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(54) **Title:** SURFACTANT RESPONSIVE EMULSION POLYMERIZED MICRO-GELS

(57) **Abstract:** A stable, aqueous composition containing a crosslinked, nonionic, amphiphilic polymer capable of forming a yield stress fluid in combination with a surfactant is disclosed. The yield stress fluid is capable of suspending insoluble materials in the presence of electrolytes, perfumes, fragrances and/or organic acid preservatives.

SURFACTANT RESPONSIVE EMULSION POLYMERIZED MICRO-GELS

FIELD OF THE DISCLOSED TECHNOLOGY

[0001] The disclosed technology relates to rheology modifiers and more specifically to a yield stress fluid comprising a surfactant responsive micro-gel. The disclosed technology also relates to the formation of a rheologically and phase stable surfactant responsive micro-gel composition that exhibits synergistic rheology profiles with electrolytes. Additionally, the disclosed technology relates to the formation of a rheologically and phase stable surfactant responsive micro-gel composition that can be used over a broad pH range to suspend particulates, insoluble materials, perfumes and fragrances in the presence of electrolytes and/or low pH organic acid preservatives.

BACKGROUND OF THE DISCLOSED TECHNOLOGY

[0002] We are surrounded in everyday life by yield stress fluids. Simply stated, yield stress fluids remain stationary until a sufficient stress is placed on the fluid at which point the fluid will flow. It can be thought of as the initial resistance to flow under stress and is also referred to as yield value. Yield stress is a measurable quantity similar to, but not dependent on viscosity. While a certain rheology modifier may thicken or enhance the viscosity of a composition in which it is included, it does not necessarily have desirable yield stress properties.

[0003] A desirable yield stress property is critical to achieving certain physical and aesthetic characteristics in a liquid medium, such as the indefinite suspension of particles, insoluble liquid droplets, or the stabilization of gas bubbles within a liquid medium. Particles dispersed in a liquid medium will remain suspended if the yield stress (yield value) of the medium is sufficient to overcome the effect of gravity or buoyancy on those particles. Insoluble liquid droplets can be prevented from rising and coalescing and gas bubbles can be suspended and uniformly distributed in a liquid medium using yield value as a formulating tool. An example of a yield stress fluid is a micro-gel rheology modifier which is used generally to adjust or modify the rheological properties of aqueous compositions. Such properties include, without limitation, viscosity, flow rate, stability to viscosity

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change over time, and the ability to suspend particles for indefinite periods of time. They are useful in a number of consumer and industrial applications. An important consumer application includes their use in the formulation of personal care products such as body washes, skin creams, toothpastes, shampoos, hair gels and other cosmetics. In industrial applications, they are useful as subterranean treatment fluids in the oil and gas industry as a component in drilling and fracturing fluids. Typically, they comprise chemically crosslinked polymers having a pH-responsive functionality that is either base or acid sensitive. The polymers may be mixed with other ingredients in a formulation and then neutralized by the addition of a neutralization agent such as an acid or a base. Acid sensitive thickeners are activated upon contact with an acidic agent, while base-sensitive thickeners are activated upon contact with an alkaline agent. Upon neutralization, the polymers swell significantly to form a randomly close-packed (RCP) jammed network of swollen cross-linked micro-gel particles imparting a desired rheological profile, i.e., yield stress, elastic modulus, and viscosity, as well as optical clarity to the formulation.

[0004] These types of rheology modifiers are well known in the art. For example, U.S. Pat. Nos. 2,798,053; 2,858,281; 3,032,538; and 4,758,641 describe cross-linked carboxylic acid polymers based on acrylic acid, maleic acid, itaconic acid or methacrylic acid monomers. U.S. Pat. No. 6,635,702 describes crosslinked alkali-swallowable acrylate copolymers comprising one or more carboxylic acid monomers and one or more non-acid vinyl monomers. U.S. Pat. No. 7,378,479 discloses a crosslinked acid-swallowable polymer containing at least one basic amino substituent that is cationic at low pH, at least one hydrophobically modified polyoxyalkylene substituent derived from an associative vinyl monomer, and at least one polyoxyalkylene substituent derived from a semihydrophobic vinyl surfactant monomer. A key feature of these pH-responsive micro-gels is the very large increase in diameter (or size) of individual cross-linked polymer particles upon neutralization. The high swelling efficiency allows formulators to achieve the desired yield stress and viscosity using relatively small amounts of polymer resulting in low cost-in-use. Dalmont, Pinprayoon and Saunders (*Langmuir* vol. 24, page 2834, 2008) show that individual particles in a micro-gel dispersion of a

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copolymer of ethyl acrylate, and methacrylic acid cross-linked with butanediol diacrylate increase in diameter by at least a factor of 3 upon pH-activation or neutralization. The level of swelling causes an increase in volume fraction of at least 27 (3^3). A jammed network is achieved upon neutralization (or activation) with a relatively low concentration of polymer (less than 3 wt.%).

[0005] Although pH-responsive micro-gels provide yield stress fluids with the high efficiency that is desired by the formulator, they suffer from a major disadvantage in that their thickening ability is greatly reduced by the presence of moderate amounts of electrolytes such as sodium chloride, calcium chloride and magnesium sulfate in the medium. They do not effectively maintain their viscosity and drastic viscosity losses in the presence of inorganic electrolytes are observed. Moreover, rheological properties are not uniform across a broad range in pH and show sharp changes as a function of pH. To overcome these difficulties, various non-ionic thickeners have been proposed. U.S. Pat. No. 4,722,962 describes non-ionic associative thickeners comprising a water-soluble monoethylenically unsaturated monomer and a non-ionic urethane monomer. These polymers provide increases in viscosity or thickening of aqueous formulations that is relatively independent of pH but the polymers are not cross-linked and the purely associative interactions do not create a yield stress.

[0006] In addition to pH-responsive micro-gels, temperature-responsive micro-gels are known in the art. Senff and Richtering (*Journal of Chemical Physics*, vol. 111, page 1705, 1999) describe the change in size of non-ionic chemically cross-linked poly (N-isopropylacrylamide) (PNIPAM) micro-gel particles as a function of temperature. The particles swell by almost a factor of 2.5 in diameter (15 times in terms of volume fraction) when the temperature is reduced from 35°C to 10°C. Although this represents a significant degree of swelling, the use of temperature to activate micro-gels is undesirable. A method of activation is needed that enables switching from a free-flowing suspension to a jammed yield stress fluid under ambient conditions.

[0007] Wu and Zhou (*Journal of Polymer Science: Part B: Polymer Physics*, vol.34, page 1597, 1996) describe the effect of surfactant on swelling of chemically cross-linked PNIPAM homo-polymer micro-gel particles in water. The use of

surfactants to activate micro-gels is attractive because many formulations contain surfactants as co-ingredients. However, the efficiency of swelling reported by Wu and Zhou is extremely low. The anionic surfactant sodium dodecyl (lauryl) sulfate increases the size of cross-linked PNIPAM particles by only a factor of 1.4 at room temperature. Furthermore, Wu and Zhou do not teach how to create a shear thinning yield stress fluid with high optical clarity.

[0008] Hidi, Napper and Sangster (*Macromolecules*, vol.28, page 6042, 1995) describe the effect of surfactant on swelling of poly (vinyl acetate) homopolymer micro-gels in water. For micro-gels that are not cross-linked they report an increase in diameter by a factor of 3 to 4 corresponding to a 30 to 60 fold change in volume of the original particles in the presence of sodium dodecyl (lauryl) sulfate. However, swelling is drastically reduced for cross-linked particles. In this case, they observe an increase in diameter by only a factor of 1.4. Once again, Hidi, Napper and Sangster do not teach how to create a shear thinning yield stress fluid with high optical clarity.

[0009] Apart from providing the necessary rheology profiles, the suspension of solids and/or insoluble materials in a phase stable system is equally important to a rheology modifier. In drilling for oil and gas, subterranean treatment fluids (e.g., drilling and fracture fluids) are typically modified with gelling agents to provide desired rheological properties. Gelling agents include any substance that is capable of increasing the viscosity of a fluid, for example, by forming a micro-gel. These agents must not only possess desirable rheological properties in terms of fluid flow and pumpability, but must also have the capability to suspend solids under both dynamic and static conditions. During active drilling operations, the drilling fluid must possess sufficient structure to carry the formation cuttings to the surface and also have the necessary shear thinning properties to be pumpable. During non-drilling periods, the drilling fluid may remain stationary in the bore hole for hours or even days at a time. During this period, settling of entrained solids can be problematic if the fluid does not have enough structure to support both large and small particulate matter.

[0010] Fracturing is used to boost the production of hydrocarbons such as petroleum or natural gas from subterranean formations. In this process, a

fracturing fluid containing a gelling agent is injected through a wellbore and forced against the formation strata by high pressure sufficient to cause the strata to crack and fracture thereby liberating the hydrocarbon trapped in the formation. The fracturing fluid also carries a proppant to the fracture site. Proppant particles remain in the fracture thereby "propping" the fracture open when the well is in production. The proppant material is typically selected from sand, sintered bauxite, glass balls, polystyrene beads and the like. Whereas sufficient rheological properties are important in treatment fluids used in fracturing, satisfactory suspending ability is necessary for the transport of the proppant materials to the fracture site within the formation.

[0011] Conditions are harsh within a subterranean formation and a gelling agent must be stable to variations in temperature, brackish environments, wide ranges of pH, and changes in shear forces.

[0012] Various problems have been encountered with subterranean treatment fluids in oil field applications, including the lack of thermal stability of the gel upon exposure to varying temperatures, pH and brackish environments, as well as high shear conditions. This can result in changes in the rheological properties of the gel which can ultimately affect the ability of the fluid to suspend bore hole cuttings and or proppant materials. If particulate materials are prematurely lost from the treatment fluid, it can have a detrimental effect on the drilling and development of the formation. Furthermore, gel instability can result in higher loss of fluid into the formation thereby diminishing the efficiency of the operation.

[0013] Personal and homecare compositions which can suspend particles and/or other water insoluble materials are very desirable. These materials impart or contribute to a variety of user benefits including but not limited to exfoliation, visual aesthetics, and/or the encapsulation and release of beneficial agents upon use. The suspension of particulate and insoluble materials as active and aesthetic agents in personal and homecare compositions is becoming increasingly popular with formulators. Typically, particles are suspended in these compositions using structuring systems such as acrylate polymers, structuring gums (e.g., xanthan gum), starch, agar, hydroxyl alkyl cellulose, etc. However, the addition of beads

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or particles to personal care compositions tends to be problematic. For example, one problem is that particles or insoluble materials very frequently tend to be of a different density than the continuous phase of the composition to which they are added. This mismatch in the density can lead to separation of the particles from the continuous phase and a lack of overall product stability. In one aspect, when added particles are less dense than that of the composition continuous phase, the particles tend to rise to the top of such phase ("creaming"). In another aspect, when the added particles have a density greater than that of the continuous phase, the particles tend to gravitate to the bottom of such phase ("settling"). When large particles are desired to be suspended (e.g., polyethylene particles, guar beads, etc.), the level of polymer used is typically increased to provide increased structure for suspended beads. A consequence of thickening a liquid to provide structure for suspended beads causes a significant increase in liquid viscosity and a corresponding decrease in pourability, a property which is not always desirable. Highly viscous products are typically difficult to apply and rinse away, especially if the shear thinning profile of the viscosity building agent is deficient. High viscosities can also adversely affect packaging, dispensing, dissolution, and the foaming and sensory properties of the product. Moreover, conventionally structured liquids are often opaque or turbid thereby obscuring the suspended beads from the consumer, which adversely affects the aesthetic appeal of the product.

[0014] Many common thickeners such as xanthan gum, carboxymethylcellulose (CMC), carrageenan, and acrylic acid homopolymers and copolymers are anionic and therefore, can react with the cationic surfactants and cause precipitation of the cationic and thickener or reduce the efficacy of the cationic surfactant. Non-ionic thickeners such as hydroxyethylcellulose (HEC) and hydroxypropylmethylcellulose (HPMC) can provide viscosity in cationic systems, however, very little suspension properties are imparted to the fluid. Cationic thickeners such as Polyquaternium-10 (cationically modified HEC) and cationic guar provide thickening in cationic systems but not suspension. Some acrylic polymers are effective at thickening cationic systems but they can be

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limited by pH, require high concentrations, have high cost-in-use, and often have narrow limits of compatibility with the cationic materials.

[0015] Anionic surfactants are often used as deterative agents in cleansers and cleaning products because of their excellent cleaning and foaming properties. Exemplary anionic surfactants traditionally utilized in these formulations include, for example, alkyl sulfates and alkyl benzene sulfonates. While the anionic surfactants and, in particular, the anionic sulfates and sulfonates are efficient deterative agents, they are severe ocular irritants and capable of causing mild to moderate dermal irritation to some sensitized persons. Accordingly, it has become increasingly important to consumers that aqueous cleansing compositions be mild in that they do not irritate the eyes and skin when in use. Manufacturers are striving to provide mild cleansing products that also incorporate insoluble benefit and/or aesthetic agents that require stable suspension. It is known that the irritation caused by anionic sulfates and sulfonates can be reduced by utilizing the ethoxylated forms thereof. While ethoxylated surfactants may mitigate ocular and skin irritation in compositions in which they are included, a major problem in using these surfactants is that it is difficult to obtain desirable yield stress properties in an ethoxylated system.

