surfactants to improve the incorporation of the fluorinated monomers would result in latex with amphiphilic components while greatly reducing the desired surface properties of fluorinated polymers. Meanwhile the removal of surfactants from the latex and isolation of the attained fluorinated particles turned out to be a high cost process, if possible at all.

As discussed in the above prior art, the isolated core-shell fluorinated particles with pure fluorinated polymer as shell and non-fluorinated polymer as core is of great value in applications as additives in various coatings. The efficient preparation of such core-shell fluorinated particles with preferably pure fluorinated polymer in the shell is in high demand. No such particles and the preparation have been reported yet.

Summary

The object underlining the present disclosure is to provide a process for preparing fluorinated core-shell-polymer particles wherein the process can be carried out in the absence of surfactants, emulsifiers, emulsifying monomers or mixtures thereof, and wherein a high amount of fluorinated monomer can be included in the polymer shell.

The object is achieved by a process for preparing fluorinated core-shell polymer particles in which the core is a non-fluorinated polymer and the shell is derived from at least 50% by weight of fluorinated monomers, by

1) synthesizing a core polymer latex by aqueous emulsion polymerization of non-fluorinated monomers forming the core polymer,

2) adding the shell-forming fluorinated monomers or mixtures of at least 50% by weight of fluorinated monomers with non-fluorinated monomers to the core polymer latex of step 1) and allowing for at least one hour of equilibration time in which essentially no polymerization of the shell monomers occurs,

3) reacting the shell-forming monomers in the mixture from step 2) to form the core-shell polymer particles,

wherein the process steps 1) to 3) are carried out under mechanical stirring in the absence of surfactants, emulsifiers, emulsifying monomers and mixtures thereof.

Preferably the shell is derived from at least 75% by weight, more preferably at least 85% by weight, more preferably at least 95% by weight, specifically at least 99% by weight or 100% by weight of fluorinated monomers.

In an aspect, there is provided a process for preparing fluorinated core-shell polymer particles in which the core is a non-fluorinated polymer and the shell is derived from 100% by weight of fluorinated monomers, by

1) synthesizing a core polymer latex by aqueous emulsion polymerization of non-fluorinated monomers forming the core polymer,

2) adding the shell-forming fluorinated monomers to the core polymer latex of step 1) and allowing for at least one hour of equilibration time in which essentially no polymerization of the shell monomers occurs,

3) reacting the shell-forming monomers in the mixture from step 2) to form the core-shell polymer particles,

wherein the process steps 1) to 3) are carried out under mechanical stirring in the absence of surfactants, emulsifiers, emulsifying monomers and mixtures thereof.

Furthermore, the object is achieved by a fluorinated core-shell-polymer particle obtainable by the above process.Furthermore, the object is achieved by a fluorinated core-shell-polymer, in which the core is a non-fluorinated polymer and the shell is derived from at least 50% by weight of fluorinated monomers, the polymer being free from surfactants, emulsifiers and emulsifying monomers.

In another aspect, there is provided a fluorinated core-shell-polymer, in which the core is a non-fluorinated polymer and the shell is derived from 100% by weight of fluorinated monomers, the polymer being free from surfactants, emulsifiers and emulsifying monomers.

In yet another aspect, there is provided a use of the fluorinated core-shell-polymers as defined herein for forming a solid water-, oil- and soil-repellent coating on solid surfaces.

In another aspect, there is provided a process for forming a solid water-, oil- and soil-repellent coating film on solid surfaces, involving the steps of

a) casting a coating film of an aqueous latex dispersion containing fluorinated

core-shell particles as defined above on a solid surface,

b) evaporating the aqueous dispersion medium and

c) annealing the coating film.

The aqueous latex dispersion may contain a mixture of fluorinated core-shell polymer particles as defined above admixed with non-fluorinated polymer particles.

The present disclosure provides fluorinated particles possessing a core-shell structure with preferably pure fluorinated polymers as shell and non-fluorinated polymers as core to overcome the drawback of the mixed systems of conventional fluorinated particles in the applications as additives in coatings, such as large quantity of fluoro component, poor compatibility and uneven surface. The present disclosure also provides a simple low cost process for the preparation of abovementioned fluorinated polymer particles.

The process comprising the 1) emulsion and/or dispersion polymerization of non-fluorinated monomers and fluorinated monomers in water medium in the absence of surfactant and/or emulsifier and/or ionic vinyl monomers, especially in a one-pot reaction process, and 2) isolation of the abovementioned fluorinated particles by removing water and volatiles.

The present disclosure is characterized by fluorinated particles possessing a core-shell structure containing preferably pure fluorinated polymers in the shell and non-fluorinated polymers in the core.

