

## Description

This invention relates to ion exchange resins, and in particular to mixed-bed ion exchange resins.

Mixed-bed ion exchange resins are well-known to be simple mixtures of the beads of an anion exchange resin with those of a cation exchange resin. When water of another liquid containing dissolved salts flows through a mixed-bed resin, the cation exchange beads exchange hydrogen ions for dissolved cations in the liquid, and the anion exchange beads typically exchange hydroxide ions for dissolved anions. This process normally continues until the available hydrogen or hydroxide ions of the resins have all been exchanged, whereupon these ions must be replaced via the process known as regeneration.

Cation exchange resins are normally regenerated with aqueous solutions of acids, while anion exchange resins are normally regenerated with aqueous solutions of bases. Exposure of the cation resin to the cations of the anion resin regenerant, or of the anion resin to the anions of the cation resin regenerant, would effectively prevent or reverse regeneration, so the resins are typically segregated prior to regeneration. The cation and anion resins are selected with sufficiently different backwash flotation rates, resulting from their densities and bead diameters, that classification of the resin bed by passing water upward through it causes vertical segregation of the two resins within the ion exchange column. Regenerants are then caused to flow within their respective separated resins.

It is well known to increase the thickness of this interface between the two resins by including a third, inert material in the mixed-bed resin composition, which during the ion exchange treatment process is intimately mixed with the ion exchange resins, but which, because of its backwash flotation rate intermediate between those of the cation resin and the anion resin, settles between these two resins during classification prior to regeneration. As disclosed in US-A-2,666,741, this separation of the cation resin from the anion resin before regeneration allows placement of liquid inlets and outlets between them, reduces the chance of the regenerant for one resin working its way into the other resin, and allows for a reduction in bed size caused by attrition of the resins. In addition, such generation processes are not currently popular.

The spacer materials, which have been useful, typically appear neutral with respect to ion exchange properties. That is, the spacer materials appear ionically neutral, having neither reactive acidic nor basic functional ion exchange sites, and have a backwash flotation rate intermediate between those of the anion and cation resins. For practical considerations, it is helpful if the density of the spacer material approaches a value intermediate between the densities of the two ion exchange resins, so that its particle size and shape may be similar to that of the resins. The

spacer material should be at least as physically stable as the ion exchange resins in order that shrinkage of the separation zone does not require addition of spacer material before replacement of the resins. The spacer material must also be resistant to attack by the influent stream and by the regenerants, which are usually solutions of strong acids and strong bases.

Materials which have been used by others as an inert spacer between the anion resins and cation resins during regeneration include beads or particles of polystyrene, polyvinyl chloride, polyethylene and hollow glass spheres. Unfortunately, said spacer material has a tendency for them to aggregate with particles of the anion exchange resin, thus causing the backwash flotation rate of both the resin and the spacer material to be changed. When this occurs, backwashing fails to sharply classify the materials in the ion exchange bed, and the subsequent regeneration is less efficient and less complete. Another problem is the cogglomeration or agglomeration of beads caused by trapped gases between beads during backwash. Such a problem causes beads to "float", thus failing to provide a sharp classification of materials in the ion exchange bed.

Mixed-bed ion exchange resin compositions are disclosed in US-A-4,151,332. Such compositions comprise particles containing in polymerized form, relative large amounts of a hydroxyalkyl methacrylate monomer. Unfortunately, such particles are prepared using polymerization techniques which can yield wide particle size distributions which lower their effectiveness after several regeneration processes. In addition, the relatively large amount of hydrophilic hydroxyalkyl methacrylate monomer which is employed can provide a tendency for the particle to be not water wettable and thus can cause cross contamination of anionic and cationic beads.

In view of the deficiencies of the prior art, it would be highly desirable to provide a particulate spacer material for separation of mixed bed ion resin interfaces, which particles have excellent settling properties when subjected to backwashing, no titratable ionic moieties, and good physical properties.

The present invention is a bead for a cation and anion mixed-bed ion exchange resin composition, which bead is an essentially spherical, hydrolytically stable polymer bead wherein said bead comprises the polymerization product of a major amount of at least one monoethylenically unsaturated hydrophobic monomer, at least one polyethylenically unsaturated monomer, and a minor amount of a monoethylenically unsaturated hydrophilic monomer such that said bead does not exhibit a titratable acid functionality greater than 0.1 meg/10 ml of resin, characterized in that the hydrophilic monomer consists of one or more ionizable monomers containing anionic or cationic moieties and optionally with an amount of hydroxyalkyl methacrylate.

