being broken.

EP 0 101 943 B1

Example 13

5 Into a 3 liter, stainless steel reactor equipped with an agitator, 35 parts by weight of 0.3 percent crosslinked styrene DVB copolymer seed particles having a particle size in the range of 180—300 μm were loaded. To the seed particles, 65 parts water, 6.5 parts DVB, 58.4 parts styrene, 0.036 percent weight (based on total monomers) TBPO, 0.025 weight percent (based on total monomers) TBPB, 0.4 part stabilizer and 0.3 part sodium dichromate were added with agitation. Water was added until the weight phase ratio, after the addition of the monomer feed, was 1.0. The reaction mixture was then heated until the temperature was 78°C and held at 78°C for 2.5 hours, at which time a monomer feed consisting of 4.5 percent DVB and 95.5 percent styrene was begun. The monomer feed continued for 6 hours until the monomer feed constituted 10 71.4 weight percent of the copolymer bead weight. The reaction was maintained at 78°C for 4.0 hours and then finished off at 110°C for 2 hours. The beads so obtained were sulfonated and have the properties described in Table II.

15

20

25

30

35

40

45

50

55

60

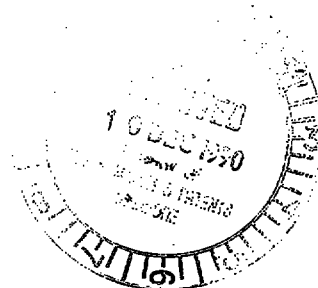
65



TABLE II

Example No.	Ave. ¹ DVB % ¹	Toluene ² Swell Crosslink %	Crush ³ Strength, grams	% Orig. ⁴ Spheres	Resin Size, μ	% Spheres ⁵ 10 Cycles Osmotic Shock Test	Dry ⁶ Weight Capacity (meq/g)	Water ⁷ Retention Capacity %
7	3.64	8.25	4040*	100	800	95	5.36	60.0
8	0.96	8.8	2600*	98+	900	50	5.16	66.5
9	5.24	12.1	1710	97	750	97	5.25	54.5
10	5.83	7.75	2100*	98+	710-850	97	5.19	53.5
11	3.0	11.25	1600*	98	800	98	5.28	61.6
12	1.71	4.15	1640	98	500-1180	98	5.35	69.8
13	5.37	N.D.	3600*	96	500-1180	95	5.23	52.6

N.D. Not determined.
1-7 See notes 1-7 from Table I.



As can be seen from the data in Table II, the sulfonated resins exhibit very high crush strength, excellent sphericity and high capacity. The copolymer beads, before the sulfonation thereof, exhibit significantly higher effective crosslink density than actual crosslink density. In addition, the sulfonated resins tested for resistance to osmotic shock exhibit very little breakage upon being subjected to 10 cycles of alternate treatments with 8 M HCl and 8 M sodium hydroxide.

Claims

1. A process for preparing crosslinked copolymer beads, the process comprising the imbibition of a monomer by polymer particles, and the process being characterized by the following steps:

(a) forming a suspension of particles of a crosslinked polymer in a continuous aqueous phase, then
(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 40 to 95 weight percent of said monomers are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

2. The process of Claim 1 wherein the monoethylenically unsaturated monomer employed in step (b) and (d) comprises a monovinyl aromatic or an alkyl ester of acrylic or methacrylic acid and the polyethylenically unsaturated monomer comprises divinylbenzene, an alkylene diacrylate or an alkylene dimethacrylate.

3. A process of Claim 1 wherein said second monomer mix is added continuously or intermittently such that the instantaneous conversion during said addition of monomer mix is at least 20 percent.

4. A process of Claim 1 which further comprises attaching active ion exchange groups to the copolymer beads to form an ion exchange resin.

5. The process of Claim 1 wherein the crosslinked copolymer bead has a core/shell morphology and the polymers of the shell have an average crosslink density which is less than or equal to the average crosslink density of the polymers of the core.