[0016] One important class of liquid rheology modifier commonly employed to thicken aqueous based surfactant containing formulations is the alkali-swellable or alkali-soluble emulsion (ASE) polymers. ASE polymers are linear or crosslinked copolymers that are synthesized from (meth)acrylic acid and alkyl acrylates. The crosslinked polymers immediately thicken upon neutralization with an inorganic or an organic base. As liquid emulsions, ASE polymers are easily processed and formulated into liquid surfactant containing formulations by the product formulator. Examples of ASE polymer thickened surfactant based formulations are set forth in U.S. Patent No. 6,635,702; International Published Application No. WO 01/19946; and European Patent No. 1 690 878 B1, which disclose the use of a polymeric thickener for aqueous compositions containing surfactants. Although these thickeners offer good viscosity, suspension and clarity properties in surfactant containing formulations at pH values near neutral (pH \geq 6.0), they become hazy at acidic pH ranges, resulting in poor clarity.

[0017] Microbial contamination from bacteria, yeast, and/or fungus in cosmetics, toiletries, personal and homecare products is very common and has been of great concern to the industry for many years. Present day surfactant containing products are typically formulated with a preservative to protect the product from decay, discoloration, or spoilage and to ensure that the product is safe for topical application to hard surface substrates and laundry items in homecare applications, and to the skin, scalp, and hair in humans and animals in personal and animal care applications. Three classes of preservative compounds that are commonly used in surfactant containing products are the formaldehyde donors such as diazolinyl urea, imidazolinyl urea, and DMDM Hydantoin; the halogenated compounds including 2,4-dichlorobenzyl-alcohol, Chloroxyleneol (4-chloro-3,5-dimethyl-phenol), Bronopol (2-bromo-2-nitropropane-1,3-diol), and iodopropynyl butyl carbamate; and the paraben compounds including methyl-paraben, ethyl-paraben, propyl-paraben, butyl-paraben, isopropyl-paraben, and benzyl-paraben.

[0018] While these preservatives have been successfully utilized in personal care products for many years, there are recent concerns by the scientific community and the public that some of these compounds may constitute health hazards. Accordingly, there is an interest in replacing the above-mentioned compounds in surfactant containing products that are topically applied to or come into contact with human skin, scalp or hair while maintaining good antimicrobial efficacy, mildness, and do not raise safety concerns.

[0019] Organic acids (e.g., sorbic, citric and benzoic), such as those used as preservatives in the food industry, have been increasingly looked at as the ideal replacement for the foregoing preservative systems in surfactant containing formulations. The antimicrobial activity of the organic acids is connected to the associated or protonated species of the acid molecule. As the pH of an organic acid containing formulation increases, dissociation of the proton occurs forming acid salts. The dissociated form of the organic acids (acid salts) have no antimicrobial activity when used alone, effectively limiting the use of organic based acids to pH values below 6 (Weber, K. 2005. New alternatives to paraben-based preservative blends. *Cosmetics & Toiletries* 120(1): 57-62).

[0020] The literature has also suggested that formulating products in the natural pH range (between about 3-5) 1) reduces the amount of preservative required in a product by enhancing preservative efficacy, 2) stabilizes and increases the effectiveness of many cosmetic active ingredients, 3) is beneficial to the repair and maintenance of skin barrier tissue, and 4) supports the natural skin flora to the exclusion of over-colonization by deleterious microorganisms (Wiechers, J.W. 2008. Formulating at pH 4-5: How lower pH benefits the skin and formulations. *Cosmetics & Toiletries* 123(12): 61-70).

[0021] U.S. Pat. No. 5,139,770 describes the use of crosslinked homopolymers of vinyl pyrrolidone in surfactant containing formulations such as conditioning shampoo to obtain relatively high viscosities. However, the patent does not teach how to create a yield stress fluid with high optical clarity that is also shear thinning.

[0022] As the industry desires new thickened surfactant based products that are formulated in the acidic pH range, there is a developing need for a rheology modifier that, when used in combination with a surfactant, provides a high clarity formulation under acidic pH conditions while maintaining a good viscosity/rheology profile, suspension (yield value), and enhanced aesthetics.

[0023] U.S. Pat. No. 5,663,258 describes the preparation of crosslinked copolymers of vinyl pyrrolidone/vinyl acetate. High viscosities are obtained when the polymer is combined with water but there is no teaching about using the polymer to create a yield stress fluid that is activated by surfactant.

[0024] U.S. Patent No. 6,645,476 discloses a water soluble polymer prepared from the free radical polymerization of a hydrophobically modified ethoxylated macromer in combination with a copolymerizable second monomer selected from unsaturated acids and their salts and/or a myriad of other monomers including N-vinyl lactams and vinyl acetate. Preferred polymers are crosslinked and are polymerized from hydrophobically modified ethoxylated macromers in combination with neutralized acrylamidomethylpropanesulfonic acid. The viscosities of 1% aqueous solutions of the polymer preferably range from 20,000 mPa·s to 100,000 mPa·s. There is no teaching of a surfactant activated polymer devoid of hydrophobically modified ethoxylated macromer repeating units

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providing a yield stress fluid exhibiting good suspension properties without a substantial increase in viscosity.

[0025] There remains a challenge to not only demonstrate the ability to effectively suspend particles within stable micro-gel containing compositions, but also exhibit desirable mildness, desirable rheology profiles, clarity and aesthetic characteristics across a wide range of temperature, pH conditions and electrolyte concentrations at low polymer usage levels. Accordingly, there is a need for a yield stress fluid based on polymer micro-gel particles wherein the concentration of polymer is no more than 5 wt.% based on the weight of the composition in which it is included and having a yield stress value of at least 1 mPa, or 0.1 Pa, wherein the yield stress, elastic modulus and optical clarity are substantially independent of pH. There is also a need to provide yield stress fluids formulated with mild surfactants such as, for example, surfactants containing ethylene oxide moieties.

SUMMARY OF THE DISCLOSED TECHNOLOGY

[0026] The present technology provides crosslinked, nonionic, amphiphilic polymers, or amphiphilic polymers for brevity, that can be swollen in the presence of a surfactant. The amphiphilic polymers can be prepared by polymerizing a monomer composition including at least one hydrophilic monomer, at least one hydrophobic monomer and an amphiphilic crosslinking monomer. The crosslinking monomer may be an amphiphilic crosslinking agent, or a mixture of an amphiphilic crosslinking agent and a conventional crosslinking agent. Surprisingly, the rheological profiles and clarity of aqueous surfactant systems containing these polymers are synergistically improved in the presence of electrolytes such as inorganic salts, acid preservatives and/or perfumes and fragrances.

[0027] In an embodiment, it has been found that amphiphilic crosslinking agents can be easily reacted into amphiphilic polymer. Amphiphilic crosslinking agents can contain more than one reactive moiety. In some embodiments the at least one reactive moiety can be an allyl group.

[0028] In another aspect, an embodiment of the disclosed technology relates to a yield stress fluid comprising a crosslinked, nonionic, amphiphilic polymer and a surfactant.

[0029] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and at least one surfactant, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, and the at least one surfactant is no more than 70 wt.% of the composition, the yield stress of the composition is at least 1 mPa, or 0.1 Pa with a shear thinning index of less than 0.5 at shear rates between about 0.1 and about 1 reciprocal seconds, and wherein the yield stress, elastic modulus and optical clarity of the composition are substantially independent of pH in the range of about 2 to about 14.

[0030] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and at least one surfactant, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, and the at least one surfactant is no more than 70 wt.% of the composition, wherein the ratio of the standard deviation to the mean of measured values for yield stress, elastic modulus and optical clarity is less than 0.3 in one aspect, and less than 0.2 in another aspect in the pH range from about 2 to about 14.

[0031] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and at least one surfactant, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, and at least one surfactant is no more than 70 wt.% of the composition, the yield stress of the composition is at least 1mPa, or 0.1 Pa with a shear thinning index of less than 0.5 at shear rates between about 0.1 and about 1 reciprocal seconds, and wherein the yield stress, elastic modulus and optical clarity of the composition are substantially independent of pH in the range of about 2 to about 14 and wherein the composition is able to suspend beads of a size between 0.5 and 1.5 mm wherein the difference in specific gravity of the beads relative to water is in the range of 0.2 to 0.5 for a period of at least 4 weeks at room temperature.

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[0032] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and one or more surfactants, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, wherein the total concentration of surfactant is no more than 70 wt.% of the composition, the yield stress of the composition is at least 1 mPa, or 0.1 Pa with a shear thinning index of less than 0.5 at shear rates between about 0.1 and about 1 reciprocal seconds, and wherein the yield stress, elastic modulus and optical clarity of the composition are substantially independent of pH in the range of about 2 to about 14 and wherein the composition is able to suspend beads of a size between 0.5 and 1.5 mm where the difference in specific gravity of the beads relative to water is in the range of 0.2 to 0.5 for a period of at least 4 weeks at room temperature and wherein one of the surfactants contains ethylene oxide moieties and said surfactant is more than 75% by weight of the total surfactant.

[0033] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and at least one surfactant, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, and the at least one surfactant is no more than 70 wt.% of the composition, the yield stress of the composition is at least 1 mPa, or 0.1 Pa with a shear thinning index of less than 0.5 at shear rates between about 0.1 and about 1 reciprocal seconds, and wherein the viscosity, yield stress, elastic modulus and optical clarity of the composition are substantially independent of pH in the range of about 2 to about 14, and wherein the rheology profiles such as viscosity and yield stress is synergistically enhanced in the presence of an electrolyte such as an inorganic salt.

[0034] In still another aspect, an embodiment of the disclosed technology relates to a thickened aqueous composition comprising a crosslinked, nonionic, amphiphilic polymer and at least one surfactant, wherein the concentration of the polymer is no more than 5 wt.% based on the total weight of the composition, and the at least one surfactant is no more than 70 wt.% of the composition, the yield stress of the composition is at least 1 mPa, or 0.1 Pa with a shear thinning index

of less than 0.5 at shear rates between about 0.1 and about 1 reciprocal seconds, and wherein the viscosity, yield stress, elastic modulus and optical clarity of the composition are maintained in the presence of a low pH organic acid preservative.

[0035] The crosslinked, nonionic, amphiphilic polymer compositions as well as the thickened aqueous fluid comprising the nonionic, amphiphilic, polymer compositions and the at least one surfactant of the disclosed technology may suitably comprise, consist of, or consist essentially of the components, elements, and process delineations described herein. The disclosed technology illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

[0036] Unless otherwise stated, all percentages, parts, and ratios expressed herein are based upon the total weight of the components contained in the compositions of the disclosed technology.

[0037] As used herein, the term "amphiphilic polymer" means that the polymeric material has distinct hydrophilic and hydrophobic portions. "Hydrophilic" typically means a portion that interacts intramolecularly with water and other polar molecules. "Hydrophobic" typically means a portion that interacts preferentially with oils, fats or other non-polar molecules rather than aqueous media.

[0038] As used herein, the term "hydrophilic monomer" means a monomer that is substantially water soluble. "Substantially water soluble" refers to a material that is soluble in distilled (or equivalent) water, at 25°C, at a concentration of about 3.5% by weight in one aspect, and soluble at about 10% by weight in another aspect (calculated on a water plus monomer weight basis).

[0039] As used herein, the term "hydrophobic monomer" means a monomer that is substantially water insoluble. "Substantially water insoluble" refers to a material that is not soluble in distilled (or equivalent) water, at 25°C, at a concentration of about 3% by weight in one aspect, and not soluble at about 2.5% by weight in another aspect (calculated on a water plus monomer weight basis).

[0040] The term "nonionic" as used herein encompasses both a monomer, monomer composition or a polymer polymerized from a monomer composition devoid of ionic or ionizable moieties ("nonionizable"), and a "substantially

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nonionic" monomer, monomer composition or polymer polymerized from a monomer composition.

[0041] An ionizable moiety is any group that can be made ionic by neutralization with an acid or a base.

[0042] An ionic or an ionized moiety is any moiety that has been neutralized by an acid or a base.

[0043] By "substantially nonionic" is meant that the monomer, monomer composition or polymer polymerized from a monomer composition contains less than 5 wt.% in one aspect, less than 3 wt.% in another aspect, less than 1 wt.% in a further aspect, less than 0.5 wt.% in a still further aspect, less than 0.1 wt.% in an additional aspect, and less than 0.05 wt.% in a further aspect, of an ionizable and/or an ionized moiety.

[0044] For the purpose of the specification the prefix "(meth)acryl" includes "acryl" as well as "methacryl". For example, the term "(meth)acrylamide" includes both acrylamide and methacrylamide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] Fig. 1 is a curve of the Brookfield viscosities versus salt concentration (NaCl) comparing surfactant formulations containing no amphiphilic polymer, the comparative amphiphilic polymer of Example 2 and the illustrative amphiphilic polymer of Example 17.

[0046] Fig. 2 is plot of yield stress versus salt concentration (NaCl) comparing surfactant formulations containing no amphiphilic polymer, the comparative amphiphilic polymer of Example 2 and the illustrative amphiphilic polymer of Example 17.

[0047] Fig. 3 is a plot of optical clarity (% transmittance at 640 nm) versus salt concentration (NaCl) comparing surfactant formulations containing no amphiphilic polymer, the comparative amphiphilic polymer of Example 2 and the illustrative amphiphilic polymer of Example 17.

[0048] Fig. 4 is a plot of Brookfield viscosity and yield value versus sodium benzoate concentration comparing surfactant formulations containing the

comparative amphiphilic polymer of Example 2 and the illustrative amphiphilic polymer of Example 17.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0049] Exemplary embodiments in accordance with the disclosed technology will be described. Various modifications, adaptations or variations of the exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the disclosed technology, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the disclosed technology.

[0050] While overlapping weight ranges for the various components and ingredients that can be contained in the compositions of the disclosed technology have been expressed for selected embodiments and aspects of the disclosed technology, it should be readily apparent that the specific amount of each component in the disclosed compositions will be selected from its disclosed range such that the amount of each component is adjusted such that the sum of all components in the composition will total 100 weight percent. The amounts employed will vary with the purpose and character of the desired product and can be readily determined by one skilled in the art.