The particles of this invention allow the skilled

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artisan to prepare improved mixed-bed ion exchange resin compositions comprising particles of an anion exchange resin, particles of a cation exchange resin, and particle beads of this invention wherein the particles of this invention have a backwash flow rate intermediate between that of the anion exchange resin particles and that of the cation exchange resin particles. Specifically, the interface particles of this invention exhibit excellent settling properties and do not aggregate causing flotation problems during backwashing. The use of particle beads of this invention allows the skilled artisan to provide a process for the effective separation of anionic and cationic exchange resins while preventing the cross contamination of such resin particles during regeneration. The use of the particles of this invention allow the skilled artisan to perform a process for preparing improved mix-bed exchange resin compositions having improved life cycles and improved resin efficiency.

The size of the bead is essentially equal to that of other like beads, such that there is a narrow particle size distribution of the uniform or homogeneous sized beads as employed. The density of the bead is essentially equal to that of like beads (i.e., the beads have a uniform or homogeneous density). The titratable acid functionality is present at greater than 0.1 meq/10 ml of resin. The bead can be wet by water thus preventing the accumulation of aqueous bubbles (which can cause flotation problems) at the surface of said bead.

Polymers useful in the practice of this invention are crosslinked polymers formed through the addition polymerization of at least one polymerizable monoethylenically unsaturated hydrophobic monomer, at least one polymerizable polyethylenically unsaturated monomer, and at least one polymerizable monoethylenically unsaturated hydrophilic monomer.

The hydrophilic monomer is most desirably a monomer containing an ionic moiety. The ionic moieties can be either anionic or cationic, although anionic moieties are much preferred. Typically suitable anionic moieties include sulfonic acid, carboxylic acid, phosphonic acid, and the like; and salts thereof. Examples of anionic hydrophilic monomers include acrylic acid, methacrylic acid, sulfoethyl methacrylate, 2-acrylamido-2-methylpropane sulfonic acid, styrene sulfonic acid; and salts thereof, as well as hydrolyzed vinylbenzyl chloride. Less preferred monomers such as hydroxyethyl methacrylate and hydroxyhexyl methacrylate, can also be employed in addition to the aforementioned hydrophilic monomers. However, it is desirable to keep monomers such as hydroxyethyl methacrylate to a minimum because such monomers are nonionic in character and the density of beads formed using such monomers is not desirable. Suitable cationic moieties typically include amines, ammonium moieties, phosphonium moieties, sulfonium moieties, and the like. Exemplary cationic moieties include  $\text{—NH}_2$ ;  $\text{—N(CH}_3)_2$ ;

$\text{—N(CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ ;  $\text{—N(CH}_3)_3^+$ ;  $\text{—N(CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ ; and the like.

The hydrophobic monomer is most desirably one that when polymerized, yields an essentially water-insoluble polymer. Such monomers include the monovinylidene aromatics such as styrene, vinyl naphthalene, and the like. Also included are the alkyl substituted styrenes such as vinyltoluene and ethylvinylbenzene. Halo-substituted styrenes such as bromo- or chlorostyrene are included. Also included are the haloolefins such as the vinyl halides (e.g., vinyl chloride). Particularly useful are the esters of  $\alpha,\beta$ -ethylenically unsaturated carboxylic acids, such as methylmethacrylate and ethylacrylate. Monomers such as vinyl acetate can be employed.

Polyethylenically unsaturated monomers are the polyvinyl monomers useful in preparing ion exchange resins and include monomers such as divinyl benzene, divinyl toluene, divinyl xylene, and divinyl naphthalene; ethylene glycol dimethacrylate; trimethylol propane triacrylate; divinylsuccinate; and the like.