6. A process for preparing crosslinked copolymer beads comprising:

(a) forming a suspension of particles of a crosslinked or noncrosslinked polymer in a continuous aqueous phase, then

(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 20 to 95 weight percent of said monomers are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

7. The process of Claim 6 wherein the monoethylenically unsaturated monomer employed in step (b) and (d) comprises a monovinyl aromatic or an alkyl ester of acrylic or methacrylic acid and the polyethylenically unsaturated monomer comprises divinylbenzene, and alkylene diacrylate or an alkylene dimethacrylate.

8. A process of Claim 6 wherein said second monomer mix is added continuously or intermittently such that the instantaneous conversion during said addition of monomer mix is at least 20 percent.

9. A process of Claim 6 which further comprises attaching active ion exchange groups to the copolymer beads to form an ion exchange resin.

10. The process of Claim 6 wherein the crosslinked copolymer bead has a core/shell morphology and the polymer of the shell have an average crosslink density which is less than or equal to the average crosslink density of the polymers of the core.

As can be seen from the data in Table II, the sulfonated resins exhibit very high crush strength, excellent sphericity and high capacity. The copolymer beads, before the sulfonation thereof, exhibit significantly higher effective crosslink density than actual crosslink density. In addition, the sulfonated resins tested for resistance to osmotic shock exhibit very little breakage upon being subjected to 10 cycles of alternate treatments with 8 M HCl and 8 M sodium hydroxide.

Claims

1. A process for preparing crosslinked copolymer beads, the process comprising the imbibition of a monomer by polymer particles, and the process being characterized by the following steps:

(a) forming a suspension of particles of a crosslinked polymer in a continuous aqueous phase, then
(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 40 to 95 weight percent of said monomers are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

2. The process of Claim 1 wherein the monoethylenically unsaturated monomer employed in step (b) and (d) comprises a monovinyl aromatic or an alkyl ester of acrylic or methacrylic acid and the polyethylenically unsaturated monomer comprises divinylbenzene, an alkylene diacrylate or an alkylene dimethacrylate.

3. A process of Claim 1 wherein said second monomer mix is added continuously or intermittently such that the instantaneous conversion during said addition of monomer mix is at least 20 percent.

4. A process of Claim 1 which further comprises attaching active ion exchange groups to the copolymer beads to form an ion exchange resin.

5. The process of Claim 1 wherein the crosslinked copolymer bead has a core/shell morphology and the polymers of the shell have an average crosslink density which is less than or equal to the average crosslink density of the polymers of the core.

6. A process for preparing crosslinked copolymer beads comprising:

(a) forming a suspension of particles of a crosslinked or noncrosslinked polymer in a continuous aqueous phase, then

(b) swelling said polymer particles with a first monomer mix comprising from 75 to 99.5 parts by weight of a monoethylenically unsaturated monomer, 0.5 to 25 parts by weight of a polyethylenically unsaturated monomer and a sufficient amount of a substantially water-insoluble free radical initiator to catalyze the polymerization of said first monomer mix and a second monomer mix, then

(c) polymerizing said first monomer mix within said polymer particles until 20 to 95 weight percent of said monomers are converted to polymer, then

(d) continue adding to said suspension a second monomer mix, which second monomer mix comprises a monoethylenically unsaturated monomer but contains essentially no free radical initiator, said addition of said second monomer mix being made under conditions including a temperature sufficient to initiate the free radical polymerization of the monomer in said second monomer mix such that said monomer mix is imbibed by said polymer particles and the polymerization of said second monomer mix within said polymer particles is catalyzed by the free radical initiator contained in said first monomer mix and wherein the monomers of the second monomer mix, when polymerized, comprise from 40 to 90 weight percent of the product copolymer beads.

7. The process of Claim 6 wherein the monoethylenically unsaturated monomer employed in step (b) and (d) comprises a monovinyl aromatic or an alkyl ester of acrylic or methacrylic acid and the polyethylenically unsaturated monomer comprises divinylbenzene, and alkylene diacrylate or an alkylene dimethacrylate.