[0051] Unexpectedly, it has been discovered that highly efficient yield stress fluids with excellent shear thinning and optical clarity over a broad pH range are obtained if certain chemically crosslinked, nonionic (or substantially nonionic), amphiphilic polymers are mixed with surfactants in water. It has been determined that crosslinking provides the right balance between mechanical rigidity of the particles and expansion in aqueous surfactant media. The crosslinked, nonionic (or substantially nonionic), amphiphilic polymers of the present technology display high surfactant activated swelling in water with increases in particle diameter of at least a factor of 2.5 in one aspect and at least 2.7 in another aspect. Furthermore, swollen micro-gels based on the polymers of the disclosed technology interact with each other in aqueous surfactant media to create soft glassy materials (SGMs) with high yield stress and shear thinning flow that is substantially

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independent of pH. Moreover, it has been unexpectedly found that inorganic salts synergistically improve the rheological profiles (e.g., viscosity and yield value) of aqueous surfactant systems in which the amphiphilic polymers of the disclosed technology have been included.

Amphiphilic Polymer

[0052] The crosslinked, nonionic, amphiphilic polymers useful in the practice of the disclosed technology are polymerized from monomer components that contain free radically polymerizable unsaturation. In one embodiment, the crosslinked, nonionic, amphiphilic polymers useful in the practice of the disclosed technology are polymerized from a monomer composition comprising at least one nonionic, hydrophilic unsaturated monomer, at least one unsaturated hydrophobic monomer, and at least one polyunsaturated crosslinking monomer. In one aspect, the copolymer can be polymerized from a monomer composition comprising any weight ratio of nonionic, hydrophilic unsaturated monomer to unsaturated hydrophobic monomer.

[0053] In one embodiment, the copolymers can be polymerized from a monomer composition typically having a hydrophilic monomer to hydrophobic monomer ratio of from about 5:95 wt.% to about 95:5 wt.%, from about 15:85 wt.% to about 85:15 wt.% in another aspect, and from about 30:70 wt.% to about 70:30 wt.% in a further aspect, based on the total weight of the hydrophilic and hydrophobic monomers present. The hydrophilic monomer component can be selected from a single hydrophilic monomer or a mixture of hydrophilic monomers, and the hydrophobic monomer component can be selected from a single hydrophobic monomer or a mixture of hydrophobic monomers.

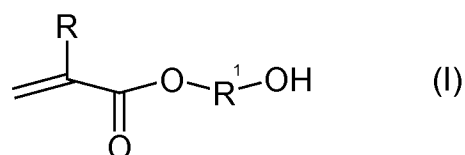
Hydrophilic Monomer

[0054] The hydrophilic monomers suitable for the preparation of the crosslinked, nonionic, amphiphilic polymer compositions of the disclosed technology are selected from but are not limited to hydroxy(C₁-C₅)alkyl (meth)acrylates; open chain and cyclic N-vinylamides (N-vinyl lactams containing 4 to 9 atoms in the lactam ring moiety, wherein the ring carbon atoms optionally

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can be substituted by one or more lower alkyl groups such as methyl, ethyl or propyl); amino group containing vinyl monomers selected from (meth)acrylamide, N-(C₁-C₅)alkyl(meth)acrylamides, N,N-di(C₁-C₅)alkyl(meth)acrylamides, N-(C₁-C₅)alkylamino(C₁-C₅)alkyl(meth)acrylamides and N,N-di(C₁-C₅)alkylamino(C₁-C₅)alkyl(meth)acrylamides, wherein the alkyl moieties on the disubstituted amino groups can be the same or different, and wherein the alkyl moieties on the monosubstituted and disubstituted amino groups can be optionally substituted with a hydroxyl group; other monomers include vinyl alcohol; vinyl imidazole; and (meth)acrylonitrile. Mixtures of the foregoing monomers also can be utilized.

[0055] The hydroxy(C₁-C₅)alkyl (meth)acrylates can be structurally represented by the following formula:



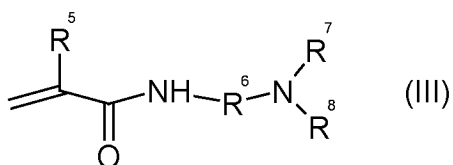
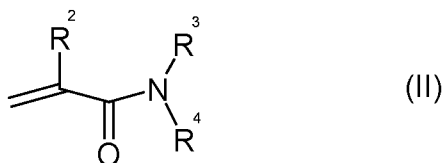
wherein R is hydrogen or methyl and R¹ is a divalent alkylene moiety containing 1 to 5 carbon atoms, wherein the alkylene moiety optionally can be substituted by one or more methyl groups. Representative monomers include 2-hydroxyethyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, and mixtures thereof.

[0056] Representative open chain N-vinylamides include N-vinylformamide, N-methyl-N-vinylformamide, N-(hydroxymethyl)-N-vinylformamide, N-vinylacetamide, N-vinylmethylacetamide, N-(hydroxymethyl)-N-vinylacetamide, and mixtures thereof.

[0057] Representative cyclic N-vinylamides (also known as N-vinyl lactams) include N-vinyl-2-pyrrolidinone, N-(1-methyl vinyl) pyrrolidinone, N-vinyl-2-piperidone, N-vinyl-2-caprolactam, N-vinyl-5-methyl pyrrolidinone, N-vinyl-3,3-dimethyl pyrrolidinone, N-vinyl-5-ethyl pyrrolidinone and N-vinyl-6-methyl piperidone, and mixtures thereof. Additionally, monomers containing a pendant N-vinyl lactam moiety can also be employed, e.g., N-vinyl-2-ethyl-2-pyrrolidone (meth)acrylate.

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[0058] The amino group containing vinyl monomers include (meth)acrylamide, diacetone acrylamide and monomers that are structurally represented by the following formulas:



[0059] Formula (II) represents N-(C₁-C₅)alkyl(meth)acrylamide or N,N-di(C₁-C₅)alkyl(meth)acrylamide wherein R² is hydrogen or methyl, R³ independently is selected from hydrogen, C₁ to C₅ alkyl and C₁ to C₅ hydroxyalkyl, and R⁴ independently is selected from is C₁ to C₅ alkyl or C₁ to C₅ hydroxyalkyl.

[0060] Formula (III) represents N-(C₁-C₅)alkylamino(C₁-C₅)alkyl(meth)acrylamide or N,N-di(C₁-C₅)alkylamino(C₁-C₅)alkyl(meth)acrylamide wherein R⁵ is hydrogen or methyl, R⁶ is C₁ to C₅ alkylene, R⁷ independently is selected from hydrogen or C₁ to C₅ alkyl, and R⁸ independently is selected from C₁ to C₅ alkyl.

[0061] Representative N-alkyl(meth)acrylamides include but are not limited to N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-propyl(meth)acrylamide, N-isopropyl(meth)acrylamide, N-tert-butyl(meth)acrylamide, N-(2-hydroxyethyl)(meth)acrylamide, N-(3-hydroxypropyl)(meth)acrylamide, and mixtures thereof.

[0062] Representative N,N-dialkyl(meth)acrylamides include but are not limited to N,N-dimethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N,N-(di-2-hydroxyethyl)(meth)acrylamide, N,N-(di-3-hydroxypropyl)(meth)acrylamide, N-methyl,N-ethyl(meth)acrylamide, and mixtures thereof.

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[0063] Representative N,N-dialkylaminoalkyl(meth)acrylamides include but are not limited to N,N-dimethylaminoethyl(meth)acrylamide, N,N-diethylaminoethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, and mixtures thereof.

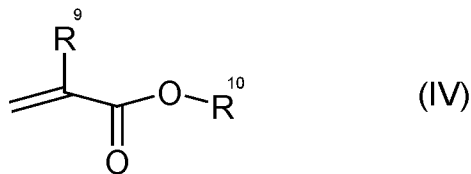
Hydrophobic Monomer

[0064] Hydrophobic monomers suitable for the preparation of the crosslinked, nonionic, amphiphilic polymer compositions of the disclosed technology are selected from but are not limited to one or more of esters of (meth)acrylic acid with alcohols containing 1 to 30 carbon atoms; vinyl esters of aliphatic carboxylic acids containing 1 to 22 carbon atoms; vinyl ethers of alcohols containing 1 to 22 carbon atoms; vinyl aromatics containing 8 to 20 carbon atoms; vinyl halides; vinylidene halides; linear or branched alpha-monoolefins containing 2 to 8 carbon atoms; an associative monomer having a hydrophobic end group containing 8 to 30 carbon atoms, and mixtures thereof.

Semi-Hydrophobic Monomer

[0065] Optionally, at least one semi-hydrophobic monomer can be used in the preparation of the amphiphilic polymers of the disclosed technology. A semi-hydrophobic monomer is similar in structure to an associative monomer, but has a substantially non-hydrophobic end group selected from hydroxyl or a moiety containing 1 to 4 carbon atoms.

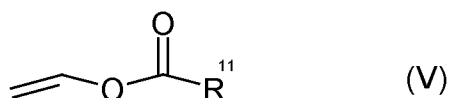
[0066] In one aspect of the disclosed technology, the esters of (meth)acrylic acid with alcohols containing 1 to 30 carbon atoms can be represented by the following formula:



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wherein R⁹ is hydrogen or methyl and R¹⁰ is C₁ to C₂₂ alkyl. Representative monomers under formula (IV) include but are not limited to methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, sec-butyl (meth)acrylate, iso-butyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, lauryl (meth)acrylate, tetradecyl (meth)acrylate, hexadecyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate, and mixtures thereof.

[0067] Vinyl esters of aliphatic carboxylic acids containing 1 to 22 carbon atoms can be represented by the following formula:



wherein R¹¹ is a C₁ to C₂₂ aliphatic group which can be an alkyl or alkenyl. Representative monomers under formula (V) include but are not limited to vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, vinyl hexanoate, vinyl 2-methylhexanoate, vinyl 2-ethylhexanoate, vinyl iso-octanoate, vinyl nonanoate, vinyl neodecanoate, vinyl decanoate, vinyl versatate, vinyl laurate, vinyl palmitate, vinyl stearate, and mixtures thereof.

[0068] In one aspect, the vinyl ethers of alcohols containing 1 to 22 carbon atoms can be represented by the following formula:



wherein R¹³ is a C₁ to C₂₂ alkyl. Representative monomers of formula (VI) include methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, 2-ethylhexyl vinyl ether, decyl vinyl ether, lauryl vinyl ether, stearyl vinyl ether, behenyl vinyl ether, and mixtures thereof.

[0069] Representative vinyl aromatic monomers include but are not limited to styrene, alpha-methylstyrene, 3-methyl styrene, 4-methyl styrene, 4-propyl

styrene, 4-tert-butyl styrene, 4-n-butyl styrene, 4-n-decyl styrene, vinyl naphthalene, and mixtures thereof.

[0070] Representative vinyl and vinylidene halides include but are not limited to vinyl chloride and vinylidene chloride, and mixtures thereof.

[0071] Representative alpha-olefins include but are not limited to ethylene, propylene, 1-butene, iso-butylene, 1-hexene, and mixtures thereof.

[0072] The associative monomer of the disclosed technology has an ethylenically unsaturated end group portion (i) for addition polymerization with the other monomers of the disclosed technology; a polyoxyalkylene mid-section portion (ii) for imparting selective hydrophilic and/or hydrophobic properties to the product polymer, and a hydrophobic end group portion (iii) for providing selective hydrophobic properties to the polymer.

[0073] The portion (i) supplying the ethylenically unsaturated end group can be a residue derived from an α,β -ethylenically unsaturated monocarboxylic acid. Alternatively, portion (i) of the associative monomer can be a residue derived from an allyl ether or vinyl ether; a nonionic vinyl-substituted urethane monomer, such as disclosed in U.S. Reissue Patent No. 33,156 or U.S. Patent No. 5,294,692; or a vinyl-substituted urea reaction product, such as disclosed in U.S. Patent No. 5,011,978; the relevant disclosures of each are incorporated herein by reference.

[0074] The mid-section portion (ii) is a polyoxyalkylene segment of about 2 to about 150 in one aspect, from about 10 to about 120 in another aspect, and from about 15 to about 60 in a further aspect of repeating C_2-C_4 alkylene oxide units. The mid-section portion (ii) includes polyoxyethylene, polyoxypropylene, and polyoxybutylene segments, and combinations thereof comprising from about 2 to about 150 in one aspect, from about 5 to about 120 in another aspect, and from about 10 to about 60 in a further aspect of ethylene, propylene and/or butylene oxide units, arranged in random or block sequences of ethylene oxide, propylene oxide and/or butylene oxide units.

[0075] The hydrophobic end group portion (iii) of the associative monomer is a hydrocarbon moiety belonging to one of the following hydrocarbon classes: a C_8-C_{30} linear alkyl, a C_8-C_{30} branched alkyl, a C_8-C_{30} carbocyclic alkyl, a C_2-C_{30}

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alkyl-substituted phenyl, an araalkyl substituted phenyl, and aryl-substituted C₂-C₃₀ alkyl groups.

[0076] Non-limiting examples of suitable hydrophobic end group portions (iii) of the associative monomers are linear or branched alkyl groups having about 8 to about 30 carbon atoms, such as capryl (C₈), iso-octyl (branched C₈), decyl (C₁₀), lauryl (C₁₂), myristyl (C₁₄), cetyl (C₁₆), cetearyl (C₁₆-C₁₈), stearyl (C₁₈), isostearyl (branched C₁₈), arachidyl (C₂₀), behenyl (C₂₂), lignoceryl (C₂₄), cerotyl (C₂₆), montanyl (C₂₈), melissyl (C₃₀), and the like.