The seed bead is a monomer swellable, spheroidal bead of a polymer derived from a monoethylenically unsaturated hydrophobic monomer and a crosslinking agent therefor, which crosslinking agent is preferably a polyethylenically unsaturated monomer. Typically, the hydrophobic monomer is styrene or methylmethacrylate. The seed bead is most desirably prepared by polymerizing the desired hydrophobic monomer or mixture of monomers with the desired polyethylenically unsaturated monomer such that the amount of polyethylenically unsaturated monomer is present in an amount from 0.1 to 2 weight percent, based on the weight of total monomer forming the seed. Such seed beads are preferably monodisperse in nature (i.e., all seed particles are of essentially the same diameter). The seed beads are prepared using techniques known in the art. For example, seed beads can be prepared by a conventional batch suspension process wherein the particle size is determined by agitation rate and the suspending agent which is selected. Alternatively, the seed bead can be prepared by the polymerization of ultrasonically generated monodispersed monomer droplets as disclosed in US—A—4,444,961.

Most desirably, beads of this invention are prepared by seed suspension polymerization techniques. For example, a seed bead is swollen with a hydrophobic monomer and polyvinyl monomer mixture and subjected to polymerization conditions. The hydrophilic properties of the resulting bead are provided to the surface of the bead by introducing a desired amount of hydrophilic monomer into the reaction mixture before polymerization is complete. This method is preferred over the preparation of a bead which is prepared and subjected to surface hydrolysis. Factors such as seed bead particle size, ratio of seed bead to monomer mixture, and the like will affect the final bead particle size and density.

The amount of polymerizable monomer relative

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to the seed bead can vary. Typically, the amount of monomer relative to the amount of seed which is employed ranges from 3:1 to 6:1, based on the weight of each of the species. Such a mixture typically yields a final bead having a diameter which is 1.5 to 2 times that of the seed bead. Although the beads can be prepared in a wide range of sizes, the preferred beads range from 75 micrometers to 2 millimeters in diameter. Such final beads typically have a wet density ranging from 1.14 to 1.19 gm/ml, preferably 1.15 gm/ml.

The monomer mixture which is employed can vary depending upon factors such as the density of the bead desired, the seed bead which is employed, the type of hydrophilic monomer which is employed, and the like. Typically, the amount of hydrophobic monomer can range from 89 to 99 weight percent based on the total weight of all monomers. The amount of polyvinyl crosslinking monomer can range from 0.05 to 10 weight percent based on all monomers. The amount of hydrophilic monomer can vary and typically range from 0.1 to 8 weight percent, preferably from 0.1 to 6, most preferably from 0.1 to less than 5, weight percent based on all monomers.

The amount of hydrophilic monomer which is employed varies with the type or character of monomer. For example, a more hydrophilic monomer can be employed in a smaller amount than a less hydrophilic monomer. For example, methacrylic acid can be employed in an amount ranging from 1 to 6, preferably 4 to 5, weight percent based on all monomers. Alternatively, a hydrophilic monomer such as sodium styrene sulfonate can be employed in an amount ranging from 0.25 to 1, preferably 0.5 to 0.7, weight percent based on all monomers.

For use in a mixed-bed ion exchange column the polymer beads of the present invention are added to the mixed cation and anion exchange resins in an amount from 5 to 15 volume percent of the total ion exchange resin volume; the preferred amount is about 10 volume percent.

A particle size of the polymer beads is chosen to give a backwash flow rate intermediate between that of the anion exchange resin and the cation exchange resin. See for example, the teachings in US 4,151,332. The polymer beads are mixed with the ion exchange resins during the loading of the column. The beads separate to form the interface separator zone during backwashing, and are remixed with the ion exchange resins for the next cycle.

The resistance of the polymer beads of this invention to clumping or aggregation with anion exchange resins is thought to relate to the presence of the hydrophilic monomers which provide good surface wettability. Because the amount of hydrophilic monomer is very small relative to the amount of hydrophobic monomer and crosslinking monomer, there is no significant ion exchange capacity. In addition, the extremely low amount of hydrophilic monomer which is present in the bead does not introduce a tendency

to swell to the bead. Furthermore, the extremely low amount of hydrophilic monomer provides increased resistance to chemical attack, and increased resistance to osmotic shock caused from expansion and contraction during regeneration.

The following examples are presented to further illustrate but not limit the scope of this invention.