8. A process of Claim 6 wherein said second monomer mix is added continuously or intermittently such that the instantaneous conversion during said addition of monomer mix is at least 20 percent.

9. A process of Claim 6 which further comprises attaching active ion exchange groups to the copolymer beads to form an ion exchange resin.

10. The process of Claim 6 wherein the crosslinked copolymer bead has a core/shell morphology and the polymer of the shell have an average crosslink density which is less than or equal to the average crosslink density of the polymers of the core.



Patentansprüche

1. Verfahren zum Herstellen von vernetzten Copolymerperlen durch Aufsaugen eines Monomers in Polymerteilchen, wobei das Verfahren durch die folgenden Schritte gekennzeichnet ist:

(a) Ausbilden einer Suspension von Teilchen eines vernetzten Polymeren in einer kontinuierlichen wäßrigen Phase, dann

(b) Quellen der Polymerteilchen mit einer ersten Monomermischung enthaltend 75 bis 99,5 Gewichtsteile eines monoethylenisch ungesättigten Monomeren, 0,5 bis 25 Gewichtsteile eines polyethylenisch ungesättigten Monomeren und eine ausreichende Menge eines im wesentlichen wasserunlöslichen, freie Radikale bildenden Starters, um die Polymerisation der ersten Monomermischung zu katalysieren, und einer zweiten Monomermischung, dann

(c) Polymerisieren der ersten Monomermischung in den Polymerteilchen, bis 40 bis 95 Gewichtsprozent der Monomeren in Polymere umgewandelt sind, dann

(d) Fortsetzen der Zugabe einer zweiten Monomermischung zu dieser Suspension, wobei die zweite Monomermischung ein monoethylenisch ungesättigtes Monomer, jedoch im wesentlichen keinen freie Radikale bildenden Starter enthält, wobei die Zugabe der zweiten Monomermischung unter Bedingungen erfolgt, die einschließen eine ausreichende Temperatur, um die frei-radikalische Polymerisation des Monomeren in der zweiten Monomermischung auszulösen, so daß die Monomermischung von den Polymerteilchen aufgesaugt wird und die Polymerisation der zweiten Monomermischung in den Polymerteilchen vom freie Radikale bildenden Starter katalysiert wird, der in der ersten Monomermischung enthalten ist, und wobei die Monomeren der zweiten Monomermischung nach der Polymerisation 40 bis 90 Gewichtsprozent der Copolymerperlen ausmachen.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das monoethylenisch ungesättigte Monomer, das in Schritt (b) und (d) verwendet wird, ein monovinylaromatisches oder ein Alkylester von Acrylsäure oder Methacrylsäure enthält und das polyethylenisch ungesättigte Monomer Divinylbenzol, ein Alkylendiacyrat oder ein Alkylendimethacrylat enthält.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die zweite Monomermischung kontinuierlich oder intermittierend zugesetzt wird, so daß die augenblickliche Umwandlung während der Zugabe der Monomermischung mindestens 20% beträgt.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß es weiterhin das Anbringen von aktiven Ionen austauschenden Gruppen an den Copolymerperlen einschließt, um ein Ionenaustauscherharz zu bilden.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die vernetzten Copolymerperlen einen Kern-/Hüllenaufbau aufweisen und die Polymeren der Hülle eine mittlere Vernetzungsdichte aufweisen, die kleiner oder gleich der mittleren Vernetzungsdichte der Polymeren des Kerns ist.