[0077] Examples of linear and branched alkyl groups having about 8 to about 30 carbon atoms that are derived from a natural source include, without being limited thereto, alkyl groups derived from hydrogenated peanut oil, soybean oil and canola oil (all predominately C₁₈), hydrogenated tallow oil (C₁₆-C₁₈), and the like; and hydrogenated C₁₀-C₃₀ terpenols, such as hydrogenated geraniol (branched C₁₀), hydrogenated farnesol (branched C₁₅), hydrogenated phytol (branched C₂₀), and the like.

[0078] Non-limiting examples of suitable C₂-C₃₀ alkyl-substituted phenyl groups include octylphenyl, nonylphenyl, decylphenyl, dodecylphenyl, hexadecylphenyl, octadecylphenyl, isooctylphenyl, sec-butylphenyl, and the like.

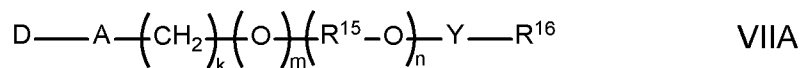
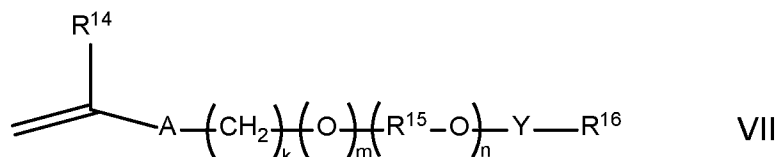
[0079] Exemplary aryl-substituted C₂-C₄₀ alkyl groups include, without limitation thereto, styryl (e.g., 2-phenylethyl), distyryl (e.g., 2,4-diphenylbutyl), tristyryl (e.g., 2,4,6-triphenylhexyl), 4-phenylbutyl, 2-methyl-2-phenylethyl, tristyrylphenolyl, and the like.

[0080] Suitable C₈-C₃₀ carbocyclic alkyl groups include, without being limited thereto, groups derived from sterols from animal sources, such as cholesterol, lanosterol, 7-dehydrocholesterol, and the like; from vegetable sources, such as phytosterol, stigmasterol, campesterol, and the like; and from yeast sources, such as ergosterol, mycosterol, and the like. Other carbocyclic alkyl hydrophobic end groups useful in the disclosed technology include, without being limited thereto, cyclooctyl, cyclododecyl, adamantyl, decahydronaphthyl, and groups derived from natural carbocyclic materials, such as pinene, hydrogenated retinol, camphor, isobornyl alcohol, and the like.

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[0081] Useful associative monomers can be prepared by any method known in the art. See, for example, U.S. Patents No. 4,421,902 to Chang *et al.*; No. 4,384,096 to Sonnabend; No. 4,514,552 to Shay *et al.*; No. 4,600,761 to Ruffner *et al.*; No. 4,616,074 to Ruffner; No. 5,294,692 to Barron *et al.*; No. 5,292,843 to Jenkins *et al.*; No. 5,770,760 to Robinson; and No. 5,412,142 to Wilkerson, III *et al.*; the pertinent disclosures of which are incorporated herein by reference.

[0082] In one aspect, exemplary associative monomers include those represented by formulas (VII) and (VIIA) as follows:

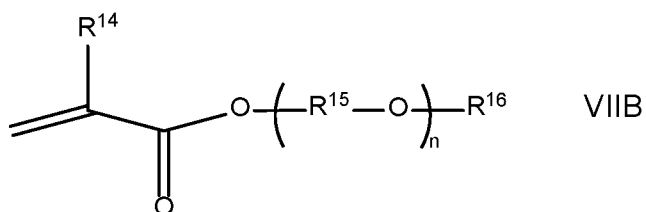


wherein R^{14} is hydrogen or methyl; A is $-\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{O}-$, $-\text{O}-$, $-\text{CH}_2\text{O}-$, $-\text{NHC}(\text{O})\text{NH}-$, $-\text{C}(\text{O})\text{NH}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{O}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{NH}-$, or $-\text{CH}_2\text{CH}_2\text{NHC}(\text{O})-$; Ar is a divalent arylene (e.g., phenylene); E is H or methyl; z is 0 or 1; k is an integer ranging from about 0 to about 30, and m is 0 or 1, with the proviso that when k is 0, m is 0, and when k is in the range of 1 to about 30, m is 1; D represents a vinyl or an allyl moiety; $(\text{R}^{15}-\text{O})_n$ is a polyoxyalkylene moiety, which can be a homopolymer, a random copolymer, or a block copolymer of C_2 - C_4 oxyalkylene units, R^{15} is a divalent alkylene moiety selected from C_2H_4 , C_3H_6 , or C_4H_8 , and combinations thereof; and n is an integer in the range of about 2 to about 150 in one aspect, from about 10 to about 120 in another aspect, and from about 15 to about 60 in a further aspect; Y is $-\text{R}^{15}\text{O}-$, $-\text{R}^{15}\text{NH}-$, $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{NH}-$, $-\text{R}^{15}\text{NHC}(\text{O})\text{NH}-$, or $-\text{C}(\text{O})\text{NHC}(\text{O})-$; R^{16} is a substituted or unsubstituted alkyl selected from a C_8 - C_{30} linear alkyl, a C_8 - C_{30}

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branched alkyl, a C₈-C₃₀ carbocyclic alkyl, a C₂-C₃₀ alkyl-substituted phenyl, an aralkyl substituted phenyl, and an aryl-substituted C₂-C₃₀ alkyl; wherein the R¹⁶ alkyl group, aryl group, phenyl group optionally comprises one or more substituents selected from the group consisting of a hydroxyl group, an alkoxy group, benzyl group phenylethyl group, and a halogen group.

[0083] In one aspect, the hydrophobically modified associative monomer is an alkoxyated (meth)acrylate having a hydrophobic group containing 8 to 30 carbon atoms represented by the following formula:



wherein R¹⁴ is hydrogen or methyl; R¹⁵ is a divalent alkylene moiety independently selected from C₂H₄, C₃H₆, and C₄H₈, and n represents an integer ranging from about 2 to about 150 in one aspect, from about 5 to about 120 in another aspect, and from about 10 to about 60 in a further aspect, (R¹⁵-O) can be arranged in a random or a block configuration; R¹⁶ is a substituted or unsubstituted alkyl selected from a C₈-C₃₀ linear alkyl, a C₈-C₃₀ branched alkyl, a C₈-C₃₀ carbocyclic alkyl, a C₂-C₃₀ alkyl-substituted phenyl, and an aryl-substituted C₂-C₃₀ alkyl.

[0084] Representative monomers under formula (VII) include lauryl polyethoxylated methacrylate (LEM), cetyl polyethoxylated methacrylate (CEM), cetearyl polyethoxylated methacrylate (CSEM), stearyl polyethoxylated (meth)acrylate, arachidyl polyethoxylated (meth)acrylate, behenyl polyethoxylated methacrylate (BEM), cerotyl polyethoxylated (meth)acrylate, montanyl polyethoxylated (meth)acrylate, melissyl polyethoxylated (meth)acrylate, phenyl polyethoxylated (meth)acrylate, nonylphenyl polyethoxylated (meth)acrylate, ω-tristyrylphenyl polyoxyethylene methacrylate, where the polyethoxylated portion of the monomer contains about 2 to about 150 ethylene oxide units in one aspect, from about 5 to about 120 in another aspect, from about 10 to about 60 in still another aspect, from 10 to 40 in a further aspect, and from 15 to 30 in a still further

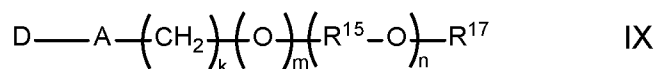
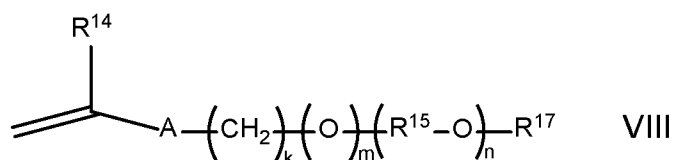
aspect; octyloxy polyethyleneglycol (8) polypropyleneglycol (6) (meth)acrylate, phenoxy polyethylene glycol (6) polypropylene glycol (6) (meth)acrylate, and nonylphenoxy polyethylene glycol polypropylene glycol (meth)acrylate.

[0085] The semi-hydrophobic monomers of the disclosed technology are structurally similar to the associative monomer described above, but have a substantially non-hydrophobic end group portion. The semi-hydrophobic monomer has an ethylenically unsaturated end group portion (i) for addition polymerization with the other monomers of the disclosed technology; a polyoxyalkylene mid-section portion (ii) for imparting selective hydrophilic and/or hydrophobic properties to the product polymer and a semi-hydrophobic end group portion (iii). The unsaturated end group portion (i) supplying the vinyl or other ethylenically unsaturated end group for addition polymerization is preferably derived from an α,β -ethylenically unsaturated mono carboxylic acid. Alternatively, the end group portion (i) can be derived from an allyl ether residue, a vinyl ether residue or a residue of a nonionic urethane monomer.

[0086] The polyoxyalkylene mid-section (ii) specifically comprises a polyoxyalkylene segment, which is substantially similar to the polyoxyalkylene portion of the associative monomers described above. In one aspect, the polyoxyalkylene portions (ii) include polyoxyethylene, polyoxypropylene, and/or polyoxybutylene units comprising from about 2 to about 150 in one aspect, from about 5 to about 120 in another aspect, and from about 10 to about 60 in a further aspect of ethylene oxide, propylene oxide, and/or butylene oxide units, arranged in random or blocky sequences.

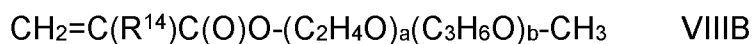
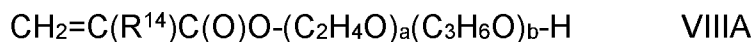
[0087] In one aspect, the semi-hydrophobic monomer can be represented by the following formulas:

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wherein R^{14} is hydrogen or methyl; A is $-\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{O}-$, $-\text{O}-$, $-\text{CH}_2\text{O}-$, $-\text{NHC}(\text{O})\text{NH}-$, $-\text{C}(\text{O})\text{NH}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{O}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{NH}-$, or $-\text{CH}_2\text{CH}_2\text{NHC}(\text{O})-$; Ar is a divalent arylene (e.g., phenylene); E is H or methyl; z is 0 or 1; k is an integer ranging from about 0 to about 30, and m is 0 or 1, with the proviso that when k is 0, m is 0, and when k is in the range of 1 to about 30, m is 1; $(\text{R}^{15}-\text{O})_n$ is a polyoxyalkylene moiety, which can be a homopolymer, a random copolymer, or a block copolymer of C_2 - C_4 oxyalkylene units, R^{15} is a divalent alkylene moiety selected from C_2H_4 , C_3H_6 , or C_4H_8 , and combinations thereof; and n is an integer in the range of about 2 to about 150 in one aspect, from about 5 to about 120 in another aspect, and from about 10 to about 60 in a further aspect; R^{17} is selected from hydrogen and a linear or branched C_1 - C_4 alkyl group (e.g., methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, and tert-butyl); and D represents a vinyl or an allyl moiety.

[0088] In one aspect, the semi-hydrophobic monomer under formula VIII can be represented by the following formulas:



wherein R^{14} is hydrogen or methyl, and "a" is an integer ranging from 0 or 2 to about 120 in one aspect, from about 5 to about 45 in another aspect, and from about 10 to about 25 in a further aspect, and "b" is an integer ranging from about 0 or 2 to about 120 in one aspect, from about 5 to about 45 in another aspect, and

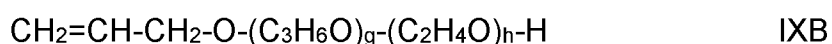
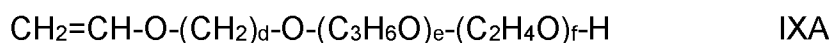
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from about 10 to about .25 in a further aspect, subject to the proviso that “a” and “b” cannot be 0 at the same time.

[0089] Examples of semi-hydrophobic monomers under formula VIIIA include polyethyleneglycol methacrylate available under the product names Blemmer[®] PE-90 (R¹⁴ = methyl, a = 2, b = 0), PE-200 (R¹⁴ = methyl, a = 4.5, b = 0), and PE-350 (R¹⁴ = methyl, a = 8, b = 0); polypropylene glycol methacrylate available under the product names Blemmer[®] PP-1000 (R¹⁴ = methyl, b = 4-6, a = 0), PP-500 (R¹⁴ = methyl, a = 0, b = 9), PP-800 (R¹⁴ = methyl, a = 0, b = 13); polyethyleneglycol polypropylene glycol methacrylate available under the product names Blemmer[®] 50PEP-300 (R¹⁴ = methyl, a = 3.5, b = 2.5), 70PEP-350B (R¹⁴ = methyl, a = 5, b = 2); polyethyleneglycol acrylate available under the product names Blemmer[®] AE-90 (R¹⁴ = hydrogen, a = 2, b = 0), AE-200 (R¹⁴ = hydrogen, a = 2, b = 4.5), AE-400 (R¹⁴ = hydrogen, a = 10, b = 0); polypropyleneglycol acrylate available under the product names Blemmer[®] AP-150 (R¹⁴ = hydrogen, a = 0, b = 3), AP-400 (R¹⁴ = hydrogen, a = 0, b = 6), AP-550 (R¹⁴ = hydrogen, a = 0, b = 9). Blemmer[®] is a trademark of NOF Corporation, Tokyo, Japan.