#### Example 1

Into a 3-liter jacketed stainless steel reactor is charged 800 g distilled water and 200 g polystyrene seed bead which is 0.3 percent crosslinked using divinylbenzene and has a 400 mesh size (420 micrometer average diameter). This mixture is agitated for 10 minutes. A mixture of 974 g methylmethacrylate, 47 g divinylbenzene, 1 g tertiary butylperoctoate and 0.6 g tertiary butylbenzoate is added to the reactor. This mixture is agitated at 150 rpm for 30 minutes in order to allow the monomer to be imbibed into the seed beads. To the mixture is added 40 g of a 1 percent aqueous sodium lauryl sulfonate solution. Then 16 g of gelatin in 860 g water is added to the reactor. The mixture is agitated for 5 minutes. To the mixture is charged 60 g methacrylic acid in 200 g water. The mixture is agitated for 10 minutes at room temperature followed by the heating of the contents at the rate of 0.5°C/minutes until the temperature reaches 80°C. The polymerization reaction is carried out at 80°C for 10 hours followed by polymerization at 110°C for 3 hours. The reaction product is cooled, washed with water, and the beads are dried at room temperature.

#### Example 2

A column is packed with 200 ml of beads as described in Example 1, 900 ml of an anion bead and 900 ml of a cation bead. The column is backwashed and air purged. The flow rate of backwashing water is adjusted to a 100 percent bed expansion and the extent of separation can be observed. After about 10 to about 20 minutes phase separation is obtained, no flotation of the beads as described in Example 1 is observed, and no cross-contamination of anion bead with cation bead are observed.

#### Example 3

Into 50 ml of water is dispersed 20 g of bead as described in Example 1. To this mixture is added a 0.2 g of an effervescent sodium bicarbonate tablet. The mixture is stirred for 30 seconds. When bubbling ceases the amount of floating bead is determined. No bead of this invention is observed to float. Conversely, a similar amount of bead which is sold under the tradename Amberlite DP-1® by the Rohm and Haas Company and which is similarly treated is observed to float in the amount of 90 percent. This indicates that the bead of this invention is much improved in resisting flotation when subjected to a gaseous phase while in use.

## Claims

1. A bead for a cation and anion mixed-bed ion exchange resin composition, which bead is an essentially spherical, hydrolytically stable polymer bead, wherein said bead comprises the polymerization product of a major amount of at least one monoethylenically unsaturated hydrophobic monomer, at least one polyethylenically unsaturated monomer, and minor amount of a monoethylenically unsaturated hydrophilic monomer such that said bead does not exhibit a titratable acid functionality greater than 0.1 meq/10 ml of resin, characterized in that the hydrophilic monomer consists of one or more ionizable monomers containing anionic or cationic moieties and optionally with an amount of hydroxyalkylmethacrylate.

2. A bead of Claim 1 comprising from 89 to 99 weight percent hydrophobic monomer, from 0.05 to 10 weight percent polyethylenically unsaturated monomer and from 0.1 to 8 weight percent hydrophilic monomer.

3. A mixed-bed ion exchange resin composition comprising:

(a) particles of anion exchange resin,  
(b) particles of a cation exchange resin, and  
(c) particles of the bead of Claim 1 wherein the particles of the bead of Claim 1 have a backwash flow rate intermediate between that of the anion exchange resin particles and that of the cation exchange resin particles.

4. A mixed-bed ion exchange resin composition of Claim 3 wherein the anion exchange resin is a basic resin and the cation exchange resin is an acidic resin.

5. A composition of Claim 3 wherein particles of (c) are present in an amount from 5 to 15 volume percent based on the total resin volume of particles of (a), (b) and (c).

6. A bead of Claim 1 which is prepared via a seed suspension polymerization technique.

7. A bead of Claim 1 wherein the hydrophilic monomer contains anionic moieties.

8. A bead of Claim 7, wherein the anionic moieties of the hydrophilic monomer are sulfonic acid, carboxylic acid, phosphonic acid and salts thereof.

9. A bead of Claim 8, wherein the anionic hydrophilic monomer is methacrylic acid.

10. A bead of Claim 1, wherein said hydrophilic monomer contains cationic moieties.

11. A bead of Claim 10, wherein the cationic moieties of the hydrophilic monomer are amines, ammonium, phosphonium or sulfonium moieties.

12. A bead of Claim 1, wherein said hydrophobic monomer is a monovinylidene aromatic monomer.

13. A bead of Claim 1, wherein said hydrophobic monomer is an ester of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid.