6. Verfahren zum Herstellen von vernetzten Copolymerperlen durch:

(a) Ausbilden einer Suspension von Teilchen eines vernetzten oder nicht vernetzten Polymeren in einer kontinuierlichen wäßrigen Phase, dann

(b) Quellen der Polymerteilchen mit einer ersten Monomermischung enthaltend 75 bis 99,5 Gewichtsteile eines monoethylenisch ungesättigten Monomeren, 0,5 bis 25 Gewichtsteile eines polyethylenisch ungesättigten Monomeren und eine ausreichende Menge eines im wesentlichen wasserunlöslichen, freie Radikale bildenden Starters, um die Polymerisation der ersten Monomermischung zu katalysieren, und einer zweiten Monomermischung, dann

(c) Polymerisieren der ersten Monomermischung in den Polymerteilchen, bis 20 bis 95 Gewichtsprozent des Monomeren in Polymer umgewandelt sind, dann

(d) Fortsetzen der Zugabe einer zweiten Monomermischung zu dieser Suspension, wobei die zweite Monomermischung ein monoethylenisch ungesättigtes Monomer, jedoch im wesentlichen keinen freie Radikale bildenden Starter enthält, wobei die Zugabe der zweiten Monomermischung unter Bedingungen erfolgt, die einschließen eine ausreichende Temperatur, um die frei-radikalische Polymerisation des Monomeren in der zweiten Monomermischung auszulösen, so daß die Monomermischung von den Polymerteilchen aufgesaugt wird und die Polymerisation der zweiten Monomermischung in den Polymerteilchen vom freie Radikale bildenden Starter katalysiert wird, der in der ersten Monomermischung enthalten ist, und wobei die Monomeren der zweiten Monomermischung nach der Polymerisation 40 bis 90 Gewichtsprozent der Copolymerperlen ausmachen.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das monoethylenisch ungesättigte Monomer, das in Schritt (b) und (d) verwendet wird, ein monovinylaromatisches oder ein Alkylester von Acrylsäure oder Methacrylsäure enthält und das polyethylenisch ungesättigte Monomer Divinylbenzol, ein Alkylendiacyrat oder ein Alkylendimethacrylat enthält.

8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die zweite Monomermischung kontinuierlich oder intermittierend zugesetzt wird, daß die augenblickliche Umwandlung während der Zugabe der Monomermischung mindestens 20% beträgt.

9. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß es weiterhin das Anbringen von aktiven Ionen austauschenden Gruppen an den Copolymerperlen einschließt, um ein Ionenaustauscherharz zu bilden.

10. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die vernetzten Copolymerperlen einen



Kern-/Hüllenaufbau aufweisen und das Polymere der Hülle eine mittlere Vernetzungsdichte aufweist, die kleiner oder gleich der mittleren Vernetzungsdichte des Polymeren des Kerns ist.