[0090] Examples of semi-hydrophobic monomers under formula VIIIB include methoxypolyethyleneglycol methacrylate available under the product names Visiomer[®] MPEG 750 MA W (R¹⁴ = methyl, a = 17, b = 0), MPEG 1005 MA W (R¹⁴ = methyl, a = 22, b = 0), MPEG 2005 MA W (R¹⁴ = methyl, a = 45, b = 0), and MPEG 5005 MA W (R¹⁴ = methyl, a = 113, b = 0) from Evonik Röhm GmbH, Darmstadt, Germany); Bisomer[®] MPEG 350 MA (R¹⁴ = methyl, a = 8, b = 0), and MPEG 550 MA (R¹⁴ = methyl, a = 12, b = 0) from GEO Specialty Chemicals, Ambler PA; Blemmer[®] PME-100 (R¹⁴ = methyl, a = 2, b = 0), PME-200 (R¹⁴ = methyl, a = 4, b = 0), PME400 (R¹⁴ = methyl, a = 9, b = 0), PME-1000 (R¹⁴ = methyl, a = 23, b = 0), PME-4000 (R¹⁴ = methyl, a = 90, b = 0).

[0091] In one aspect, the semi-hydrophobic monomer set forth in formula IX can be represented by the following formulas:



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wherein d is an integer of 2, 3, or 4; e is an integer in the range of from about 1 to about 10 in one aspect, from about 2 to about 8 in another aspect, and from about 3 to about 7 in a further aspect; f is an integer in the range of from about 5 to about 50 in one aspect, from about 8 to about 40 in another aspect, and from about 10 to about 30 in a further aspect; g is an integer in the range of from 1 to about 10 in one aspect, from about 2 to about 8 in another aspect, and from about 3 to about 7 in a further aspect; and h is an integer in the range of from about 5 to about 50 in one aspect, and from about 8 to about 40 in another aspect; e, f, g, and h can be 0 subject to the proviso that e and f cannot be 0 at the same time, and g and h cannot be 0 at the same time.

[0092] Monomers under formulas IXA and IXB are commercially available under the trade names Emulsogen[®] R109, R208, R307, RAL109, RAL208, and RAL307 sold by Clariant Corporation; BX-AA-E5P5 sold by Bimax, Inc.; and combinations thereof. EMULSOGEN[®] R109 is a randomly ethoxylated/propoxylated 1,4-butanediol vinyl ether having the empirical formula $\text{CH}_2=\text{CH}-\text{O}(\text{CH}_2)_4\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{10}\text{H}$; Emulsogen[®] R208 is a randomly ethoxylated/propoxylated 1,4-butanediol vinyl ether having the empirical formula $\text{CH}_2=\text{CH}-\text{O}(\text{CH}_2)_4\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{20}\text{H}$; Emulsogen[®] R307 is a randomly ethoxylated/propoxylated 1,4-butanediol vinyl ether having the empirical formula $\text{CH}_2=\text{CH}-\text{O}(\text{CH}_2)_4\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{30}\text{H}$; Emulsogen[®] RAL109 is a randomly ethoxylated/propoxylated allyl ether having the empirical formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{10}\text{H}$; Emulsogen[®] RAL208 is a randomly ethoxylated/propoxylated allyl ether having the empirical formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{20}\text{H}$; Emulsogen[®] RAL307 is a randomly ethoxylated/propoxylated allyl ether having the empirical formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_4(\text{C}_2\text{H}_4\text{O})_{30}\text{H}$; and BX-AA-E5P5 is a randomly ethoxylated/propoxylated allyl ether having the empirical formula $\text{CH}_2=\text{CHCH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_5(\text{C}_2\text{H}_4\text{O})_5\text{H}$.

[0093] In the associative and semi-hydrophobic monomers of the disclosed technology, the polyoxyalkylene mid-section portion contained in these monomers can be utilized to tailor the hydrophilicity and/or hydrophobicity of the polymers in which they are included. For example, mid-section portions rich in ethylene oxide

moieties are more hydrophilic while mid-section portions rich in propylene oxide moieties are more hydrophobic. By adjusting the relative amounts of ethylene oxide to propylene oxide moieties present in these monomers the hydrophilic and hydrophobic properties of the polymers in which these monomers are included can be tailored as desired.

[0094] The amount of associative and/or semi-hydrophobic monomer utilized in the preparation of the polymers of the disclosed technology can vary widely and depends, among other things, on the final rheological and aesthetic properties desired in the polymer. When utilized, the monomer reaction mixture contains one or more monomers selected from the associative and/or semi-hydrophobic monomers disclosed above in amounts ranging from about 0.01 to about 15 wt.% in one aspect, from about 0.1 wt.% to about 10 wt.% in another aspect, from about 0.5 to about 8 wt.% in still another aspect and from about 1, 2 or 3 to about 5 wt.% in a further aspect, based on the weight of the total monomers.

Ionizable Monomer

[0095] In one aspect of the disclosed technology, the crosslinked, nonionic, amphiphilic polymer compositions of the disclosed technology can be polymerized from a monomer composition including 0 to 5 wt.% of an ionizable and/or ionized monomer, based on the weight of the total monomers, so long as the yield stress value of the yield stress fluids in which the polymers of the disclosed technology are included are not deleteriously affected (i.e., the yield stress value of the fluid does not fall below 1 mPa, or 0.1 Pa).

[0096] In another aspect, the amphiphilic polymer compositions of the disclosed technology can be polymerized from a monomer composition comprising less than 3 wt.% in one aspect, less than 1 wt.% in a further aspect, less than 0.5 wt.% in a still further aspect, less than 0.1 wt.% in an additional aspect, and less than 0.05 wt.% in a further aspect, of an ionizable and/or an ionized moiety, based on the weight of the total monomers.

[0097] Ionizable monomers include monomers having a base neutralizable moiety and monomers having an acid neutralizable moiety. Base neutralizable monomers include olefinically unsaturated monocarboxylic and dicarboxylic acids

and their salts containing 3 to 5 carbon atoms and anhydrides thereof. Examples include (meth)acrylic acid, itaconic acid, maleic acid, maleic anhydride, and combinations thereof. Other acidic monomers include styrenesulfonic acid, acrylamidomethylpropanesulfonic acid (AMPS[®] monomer), vinylsulfonic acid, vinylphosphonic acid, allylsulfonic acid, methallylsulfonic acid; and salts thereof.

[0098] Acid neutralizable monomers include olefinically unsaturated monomers which contain a basic nitrogen atom capable of forming a salt or a quaternized moiety upon the addition of an acid. For example, these monomers include vinylpyridine, vinylpiperidine, vinylimidazole, vinylmethylimidazole, dimethylaminomethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminomethyl (meth)acrylate and methacrylate, dimethylaminoneopentyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, and diethylaminoethyl (meth)acrylate.

Crosslinking Monomer

[0099] In one embodiment, the crosslinked, nonionic, amphiphilic polymers useful in the practice of the disclosed technology are polymerized from a monomer composition comprising a first monomer comprising at least one nonionic, hydrophilic unsaturated monomer, at least one nonionic, unsaturated hydrophobic monomer, and mixtures thereof, and a third monomer comprising at least one polyunsaturated crosslinking monomer. The crosslinking monomer(s) is utilized to polymerize covalent crosslinks into the polymer backbone. The crosslinking monomer can be an amphiphilic crosslinking agent or a mixture of an amphiphilic crosslinking agent and a conventional crosslinking agent.

[0100] The crosslinking monomer can be an amphiphilic crosslinking agent. The amphiphilic crosslinking agent is utilized to polymerize covalent crosslinks into the amphiphilic polymer backbone. In some instances, conventional crosslinking agents can affect the volume expansion or swelling of micro-gel particles in fluids containing surfactants. For example, a high level of conventional crosslinking agent could provide a high yield stress but the limited expansion of the micro-gels would result in undesirably high polymer use levels and low optical clarity. On the other hand, a low level of conventional crosslinking agents could give high optical

clarity but low yield stress. It is desirable that polymeric micro-gels allow maximum swelling while maintaining a desirable yield stress, and it has been found that the use of amphiphilic crosslinking agents in place of, or in conjunction with conventional crosslinking agents can provide just these benefits. In addition, it has been found that the amphiphilic crosslinking agent can be easily reacted into the amphiphilic polymer. Often, certain processing techniques, such as staging, can be required with conventional crosslinking agents to achieve the proper balance of optical clarity and yield stress. In contrast, it has been found that amphiphilic crosslinking agents can simply be added in a single stage with the monomer mixture.

[0101] Amphiphilic crosslinking agents are a subset of compounds known in the art as reactive surfactants. Reactive surfactants are surface acting agents containing at least one reactive moiety so that they can covalently link to the surface of polymeric particles. By linking to particles, the reactive surfactants can improve the colloidal stability of latex particles due to the surfactant's resistance to desorbing from the particle surface. Reactive surfactants in the art commonly only have, or only need, one reactive moiety to prevent such desorption.

[0102] As a subset of reactive surfactants, amphiphilic crosslinking agents as used herein are those compounds or mixtures thereof that include more than one reactive moiety. It has surprisingly been found that such amphiphilic crosslinking agents not only can be employed to improve stability of particles, but can be efficiently employed to prepare yield stress fluids as described herein.

[0103] The art is replete with disclosures on various types of reactive surfactants, and one of ordinary skill in the art could readily determine which include more than one reactive moiety such that they can be employed herein as amphiphilic crosslinking agents without undue experimentation. Exemplary non-limiting amphiphilic crosslinking agents can be seen, for example, in US 3,541,138 (issued Nov. 17, 1970 to Emmons et al.), US 6,262,152 (issued Jul. 17, 2001 to Fryd et al.), US 8,354,488 (issued Jan. 15, 2013 to Li et al.), WO2002/100525 (published Dec. 19, 2002 to Syngenta), and the like.

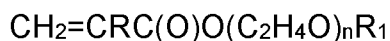
[0104] The amphiphilic crosslinking agent contains a hydrophobic moiety and a hydrophilic moiety. The hydrophobic moiety will provide solubility in oils,

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and the hydrophilic moiety will provide water solubility. Hydrophobic and hydrophilic moieties are well known to those skilled in the art.

[0105] Non-limiting examples of hydrophobic moieties of the amphiphilic crosslinking agent can be derived from functional groups such as alkyl, aryl, and alkyl aryl acrylates or methacrylates having 1-12 carbon atoms in the alkyl group and/or 6-12 carbons in the aryl group such as methyl, ethyl, butyl, propyl, isobutyl, hexyl, 2-ethyl hexyl, nonyl, lauryl, isobornyl, benzyl acrylates and methacrylates and the like; polymerizable vinyl aromatic monomers such as styrene, alpha methyl styrene, vinyl toluene and the like; and aliphatic hydrocarbon monomers such as isoprene and butadiene. Regardless of the constituent functional groups from which the hydrophobic moiety of the amphiphilic crosslinking agent is derived, the hydrophobic moiety will have limited solubility in water, which one of ordinary skill in the art would readily envisage. Examples of functional groups for preparing hydrophobic moieties can include, for example, alkyl phenols, stearyls, lauryls, tri-styryl phenols, groups derived from natural oils, and the like.

[0106] Non-limiting examples of hydrophilic moieties of the amphiphilic crosslinking agent can be functional groups such as ethoxylates, hydroxyls, amidos, aminos, phosphates, phosphonates, sulfates, sulfonates, carboxylates and the like. Such hydrophilic moieties of the amphiphilic crosslinking agent can be derived from, for example, acid monomers such as acrylic acid, methacrylic acid, acrylamidomethylpropane sulfonic acid, itaconic acid, maleic acid and styrene sulfonic acid and esters thereof; amine-containing monomers such as 2-dimethylaminoethyl methacrylate, 2-dimethylaminoethyl acrylate, 2-diethylaminoethyl methacrylate, and 2-diethylaminoethyl acrylate; and monomers having oligoether moieties of the general formula:



wherein R=H or methyl; R₁=alkyl of 1 to 4 carbon atoms, aryl of 6 to 12 carbon atoms, or alkyl-aryl, and n=1 to 20, examples of which include ethoxyethyl methacrylate, butoxyethyl methacrylate, ethoxytriethylene methacrylate, methoxy-polyethylene glycol methacrylate, and 2-ethoxytriethylene glycol methacrylate.

[0107] Additionally, the amphiphilic crosslinking agent contains multiple crosslinking moieties. Non-limiting examples of crosslinking moieties can include those shown in Table A below.

Table A

Functional Group	Crosslinking Group
epoxy	amine, anhydride, acid, phenolic, hydroxyl, N-methylol, aldehyde, acetoacetoxy
hydroxyl	isocyanate, epoxide, N-methylol, anhydride, ester
anhydride	epoxide, amine, hydroxyl
cyclic carbonate	Amine
activated allyl	amine, radical inhibitor
amine	aldehyde, epoxide, anhydride, isocyanate, ester, acetoacetoxy, activated allyl
silane, silicate, silanol, silicone	hydroxyl, water, acid, isocyanate, silane, silicate
imine	aldehyde, epoxide, anhydride, isocyanate, ester, acetoacetoxy, activated allyl

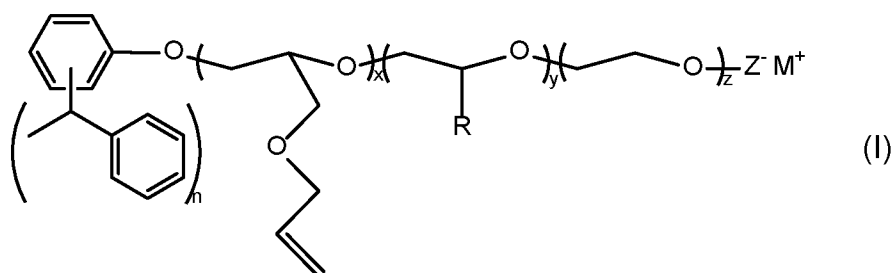
[0108] Further non-limiting examples of crosslinking moieties can include unsaturated moieties. In an embodiment, the amphiphilic crosslinking agent contains more than one unsaturated moiety, or at least two unsaturated moieties. In one aspect, the amphiphilic crosslinking agent is a polyunsaturated compound containing at least 2 unsaturated moieties. In another aspect, the amphiphilic crosslinking agent contains at least 3 unsaturated moieties.