14. A bead of Claim 1 having a diameter from 75 micrometers to 2 millimeters.

15. A bead of Claim 1 having a wet density ranging from 1.14 to 1.19 g/ml.

16. A bead of Claim 1 wherein said hydrophilic monomer comprises from 0.1 to 6 weight percent of said bead, based on all monomers.

17. A bead of Claim 1, wherein the hydrophilic properties of said bead are provided to the surface of the bead.

18. A bead of Claim 1, wherein the hydrophilic properties of said bead are provided to the surface of the bead by subjecting the bead to surface hydrolysis.

## Patentansprüche

1. Perle für Kationen- und Anionenmischbettionenaustauscherharzzusammensetzung, wobei die Perle im wesentlichen eine kugelförmige, hydrolysestabile Polymerperle ist und die Perle das Polymerisationsprodukt eines Hauptteils mindestens eines monoethylenisch ungesättigten hydrophoben Monomers, mindestens eines polyethylenisch ungesättigten Monomers und einer kleinen Menge eines monoethylenisch ungesättigten hydrophilen Monomers enthält, so daß die Perle keine titrierbare saure Funktion von mehr als 0,1 meq/10 ml Harz aufweist, dadurch gekennzeichnet, daß das hydrophile Monomer im wesentlichen aus ein oder mehreren ionisierbaren Monomeren besteht, die anionische oder kationische Gruppen enthalten und ggf. einen Anteil an Hydroxyalkylmethacrylat.

2. Perle nach Anspruch 1, dadurch gekennzeichnet, daß sie von 89 bis 99 Gew.-% hydrophobes Monomer, von 0,05 bis 10 Gew.-% polyethylenisch ungesättigtes Monomer und von 0,1 bis 8 Gew.-% hydrophiles Monomer enthält.

3. Mischbettionenaustauscherharzzusammensetzung enthaltend

(a) Teilchen Anionenaustauscherharz,  
(b) Teilchen Kationenaustauscherharz und  
(c) Teilchen aus der Perle von Anspruch 1, wobei die Teilchen der Perle von Anspruch 1 eine Rückspülgeschwindigkeit zwischen der der Anionenaustauscherharzteilchen und der der Kationenaustauscherharzteilchen aufweisen.

4. Mischbettionenaustauscherharzzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß das Anionenaustauscherharz ein basisches Harz und das Kationenaustauscherharz ein saures Harz ist.

5. Zusammensetzung nach Anspruch 3, dadurch gekennzeichnet, daß die Teilchen von (c) in einer Menge von 5 bis 15 Vol.-% bezogen auf Harzgesamtvolumen der Teilchen von (a), (b) und (c), vorhanden sind.

6. Perle nach Anspruch 1, dadurch gekennzeichnet, daß sie durch Keimsuspensionspolymerisation hergestellt ist.

7. Perle nach Anspruch 1, dadurch gekennzeichnet, daß das hydrophile Monomer anionische Gruppen enthält.

8. Perle nach Anspruch 7, dadurch gekennzeichnet, daß die anionischen Gruppen des hydrophilen Monomers Sulfonsäuregruppen, Carbonsäuregruppen, Phosphonsäuregruppen und Salze derselben sind.



9. Perle nach Anspruch 8, dadurch gekennzeichnet, daß das anionische hydrophile Monomer Methacrylsäure ist.

10. Perle nach Anspruch 1, dadurch gekennzeichnet, daß das hydrophile Monomer kationische Gruppen enthält.

11. Perle nach Anspruch 10, dadurch gekennzeichnet, daß die kationischen Gruppen des hydrophilen Monomers Amingruppen, Ammoniumgruppen, Phosponium- oder Sulfoniumgruppen sind.

12. Perle nach Anspruch 1, dadurch gekennzeichnet, daß das hydrophobe Monomer ein monovinylidenaromatisches Monomer ist.

13. Perle nach Anspruch 1, dadurch gekennzeichnet, daß das hydrophobe Monomer ein Ester einer  $\alpha,\beta$ -ethylenisch ungesättigten Carbonsäure ist.

14. Perle nach Anspruch 1, dadurch gekennzeichnet, daß sie einen Durchmesser von 75  $\mu\text{m}$  bis 2 mm aufweist.

15. Perle nach Anspruch 1, dadurch gekennzeichnet, daß sie eine Naßdichte im Bereich von 1,14 bis 1,19 g/ml aufweist.

16. Perle nach Anspruch 1, dadurch gekennzeichnet, daß das hydrophile Monomer von 0,1 bis 6 Gew.-% der Perle bezogen auf Gesamtmonomere, beträgt.