Revendications

- 5 1. Procédé de préparation de perles de copolymère réticulé, comprenant l'imprégnation de particules de polymère par un monomère, et caractérisé par les stades suivants:
(a) formation d'une suspension de particules d'un polymère réticulé dans une phase aqueuse continue, puis
- 10 (b) gonflement desdites particules de polymère avec un premier mélange de monomères comprenant de 75 à 99,5 parties en poids d'un monomère à insaturation monoéthylénique, de 0,5 à 25 parties en poids d'un monomère à insaturation polyéthylénique et une quantité suffisante d'un amorceur de radicaux libres, pratiquement insoluble dans l'eau, pour catalyser la polymérisation dudit premier mélange de monomères et d'un second mélange de monomères, puis
- 15 (c) polymérisation dudit premier mélange de monomères au sein desdites particules de polymère jusqu'à ce que 40 à 95% en poids desdits monomères soient transformés en polymère, puis
(d) addition à ladite suspension d'un second mélange de monomères, qui comprend un monomère à insaturation monoéthylénique mais ne renferme pratiquement pas d'amorceur de radicaux libres, ladite addition dudit second monomère étant réalisées à une température suffisante pour amorcer la
- 20 polymérisation radicalaire du monomère dans ledit second mélange de monomères, de telle sorte que ledit mélange de monomères imprègne lesdites particules de polymère et que la polymérisation dudit second mélange de monomères au sein desdites particules de polymère soit catalysée par l'amorceur de radicaux libres dudit premier mélange de monomères, et les monomères du second mélange de monomères, lorsqu'ils sont polymérisés, constituant de 40 à 90% en poids des perles de copolymère produites.
- 25 2. Procédé de la revendication 1, dans lequel le monomère à insaturation monoéthylénique utilisé aux stades (b) et (d) comprend un monovinylaromatique ou un ester alkylique d'acide acrylique ou méthacrylique, et le monomère à insaturation polyéthylénique comprend le divinylbenzène, un diacrylate d'alkylène ou un diméthacrylate d'alkylène.
3. Procédé de la revendication 1, dans lequel ledit second mélange de monomères est ajouté en
- 30 continu ou en discontinu, de façon que le taux de transformation instantanée pendant ladite addition du mélange de monomères soit d'au moins 20%.
4. Procédé de la revendication 1, qui comporte en outre la fixation de groupes échangeurs d'ions actifs aux perles de copolymère pour former une résine échangeuse d'ions.
5. Procédé de la revendication 1, dans lequel la perle de copolymère réticulé présente une morphologie
- 35 noyau/enveloppe et les polymères de l'enveloppe ont une densité moyenne de réticulation inférieure ou égale à la densité moyenne de réticulation des polymères du noyau.
6. Procédé de préparation de perles de copolymère réticulé comprenant:
(a) formation d'une suspension de particules d'un polymère réticulé ou non-réticulé dans une phase
- 40 aqueuse continue, puis
(b) gonflement desdites particules de polymère avec un premier mélange de monomères comprenant de 75 à 99,5 parties en poids d'un monomère à insaturation monoéthylénique, de 0,5 à 25 parties en poids d'un monomère à insaturation polyéthylénique et une quantité suffisante d'un amorceur de radicaux libres, pratiquement insoluble dans l'eau, pour catalyser la polymérisation dudit premier mélange de monomères et d'un second mélange de monomères, puis
- 45 (c) polymérisation dudit premier mélange de monomères au sein desdites particules jusqu'à ce que 20 à 95% en poids desdits monomères soient transformés en polymère, puis
(d) addition en continu à ladite suspension d'un second mélange de monomères, qui comprend un monomère à insaturation monoéthylénique, mais ne renferme pratiquement pas d'amorceur de radicaux libres, ladite addition dudit second mélange de monomères étant réalisées à une température suffisante pour
- 50 amorcer la polymérisation radicalaire du monomère dans ledit second mélange de monomères, de telle sorte que ledit mélange de monomères imprègne lesdites particules de polymères et que la polymérisation dudit second mélange de monomères au sein desdites particules de polymère soit catalysée par l'amorceur de radicaux libres dudit premier mélange de monomères, et les monomères du second mélange de monomères, lorsqu'ils sont polymérisés, constituant de 40 à 90% en poids des perles de
- 55 copolymère produites.
7. Procédé de la revendication 6, dans lequel le monomère à insaturation monoéthylénique utilisé aux stades (b) et (d) comprend un monovinylaromatique ou un ester alkylique d'acide acrylique ou méthacrylique, et le monomère à insaturation polyéthylénique comprend le divinylbenzène et un diacrylate d'alkylène ou un diméthacrylate d'alkylène.
- 60 8. Procédé de la revendication 6, dans lequel ledit second mélange de monomères est ajouté en continu ou en discontinu, de façon que le taux de transformation instantanée pendant ladite addition du mélange de monomères soit d'au moins 20%.
9. Procédé de la revendication 6, qui comporte en outre la fixation des groupes échangeurs d'ions actifs aux perles de copolymère pour former une résine échangeuse d'ions.
- 65 10. Procédé de la revendication 6, dans lequel la perle de copolymère réticulé présente une



EP 0 101 943 B1

morphologie noyau/enveloppe et les polymères de l'enveloppe ont une densité moyenne de réticulation inférieure ou égale à la densité moyenne de réticulation des polymères du noyau.

5

10

15

20

25

30

35

40

45

50

55

60

65