[0109] Mixtures of two or more amphiphilic crosslinking agents can also be utilized to crosslink the nonionic, amphiphilic polymers. In one aspect, the mixture of amphiphilic crosslinking agent contains more than one unsaturated moieties, or an average of 1.5 or 2 unsaturated moieties. In another aspect, the mixture of amphiphilic crosslinking agents contains an average of 2.5 unsaturated moieties. In still another aspect, the mixture of amphiphilic crosslinking agents contains an average of about 3 unsaturated moieties. In a further aspect, the mixture of amphiphilic crosslinking agents contains an average of about 3.5 unsaturated moieties.

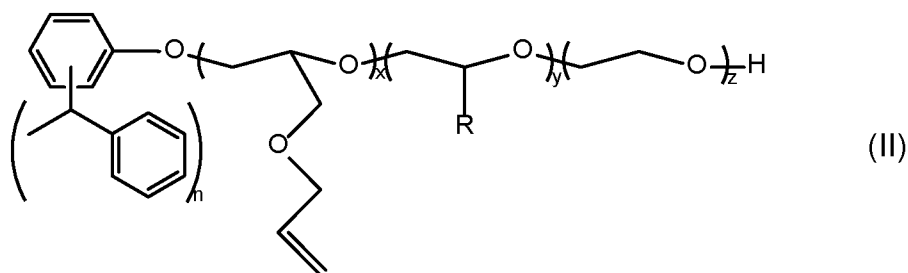
[0110] In one aspect, exemplary amphiphilic crosslinking agents suitable for use with the present technology can include, but not be limited to, compounds

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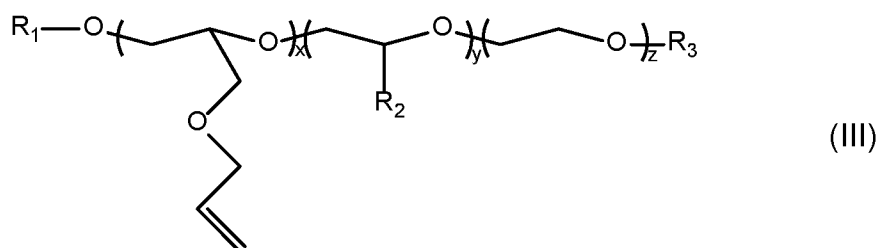
such as those disclosed in US 2013/0047892 (published Feb. 28, 2013 to Palmer, Jr. et al.), represented by the following formulas:



where R=CH₃, CH₂CH₃, C₆H₅, or C₁₄H₂₉; n=1, 2, or 3; x is 2-10, y is 0-200, z is 4-200, more preferably from about 5 to 60, and most preferably from about 5 to 40; Z can be either SO₃⁻ or PO₃²⁻, and M⁺ is Na⁺, K⁺, NH₄⁺, or an alkanolamine such as, for example, monoethanolamine, diethanolamine, and triethanolamine;



where R=CH₃, CH₂CH₃, C₆H₅, or C₁₄H₂₉; n=1, 2, 3; x is 2-10, y is 0-200, z is 4-200, more preferably from about 5 to 60, and most preferably from about 5 to 40;



where R₁ is a C₁₀₋₂₄ alkyl, alkaryl, alkenyl, or cycloalkyl, R₂=CH₃, CH₂CH₃, C₆H₅, or C₁₄H₂₉; x is 2-10, y is 0-200, z is 4-200, more preferably from about 5 to 60, and most preferably from about 5 to 40; and R₃ is H or Z⁻ M⁺ Z can be either SO₃⁻ or

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PO_3^{2-} , and M^+ is Na^+ , K^+ , NH_4^+ , or an alkanolamine such as, for example, monoethanolamine, diethanolamine, and triethanolamine.

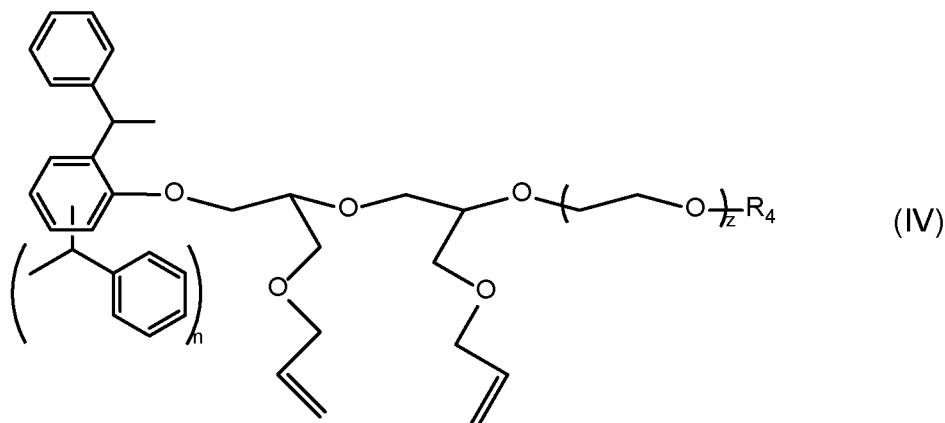
[0111] The foregoing amphiphilic crosslinking agents conforming to formulas (I), (II), (III), (IV) and (V) are disclosed in U.S. Patent Application Publication No. US 2014/0114006, the disclosure of which is herein incorporated by reference, and are commercially available under the E-Sperse™ RS Series trade name (e.g., product designations RS-1617, RS-1618, RS-1684) from Ethox Chemicals, LLC.

[0112] In one embodiment, the amphiphilic crosslinking agent can be used in an amount ranging from about 0.01 to about 3 wt.% in one aspect, from about 0.05 to about 0.1 wt.% in another aspect, and from about 0.1 to about 0.75 wt.% in a further aspect, based on the total weight of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymers of the disclosed technology. Stated another way, the amount of amphiphilic crosslinking agent and/or conventional crosslinking monomer discussed below can be calculated on the basis of parts by wt. (100% active material) per 100 parts by wt. (100% active material) of total monounsaturated monomers utilized to prepare the polymer of the disclosed technology.

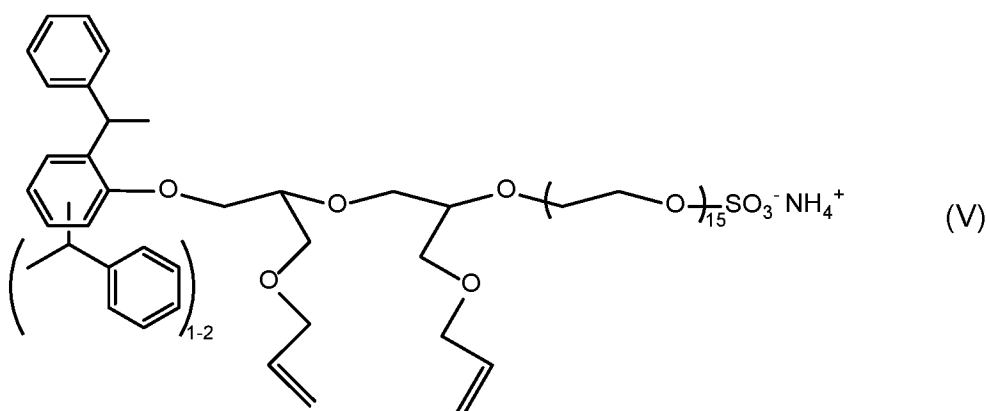
[0113] In another embodiment, the amphiphilic crosslinking agent can contain an average of about 1.5 or 2 unsaturated moieties and can be used in an amount ranging from about 0.01 to about 3 wt.% in one aspect, from about 0.02 to about 1 wt.% in another aspect, from about 0.05 to about 0.75 wt.% in a further aspect, and from about 0.075 to about 0.5 wt.% in a still further aspect, and from about 0.1 to about 0.15 wt.% in another aspect, based upon the total weight of the of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymers of the disclosed technology.

[0114] In one aspect, the amphiphilic crosslinking agent is selected from compounds of formulas (III), (IV) or (V).

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where n is 1 or 2; z is 4 to 40 in one aspect, 5 to 38 in another aspect, and 10 to 20 in a further aspect; and R₄ is H, SO₃⁻M⁺ or PO₃⁻M⁺, and M is selected from Na, K, and NH₄.



[0115] In one embodiment, the crosslinking monomer can include a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent. These are relatively low molecular weight polyunsaturated compounds (less than 300 Daltons). In one aspect, the conventional crosslinking agent is a polyunsaturated compound containing at least 2 unsaturated moieties. In another aspect, the conventional crosslinking agent contains at least 3 unsaturated moieties. Exemplary polyunsaturated compounds include di(meth)acrylate compounds such as ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-butylene glycol di(meth)acrylate, 1,6-hexanediol

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di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 2,2'-bis(4-(acryloxy-propyloxyphenyl)propane, and 2,2'-bis(4-(acryloxydiethoxy-phenyl)propane; tri(meth)acrylate compounds such as, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, and tetramethylolmethane tri(meth)acrylate; tetra(meth)acrylate compounds such as ditrimethylolpropane tetra(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, and pentaerythritol tetra(meth)acrylate; hexa(meth)acrylate compounds such as dipentaerythritol hexa(meth)acrylate; allyl compounds such as allyl (meth)acrylate, diallylphthalate, diallyl itaconate, diallyl fumarate, and diallyl maleate; polyallyl ethers of sucrose having from 2 to 8 allyl groups per molecule, polyallyl ethers of pentaerythritol such as pentaerythritol diallyl ether, pentaerythritol triallyl ether, and pentaerythritol tetraallyl ether, and combinations thereof; polyallyl ethers of trimethylolpropane such as trimethylolpropane diallyl ether, trimethylolpropane triallyl ether, and combinations thereof. Other suitable polyunsaturated compounds include divinyl glycol, divinyl benzene, and methylenebisacrylamide.

[0116] In another aspect, suitable polyunsaturated monomers can be synthesized via an esterification reaction of a polyol made from ethylene oxide or propylene oxide or combinations thereof with unsaturated anhydride such as maleic anhydride, citraconic anhydride, itaconic anhydride, or an addition reaction with unsaturated isocyanate such as 3-isopropenyl- α - α -dimethylbenzene isocyanate.

[0117] Mixtures of two or more of the foregoing polyunsaturated compounds can also be utilized to crosslink the nonionic, amphiphilic polymers. In one aspect, the mixture of conventional unsaturated crosslinking monomer contains an average of 2 unsaturated moieties. In another aspect, the mixture of conventional crosslinking agents contains an average of 2.5 unsaturated moieties. In still another aspect, the mixture of conventional crosslinking agents contains an average of about 3 unsaturated moieties. In a further aspect, the mixture of conventional crosslinking agents contains an average of about 3.5 unsaturated moieties.

[0118] In one embodiment, the conventional crosslinking agent component can be used in an amount ranging from about 0.01 to about 1 wt.% in one aspect, from about 0.05 to about 0.75 wt.% in another aspect, and from about 0.1 to about 0.5 wt.% in a further aspect, based on the total weight of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymers of the disclosed technology.

[0119] In another embodiment of the disclosed technology, the conventional crosslinking agent component contains an average of about 3 unsaturated moieties and can be used in an amount ranging from about 0.01 to about 0.3 wt.% in one aspect, from about 0.02 to about 0.25 wt.% in another aspect, from about 0.05 to about 0.2 wt.% in a further aspect, and from about 0.075 to about 0.175 wt.% in a still further aspect, and from about 0.1 to about 0.15 wt.% in another aspect, based upon the total weight of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymers of the disclosed technology.

[0120] In one aspect, the conventional crosslinking agent is selected from trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, pentaerythritol triallylether and polyallyl ethers of sucrose having 3 allyl groups per molecule.

[0121] In another aspect, the nonionic amphiphilic polymer can be crosslinked with a combination of a conventional crosslinking agent and an amphiphilic crosslinking agent. The conventional crosslinking agent and amphiphilic crosslinking agent can be used in a total amount ranging from about 0.01 to about 1 wt.% in one aspect, from about 0.05 to about 0.75 wt.% in another aspect, and from about 0.1 to about 0.5 wt.% in a further aspect, based on the total weight of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymers of the disclosed technology.

[0122] In another embodiment, the combination of the conventional crosslinking agent and amphiphilic crosslinking agent can contain an average of about 2 or 3 unsaturated moieties and can be used in an amount ranging from about 0.01 to about 2 wt.% in one aspect, from about 0.02 to about 0.3 wt.% in another aspect, from about 0.05 to about 0.2 wt.% in a further aspect, and from about 0.075 to about 0.175 wt.% in a still further aspect, and from about 0.1 to

about 0.15 wt.% in another aspect, based upon the total weight of the of the monounsaturated monomers utilized to prepare the nonionic, amphiphilic polymer of the disclosed technology.

[0123] In one aspect, the combination of the conventional crosslinking agent and amphiphilic crosslinking agent can include conventional crosslinking agents selected from selected from trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, tetramethylmethane tri(meth)acrylate, pentaerythritol triallylether and polyallyl ethers of sucrose having 3 allyl groups per molecule, and combinations thereof, and amphiphilic crosslinking agents selected from compounds of formula (III), (V), and combinations thereof.