17. Perle nach Anspruch 1, dadurch gekennzeichnet, daß die hydrophilen Eigenschaften der Perle an der Perlenoberfläche ausgebildet sind.

18. Perle nach Anspruch 1, dadurch gekennzeichnet, daß die hydrophilen Eigenschaften der Perle an der Perlenoberfläche durch Oberflächenhydrolyse der Perle erzeugt sind.

#### Revendications

1. Perle pour une composition de résine échangeuse d'ions, cations et anions et lit mixte, laquelle perle est une perle pratiquement sphérique, en un polymère stable vis-à-vis de l'hydrolyse, ladite perle comprenant le produit de polymérisation d'une quantité majeure d'au moins un monomère hydrophobe à insaturation monoéthylénique, d'au moins un monomère à insaturation polyéthylénique, et d'une quantité mineure d'un monomère hydrophile à insaturation monoéthylénique, de façon que ladite perle ne présente pas une fonctionnalité acid, dosable supérieure à 0,1 meq/10 ml de résine, caractérisée en ce que le monomère hydrophile consiste en un ou plusieurs monomère(s) ionisable(s) contenant des fragments anioniques ou cationiques, avec éventuellement une certaine quantité de méthacrylate d'hydroxyalkyle.

2. Perle de la revendication 1, comprenant de 89 à 99% en poids de monomère hydrophobe, de 0,05 à 10% en poids de monomère à insaturation polyéthylénique et de 0,1 à 8% en poids de monomère hydrophile.

3. Composition de résine échangeuse d'ions en lit mixte, comprenant:

(a) des particules de résine échangeuse d'anions,

(b) des particules de résine échangeuse de cations, et

(c) des particules perles de la revendication 1, dans laquelle les particules perles de la revendication 1 ont une vitesse d'écoulement en lavage à contre-courant intermédiaire entre celle des particules de résine échangeuse d'anion et celle des particules de résine échangeuse de cation.

4. Composition de résine échangeuse d'ions en lit mixte de la revendication 3, dans laquelle la résine échangeuse d'ions est une résine basique et la résine échangeuse de cations est une résine acide.

5. Composition de la revendication 3, dans laquelle les particules de (c) sont présentes en une quantité de 5 à 15% en volume par rapport au volume de résine total des particules (a), (b) et (c).

6. Perle de la revendication 1, qui est préparée selon une technique de polymérisation en suspension à partir de germes.

7. Perle de la revendication 1, dans laquelle le monomère hydrophile contenant des fragments anioniques.

8. Perle de la revendication 7, dans laquelle les fragments anioniques du monomère hydrophile sont des groupes acide sulfonique, acide carboxylique, acide phosphonique, ou des sels de ceux-ci.

9. Perle de la revendication 8, dans laquelle le monomère hydrophile anionique est l'acide méthacrylique.

10. Perle de la revendication 1, dans laquelle ledit monomère hydrophile contient des fragments cationiques.

11. Perle de la revendication 10, dans laquelle les fragments cationiques du monomère hydrophile sont des groupes amine, ammonium, phosphonium ou sulfonium.

12. Perle de la revendication 1, dans laquelle ledit monomère hydrophobe est un monomère monovinylidène-aromatique.

13. Perle de la revendication 1, dans laquelle ledit monomère hydrophobe est un ester d'un acide carboxylique à insaturation  $\alpha,\beta$ -éthylénique.

14. Perle de la revendication 1, qui présente un diamètre de 75  $\mu\text{m}$  à 2 mm.

15. Perle de la revendication 1, qui présente une densité à l'état mouillé allant de 1,14 à 1,19 g/ml.

16. Perle de la revendication 1, dans laquelle ledit monomère hydrophile constitue de 0,1 à 6% en poids de ladite perle, par rapport à l'ensemble des monomères.

17. Perle de la revendication 1, dans laquelle les propriétés hydrophiles de ladite perle sont conférés à la surface de la perle.

18. Perle de la revendication 1, dans laquelle on confère les propriétés hydrophiles de ladite perle à la surface de la perle en soumettant la perle à une hydrolyse de surface.