The present disclosure is also characterized by the absence of surfactant and/or emulsifier and/or ionic vinyl monomers in the preparation of the non-fluorinated polymer core and the fluorinated polymer shell.

The present disclosure is also characterized by the heterogeneous polymerization of non-fluorinated monomers and fluorinated monomers in a water medium.

The present disclosure is also characterized by the highly efficient preparation of abovementioned core-shell fluorinated particles from high fluorinated content monomers.

The abovementioned core-shell fluorinated particles have a wide application as additives for various coatings (such as water-borne coatings, organic coatings, powder coatings and surface varnishing materials), for high performance inks and for plastic devices from an extruding process.

Detailed description of the invention

This invention provides fluorinated particles with core-shell structure containing fluorinated polymers in the shell and non-fluorinated polymers in the core. As distinguished from other systems with related polymer composites which are always in a mixture of solid or dispersion in water, this invention provides fluorinated particles which have many advantages in practical applications, such as improved surface properties, easy application and wide application-range due to the lack of interference from impurities.

This invention also provides fluorinated particles with polymers from only fluorinated monomers as shell which greatly improves the efficiency of fluorinated polymers with regards to obtaining desired surface properties such as water repellence, oil repellence, weather durability and chemical resistance, compared with those particles with the copolymers of fluorinated monomers and non-fluorinated monomers in the shell.

In the process for preparing the fluorinated core-shell-polymer particles the core is a non-fluorinated polymer and the shell is derived from at least 50% by weight of fluorinated monomers, by

1) synthesizing a core polymer latex by aqueous emulsion polymerization of non-fluorinated monomers forming the core polymer,

2) adding the shell-forming fluorinated monomers or mixtures of at least 50% by weight of fluorinated monomers with non-fluorinated monomers to the core polymer latex of step 1) and allowing for at least one hour of equilibration time in which essentially no polymerization of the shell monomers occurs,

Claims

1. A process for preparing fluorinated core-shell polymer particles in which the core is a non-fluorinated polymer and the shell is derived from 100% by weight of fluorinated monomers, by

1) synthesizing a core polymer latex by aqueous emulsion polymerization of non-fluorinated monomers forming the core polymer,

2) adding the shell-forming fluorinated monomers to the core polymer latex of step 1) and allowing for at least one hour of equilibration time in which essentially no polymerization of the shell monomers occurs,

3) reacting the shell-forming monomers in the mixture from step 2) to form the core-shell polymer particles,

wherein the process steps 1) to 3) are carried out under mechanical stirring in the absence of surfactants, emulsifiers, emulsifying monomers and mixtures thereof.

2. The process according to claim 1, wherein the synthesizing to form the core polymer latex in step 1) and the reacting of the shell-forming monomers in step 3) are free-radical polymerizations.

3. The process according to claim 2, wherein in steps 1) and 3), but not in step 2), free-radical polymerization starter is added to perform the free-radical polymerizations.

4. The process according to any one of claims 1 to 3, wherein the non-fluorinated monomers for forming the core polymer are selected from the group consisting of acrylate-based monomers, methacrylate-based monomers, styrene-based monomers, vinyl-based monomers and mixtures thereof.

5. The process according to claim 4, wherein the non-fluorinated monomers are selected from C_{1-12}-alkyl(meth)acrylates.

6. The process according to any one of claims 1 to 5, wherein the fluorinated monomers are selected from alkyl(meth)acrylates having fluorinated alkyl residues.

7. The process according to any one of claims 1 to 6, wherein the average particle diameter is in the range of from 80 to 800 nm.

8. A fluorinated core-shell-polymer, in which the core is a non-fluorinated polymer and the shell is derived from 100% by weight of fluorinated monomers, the polymer being free from surfactants, emulsifiers and emulsifying monomers.

9. A fluorinated core-shell-polymer according to claim 8 having the features as defined in any one of claims 4 to 7.

10. Use of fluorinated core-shell-polymers as defined in any one of claims 8 to 9 for forming a solid water-, oil- and soil-repellent coating on solid surfaces.

11. Process for forming a solid water-, oil- and soil-repellent coating film on solid surfaces, involving the steps of

a) casting a coating film of an aqueous latex dispersion containing fluorinated core-shell-polymer particles as defined in any one of claims 8 to 9, on a solid surface,

b) evaporating the aqueous dispersion medium and

c) annealing the coating film.

12. The process as claimed in claim 11, wherein the aqueous latex dispersion contains a mixture of fluorinated core-shell-polymer particles as defined in any one of claims 8 to 9 admixed with non-fluorinated polymer particles.