Amphiphilic Polymer Synthesis

[0124] The crosslinked, nonionic, amphiphilic polymer of the disclosed technology can be made using conventional free-radical emulsion polymerization techniques. The polymerization processes are carried out in the absence of oxygen under an inert atmosphere such as nitrogen. The polymerization can be carried out in a suitable solvent system such as water. Minor amounts of a hydrocarbon solvent, organic solvent, as well as mixtures thereof can be employed. The polymerization reactions are initiated by any means which results in the generation of a suitable free-radical. Thermally derived radicals, in which the radical species is generated from thermal, homolytic dissociation of peroxides, hydroperoxides, persulfates, percarbonates, peroxyesters, hydrogen peroxide and azo compounds can be utilized. The initiators can be water soluble or water insoluble depending on the solvent system employed for the polymerization reaction.

[0125] The initiator compounds can be utilized in an amount of up to 30 wt.% in one aspect, 0.01 to 10 wt.% in another aspect, and 0.2 to 3 wt.% in a further aspect, based on the total weight of the dry polymer.

[0126] Exemplary free radical water soluble initiators include, but are not limited to, inorganic persulfate compounds, such as ammonium persulfate, potassium persulfate, and sodium persulfate; peroxides such as hydrogen peroxide, benzoyl peroxide, acetyl peroxide, and lauryl peroxide; organic hydroperoxides, such as cumene hydroperoxide and t-butyl hydroperoxide;

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organic peracids, such as peracetic acid, and water soluble azo compounds, such as 2,2'-azobis(tert-alkyl) compounds having a water solubilizing substituent on the alkyl group. Exemplary free radical oil soluble compounds include, but are not limited to 2,2'-azobisisobutyronitrile, and the like. The peroxides and peracids can optionally be activated with reducing agents, such as sodium bisulfite, sodium formaldehyde, or ascorbic acid, transition metals, hydrazine, and the like.

[0127] In one aspect, azo polymerization catalysts include the Vazo[®] free-radical polymerization initiators, available from DuPont, such as Vazo[®] 44 (2,2'-azobis(2-(4,5-dihydroimidazolyl)propane), Vazo[®] 56 (2,2'-azobis(2-methylpropionamidine) dihydrochloride), Vazo[®] 67 (2,2'-azobis(2-methylbutyronitrile)), and Vazo[®] 68 (4,4'-azobis(4-cyanovaleric acid)).

[0128] Optionally, the use of known redox initiator systems as polymerization initiators can be employed. Such redox initiator systems include an oxidant (initiator) and a reductant. Suitable oxidants include, for example, hydrogen peroxide, sodium peroxide, potassium peroxide, t-butyl hydroperoxide, t-amyl hydroperoxide, cumene hydroperoxide, sodium perborate, perphosphoric acid and salts thereof, potassium permanganate, and ammonium or alkali metal salts of peroxydisulfuric acid, typically at a level of 0.01% to 3.0% by weight, based on dry polymer weight, are used. Suitable reductants include, for example, alkali metal and ammonium salts of sulfur-containing acids, such as sodium sulfite, bisulfite, thiosulfate, hydrosulfite, sulfide, hydrosulfide or dithionite, formadinesulfinic acid, hydroxymethanesulfonic acid, acetone bisulfite, amines such as ethanolamine, glycolic acid, glyoxylic acid hydrate, ascorbic acid, isoascorbic acid, lactic acid, glyceric acid, malic acid, 2-hydroxy-2-sulfinatoacetic acid, tartaric acid and salts of the preceding acids typically at a level of 0.01% to 3.0% by weight, based on dry polymer weight, is used. In one aspect, combinations of peroxodisulfates with alkali metal or ammonium bisulfites can be used, for example, ammonium peroxodisulfate and ammonium bisulfite. In another aspect, combinations of hydrogen peroxide containing compounds (t-butyl hydroperoxide) as the oxidant with ascorbic or erythorbic acid as the reductant can be utilized. The ratio of peroxide-containing compound to reductant is within the range from 30:1 to 0.05:1.

[0129] In emulsion polymerization processes it can be advantageous to stabilize the monomer/polymer droplets or particles by means of surface active auxiliaries. Typically, these are emulsifiers or protective colloids. Emulsifiers used can be anionic, nonionic, cationic or amphoteric. Examples of anionic emulsifiers are alkylbenzenesulfonic acids, sulfonated fatty acids, sulfosuccinates, fatty alcohol sulfates, alkylphenol sulfates and fatty alcohol ether sulfates. Examples of usable nonionic emulsifiers are alkylphenol ethoxylates, primary alcohol ethoxylates, fatty acid ethoxylates, alkanolamide ethoxylates, fatty amine ethoxylates, EO/PO block copolymers and alkylpolyglucosides. Examples of cationic and amphoteric emulsifiers used are quaternized amine alkoxyates, alkylbetaines, alkylamidobetaines and sulfobetaines.

[0130] Examples of typical protective colloids are cellulose derivatives, polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and propylene glycol, polyvinyl acetate, poly(vinyl alcohol), partially hydrolyzed poly(vinyl alcohol), polyvinyl ether, starch and starch derivatives, dextran, polyvinylpyrrolidone, polyvinylpyridine, polyethyleneimine, polyvinylimidazole, polyvinylsuccinimide, polyvinyl-2-methylsuccinimide, polyvinyl-1,3-oxazolid-2-one, polyvinyl-2-methylimidazoline and maleic acid or anhydride copolymers. The emulsifiers or protective colloids are customarily used in concentrations from 0.05 to 20 wt.%, based on the weight of the total monomers.

[0131] The polymerization reaction can be carried out at temperatures ranging from 20 to 200°C in one aspect, from 50 to 150°C in another aspect, and from 60 to 100°C in a further aspect.

[0132] The polymerization can be carried out the presence of chain transfer agents. Suitable chain transfer agents include, but are not limited to, thio- and disulfide containing compounds, such as C₁-C₁₈ alkyl mercaptans, such as tert-butyl mercaptan, n-octyl mercaptan, n-dodecyl mercaptan, tert-dodecyl mercaptan, hexadecyl mercaptan, octadecyl mercaptan; mercaptoalcohols, such as 2-mercaptoethanol, 2-mercaptoopropanol; mercaptocarboxylic acids, such as mercaptoacetic acid and 3-mercaptopropionic acid; mercaptocarboxylic acid esters, such as butyl thioglycolate, isooctyl thioglycolate, dodecyl thioglycolate, isooctyl 3-mercaptopropionate, and butyl 3-mercaptopropionate; thioesters; C₁-

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C₁₈ alkyl disulfides; aryldisulfides; polyfunctional thiols such as trimethylolpropane-tris-(3-mercaptopropionate), pentaerythritol-tetra-(3-mercaptopropionate), pentaerythritol-tetra-(thioglycolate), pentaerythritol-tetra-(thiolactate), dipentaerythritol-hexa-(thioglycolate), and the like; phosphites and hypophosphites; C₁-C₄ aldehydes, such as formaldehyde, acetaldehyde, propionaldehyde; haloalkyl compounds, such as carbon tetrachloride, bromotrichloromethane, and the like; hydroxylammonium salts such as hydroxylammonium sulfate; formic acid; sodium bisulfite; isopropanol; and catalytic chain transfer agents such as, for example, cobalt complexes (e.g., cobalt (II) chelates).

[0133] The chain transfer agents are generally used in amounts ranging from 0.1 to 10 wt.%, based on the total weight of the monomers present in the polymerization medium.

Emulsion Process

[0134] In one exemplary aspect of the disclosed technology, the crosslinked, nonionic, amphiphilic polymer is polymerized via an emulsion process. The emulsion process can be conducted in a single reactor or in multiple reactors as is well-known in the art. The monomers can be added as a batch mixture or each monomer can be metered into the reactor in a staged process. A typical mixture in emulsion polymerization comprises water, monomer(s), an initiator (usually water-soluble) and an emulsifier. The monomers may be emulsion polymerized in a single-stage, two-stage or multi-stage polymerization process according to well-known methods in the emulsion polymerization art. In a two-stage polymerization process, the first stage monomers are added and polymerized first in the aqueous medium, followed by addition and polymerization of the second stage monomers. The aqueous medium optionally can contain an organic solvent. If utilized, the organic solvent is less than about 5 wt.% of the aqueous medium. Suitable examples of water-miscible organic solvents include, without limitation, esters, alkylene glycol ethers, alkylene glycol ether esters, lower molecular weight aliphatic alcohols, and the like.

[0135] To facilitate emulsification of the monomer mixture, the emulsion polymerization is carried out in the presence of at least one stabilizing surfactant. The term “stabilizing surfactant” is used in the context of surfactants employed to facilitate emulsification. In one embodiment, the emulsion polymerization is carried out in the presence of stabilizing surfactant (active weight basis) ranging in the amount of about 0.2% to about 5% by weight in one aspect, from about 0.5% to about 3% in another aspect, and from about 1% to about 2% by weight in a further aspect, based on a total monomer weight basis. The emulsion polymerization reaction mixture also includes one or more free radical initiators which are present in an amount ranging from about 0.01% to about 3% by weight based on total monomer weight. The polymerization can be performed in an aqueous or aqueous alcohol medium. Stabilizing surfactants for facilitating the emulsion polymerization include anionic, nonionic, amphoteric, and cationic surfactants, as well as reactive derivatives thereof, and mixtures thereof. By “reactive derivatives thereof” it is meant surfactants, or mixtures of surfactants, having on average less than one reactive moiety. Most commonly, anionic and nonionic surfactants can be utilized as stabilizing surfactants as well as mixtures thereof.

[0136] Suitable anionic surfactants for facilitating emulsion polymerizations are well known in the art and include, but are not limited to (C₆-C₁₈) alkyl sulfates, (C₆-C₁₈) alkyl ether sulfates (e.g., sodium lauryl sulfate and sodium laureth sulfate), amino and alkali metal salts of dodecylbenzenesulfonic acid, such as sodium dodecyl benzene sulfonate and dimethylethanolamine dodecylbenzenesulfonate, sodium (C₆-C₁₆) alkyl phenoxy benzene sulfonate, disodium (C₆-C₁₆) alkyl phenoxy benzene sulfonate, disodium (C₆-C₁₆) di-alkyl phenoxy benzene sulfonate, disodium laureth-3 sulfosuccinate, sodium dioctyl sulfosuccinate, sodium di-sec-butyl naphthalene sulfonate, disodium dodecyl diphenyl ether sulfonate, disodium n-octadecyl sulfosuccinate, phosphate esters of branched alcohol ethoxylates, and the like, as well as reactive derivatives thereof.

[0137] Nonionic surfactants suitable for facilitating emulsion polymerizations are well known in the polymer art, and include, without limitation, linear or

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branched C₈-C₃₀ fatty alcohol ethoxylates, such as capryl alcohol ethoxylate, lauryl alcohol ethoxylate, myristyl alcohol ethoxylate, cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, cetearyl alcohol ethoxylate, sterol ethoxylate, oleyl alcohol ethoxylate, and, behenyl alcohol ethoxylate; alkylphenol alkoxyates, such as octylphenol ethoxylates; and polyoxyethylene polyoxypropylene block copolymers, and the like, as well as reactive derivatives thereof. Additional fatty alcohol ethoxylates suitable as non-ionic surfactants are described below. Other useful nonionic surfactants include C₈-C₂₂ fatty acid esters of polyoxyethylene glycol, ethoxylated mono- and diglycerides, sorbitan esters and ethoxylated sorbitan esters, C₈-C₂₂ fatty acid glycol esters, block copolymers of ethylene oxide and propylene oxide, and combinations thereof, as well as reactive derivatives thereof. The number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect.

[0138] Optionally, other emulsion polymerization additives and processing aids which are well known in the emulsion polymerization art, such as auxiliary emulsifiers, protective colloids, solvents, buffering agents, chelating agents, inorganic electrolytes, polymeric stabilizers, biocides, and pH adjusting agents can be included in the polymerization system.

[0139] In one embodiment of the disclosed technology, the protective colloid or auxiliary emulsifier is selected from poly(vinyl alcohol) that has a degree of hydrolysis ranging from about 80 to 95 % in one aspect, and from about 85 to 90 % in another aspect.

[0140] In a typical two stage emulsion polymerization, a mixture of the monomers is added to a first reactor under inert atmosphere to a solution of emulsifying surfactant (e.g., anionic surfactant) in water. Optional processing aids can be added as desired (e.g., protective colloids, auxiliary emulsifier(s)). The contents of the reactor are agitated to prepare a monomer emulsion. To a second reactor equipped with an agitator, an inert gas inlet, and feed pumps are added under inert atmosphere a desired amount of water and additional anionic surfactant and optional processing aids. The contents of the second reactor are heated with mixing agitation. After the contents of the second reactor reaches a

temperature in the range of about 55 to 98°C, a free radical initiator is injected into the so formed aqueous surfactant solution in the second reactor, and the monomer emulsion from the first reactor is gradually metered into the second reactor over a period typically ranging from about one half to about four hours. The reaction temperature is controlled in the range of about 45 to about 95°C. After completion of the monomer addition, an additional quantity of free radical initiator can optionally be added to the second reactor, and the resulting reaction mixture is typically held at a temperature of about 45 to 95°C for a time period sufficient to complete the polymerization reaction to obtain the polymer emulsion.

[0141] In one aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to about 60 wt.% of at least one C₁-C₄ hydroxyalkyl (meth)acrylate (e.g., hydroxyethyl methacrylate); from about 10 to about 70 wt.% of at least one C₁-C₁₂ alkyl (meth)acrylate in one aspect or from about 10 to about 70 wt.% of at least one C₁-C₅ alkyl (meth)acrylate in another aspect; from about 0, 1, 5 or 15 to about 40 wt.% of at least one vinyl ester of a C₁-C₁₀ carboxylic acid, from about 0, 1 or 15 to about 30 wt.% of a vinyl lactam (e.g., vinyl pyrrolidone); from about 0, 0.1, 1, 5, or 7 to about 15 wt.% of at least one associative and/or a semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based upon the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0142] In another aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to about 50 wt.% at least one C₁-C₄ hydroxyalkyl (meth)acrylate (e.g., hydroxyethyl methacrylate); from about 10 to about 30 wt.% ethyl acrylate; from about 10 to about 35 wt.% butyl acrylate; from about 0 or 15 to about 25 wt.% of a vinyl ester of a C₁-C₅ carboxylic acid selected

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from vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, and vinyl valerate; from about 0, 1 or 15 to about 30 wt.% of vinyl pyrrolidone; and from about 0, 0.1, 1, 5 or 7 to about 15 wt.% of at least one associative monomer and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 in another aspect, and from about 0.5 to about 1 in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0143] In another embodiment, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to about 50 wt.% of hydroxyethyl methacrylate; from about 10 to about 30 wt.% ethyl acrylate; from about 10 to about 30 wt.% butyl acrylate; from about 0, 1, or 15 to about 25 wt.% of vinyl pyrrolidone; from about 0 or 15 to about 25 wt.% of vinyl acetate; from about 0, 0.1, 1, 5 or 7 to about 10 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0144] In another embodiment, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to 50 wt.% of hydroxyethyl methacrylate; from about 10 to about 40 wt.% ethyl acrylate; from about 10 to about 20 wt.% butyl acrylate; from about 0.1 to about 10 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer

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weight percentages are based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0145] In one aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to 50 wt.% of hydroxyethyl methacrylate; from about 10 to about 30 wt.% ethyl acrylate; from about 10 to about 30 wt.% butyl acrylate; from about 1 to about 10 or 15 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0146] In one aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 40 to 50 wt.% of hydroxyethyl methacrylate; from about 10 to about 20 wt.% ethyl acrylate; from about 20 to about 30 wt.% butyl acrylate; from about 5 or 6 to about 15 wt.% of at least one associative monomer selected from from lauryl polyethoxylated (meth)acrylate, cetyl polyethoxylated (meth)acrylate, ceteryl polyethoxylated (meth)acrylate, stearyl polyethoxylated (meth)acrylate, arachidyl polyethoxylated (meth)acrylate, behenyl polyethoxylated (meth)acrylate, cerotyl polyethoxylated (meth)acrylate, montanyl polyethoxylated (meth)acrylate, melissyl polyethoxylated (meth)acrylate, where the polyethoxylated portion of the monomer contains about 2 to about 50 ethylene oxide units (wherein all monomer weight percentages are

based on the weight of the total monomers); and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent.

[0147] In one aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to 35 wt.% of hydroxyethyl methacrylate, from about 10 to about 30 wt.% ethyl acrylate, from about 10 to about 30 wt.% butyl acrylate, from about 15 to about 25 wt.% of vinyl pyrrolidone, from about 15 to about 25 wt.% of vinyl acetate (wherein all monomer weight percentages are based on the weight of the total monomers), and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

[0148] In one aspect, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are selected from an emulsion polymer polymerized from a monomer mixture comprising from about 20 to 40 wt.% of hydroxyethyl methacrylate, from about 10 to about 30 wt.% ethyl acrylate, from about 10 to about 30 wt.% butyl acrylate, from about 15 to about 25 wt.% of vinyl pyrrolidone, and from about 1 to about 5 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers), and from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer), wherein the at least one crosslinker is selected from an amphiphilic crosslinking

agent or a combination of an amphiphilic crosslinking agent and a conventional crosslinking agent as defined herein.

Yield Stress Fluids

[0149] In one exemplary aspect of the disclosed technology, the yield stress fluid comprises: i) at least one crosslinked, nonionic amphiphilic polymer(s) described previously; ii) at least one surfactant selected from at least one anionic surfactant, at least one cationic surfactant, at least one amphoteric surfactant, at least one nonionic surfactant, and combinations thereof; and iii) water.

[0150] In another exemplary aspect of the disclosed technology, the yield stress fluid comprises: i) at least one crosslinked, nonionic amphiphilic polymer(s) described previously; ii) at least one anionic surfactant; and iii) water.

[0151] In another exemplary aspect of the disclosed technology, the yield stress fluid comprises: i) at least one crosslinked, nonionic amphiphilic polymer(s) described previously; ii) at least one anionic surfactant and at least one amphoteric surfactant; and iii) water.

[0152] Surprisingly, the present amphiphilic polymers can be activated by a surfactant to provide a stable yield stress fluid with desirable rheological and aesthetic properties with the ability to suspend particulate and insoluble materials in an aqueous medium for indefinite periods of time independent of pH. The yield stress value, elastic modulus and optical clarity are substantially independent of pH in the compositions in which they are included. The yield stress fluid of the disclosed technology is useful in the pH range of from about 2 to about 14 in one aspect, from about 3 to 11 in another aspect, and from about 4 to about 9 in a further aspect. Unlike the pH-responsive crosslinked polymers (acid or base sensitive) that require neutralization with an acid or a base to impart a desired rheological profile, the crosslinked, nonionic, amphiphilic polymers of the disclosed technology are substantially independent of pH. By substantially independent of pH is meant that the yield stress fluid within which the polymer of the disclosed technology is included imparts a desired rheological profile (e.g., a yield stress of at least 1 mPa (0.001 Pa) in one aspect, at least at least 0.5 Pa in another aspect, at least 1 Pa in still another aspect, and

at least 2 Pa in a further aspect) across a wide pH range (e.g., from about 2 to about 14) wherein the standard deviation in yield stress values across the pH range is less than 1 Pa in one aspect, less than 0.5 Pa in another aspect, and less than 0.25 Pa in a further aspect of the disclosed technology.

[0153] In one exemplary aspect of the disclosed technology, the yield stress fluid comprises at least one crosslinked, nonionic, amphiphilic polymer, at least one anionic surfactant, an optional nonionic surfactant, and water.

[0154] In another exemplary aspect, the yield stress fluid comprises at least one crosslinked, nonionic amphiphilic polymer, at least one anionic surfactant, at least one amphoteric surfactant, an optional nonionic surfactant, and water.

[0155] In still another exemplary aspect, the yield stress fluid comprises at least one crosslinked, nonionic, amphiphilic polymer, at least one anionic ethoxylated surfactant, an optional nonionic surfactant, and water. In one aspect, the average degree of ethoxylation in the anionic surfactant can range from about 1 to about 3. In another aspect, the average degree of ethoxylation is about 2.

[0156] In a further exemplary aspect, the yield stress fluid comprises at least one crosslinked, nonionic, amphiphilic polymer, at least one anionic ethoxylated surfactant, at least one amphoteric surfactant, an optional nonionic surfactant, and water. In one aspect, the average degree of ethoxylation in the anionic surfactant can range from about 1 to about 3. In another aspect, the average degree of ethoxylation is about 2.

[0157] In a still further exemplary aspect, the yield stress fluid comprises at least one crosslinked, nonionic, amphiphilic polymer, at least one anionic non-ethoxylated surfactant, at least one anionic ethoxylated surfactant, an optional nonionic surfactant, and water. In one aspect, the average degree of ethoxylation in the anionic surfactant can range from about 1 to about 3. In another aspect, the average degree of ethoxylation is about 2.

[0158] In another exemplary aspect, the yield stress fluid comprises at least one crosslinked, nonionic, amphiphilic polymer, at least one anionic non-ethoxylated surfactant, at least one anionic ethoxylated surfactant, at least one amphoteric surfactant, an optional nonionic surfactant, and water. In one aspect,

the average degree of ethoxylation in the anionic surfactant can range from about 1 to about 3. In another aspect, the average degree of ethoxylation is about 2.

[0159] The amount of amphiphilic polymer utilized in formulating the yield stress fluid of the disclosed technology ranges from about 0.5 to about 5 wt.% polymer solids (100 % active polymer) based on the weight of the total composition. In another aspect, the amount of amphiphilic polymer utilized in the formulation ranges from about 0.75 wt.% to about 3.5 wt.%. In still another aspect, the amount of amphiphilic polymer employed in the yield stress fluid ranges from about 1 to about 3 wt.%. In a further aspect, the amount of amphiphilic polymer employed in the yield stress fluid ranges from about 1.5 wt.% to about 2.75 wt.%. In a still further aspect, the amount of amphiphilic polymer utilized in the yield stress fluid ranges from about 2 to about 2.5 wt.%. The crosslinked, nonionic, amphiphilic polymer utilized in formulating the yield stress fluids of the disclosed technology is an emulsion polymer.

[0160] The yield stress fluids can be prepared by adding an activating surfactant. The activating surfactants utilized to formulate the yield stress fluids of the disclosed technology can be selected from anionic surfactants, cationic surfactants, amphoteric surfactants, nonionic surfactants, and mixtures thereof. The term "activating surfactant" is employed in the context of surfactants employed to activate the amphiphilic polymer to create the yield stress fluid. Some activating surfactants may also be stabilizing surfactants. Various non-limiting examples of activating surfactants are presented below.

[0161] Non-limiting examples of anionic surfactants are disclosed in *McCutcheon's Detergents and Emulsifiers*, North American Edition, 1998, published by Allured Publishing Corporation; and *McCutcheon's, Functional Materials*, North American Edition (1992); both of which are incorporated by reference herein in their entirety. The anionic surfactant can be any of the anionic surfactants known or previously used in the art of aqueous surfactant compositions. Suitable anionic surfactants include but are not limited to alkyl sulfates, alkyl ether sulfates, alkyl sulphonates, alkaryl sulfonates, α -olefin-sulphonates, alkylamide sulphonates, alkarylpolyether sulphates, alkylamidoether sulphates, alkyl monoglyceryl ether sulfates, alkyl monoglyceride sulfates, alkyl

monoglyceride sulfonates, alkyl succinates, alkyl sulfosuccinates, alkyl sulfosuccinamates, alkyl ether sulphosuccinates, alkyl amidosulfosuccinates; alkyl sulphoacetates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, alkyl amidoethercarboxylates, N-alkylamino acids, N-acyl amino acids, alkyl peptides, N-acyl taurates, alkyl isethionates, carboxylate salts wherein the acyl group is derived from fatty acids; and the alkali metal, alkaline earth metal, ammonium, amine, and triethanolamine salts thereof.

[0162] In one aspect, the cation moiety of the foregoing salts is selected from sodium, potassium, magnesium, ammonium, mono-, di- and triethanolamine salts, and mono-, di-, and tri-isopropylamine salts. The alkyl and acyl groups of the foregoing surfactants contain from about 6 to about 24 carbon atoms in one aspect, from 8 to 22 carbon atoms in another aspect and from about 12 to 18 carbon atoms in a further aspect and can be saturated or unsaturated. The aryl groups in the surfactants are selected from phenyl or benzyl. The ether containing surfactants set forth above can contain from 1 to 10 ethylene oxide and/or propylene oxide units per surfactant molecule in one aspect, and from 1 to 3 ethylene oxide units per surfactant molecule in another aspect.

[0163] Examples of suitable anionic surfactants include but are not limited to the sodium, potassium, lithium, magnesium, and ammonium salts of laureth sulfate, trideceth sulfate, myreth sulfate, C₁₂-C₁₃ pareth sulfate, C₁₂-C₁₄ pareth sulfate, and C₁₂-C₁₅ pareth sulfate, ethoxylated with 1, 2, 3, 4 or 5 moles of ethylene oxide; sodium, potassium, lithium, magnesium, ammonium, and triethanolamine lauryl sulfate, coco sulfate, tridecyl sulfate, myristyl sulfate, cetyl sulfate, cetearyl sulfate, stearyl sulfate, oleyl sulfate, and tallow sulfate, disodium lauryl sulfosuccinate, disodium laureth sulfosuccinate, sodium cocoyl isethionate, sodium C₁₂-C₁₄ olefin sulfonate, sodium laureth-6 carboxylate, sodium methyl cocoyl taurate, sodium cocoyl glycinate, sodium myristyl sarcosinate, sodium dodecylbenzene sulfonate, sodium cocoyl sarcosinate, sodium cocoyl glutamate, potassium myristoyl glutamate, triethanolamine monolauryl phosphate, and fatty acid soaps, including the sodium, potassium, ammonium, and triethanolamine salts of a saturated and unsaturated fatty acids containing from about 8 to about 22 carbon atoms.

[0164] The cationic surfactants can be any of the cationic surfactants known or previously used in the art of aqueous surfactant compositions. Useful cationic surfactants can be one or more of those described, for example, in *McCutcheon's Detergents and Emulsifiers*, North American Edition, 1998, supra, and *Kirk-Othmer, Encyclopedia of Chemical Technology*, 4th Ed., Vol. 23, pp. 478-541, the contents of which are herein incorporated by reference. Suitable classes of cationic surfactants include but are not limited to alkyl amines, alkyl imidazolines, ethoxylated amines, quaternary compounds, and quaternized esters. In addition, alkyl amine oxides can function as a cationic surfactant at a low pH.

[0165] Alkylamine surfactants can be salts of primary, secondary and tertiary fatty C₁₂-C₂₂ alkylamines, substituted or unsubstituted, and substances sometimes referred to as "amidoamines". Non-limiting examples of alkylamines and salts thereof include dimethyl cocamine, dimethyl palmitamine, dioctylamine, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated stearylamine, dihydroxy ethyl stearylamine, arachidylbehenylamine, dimethyl lauramine, stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride, and amodimethicone.

[0166] Non-limiting examples of amidoamines and salts thereof include stearamido propyl dimethyl amine, stearamidopropyl dimethylamine citrate, palmitamidopropyl diethylamine, and cocamidopropyl dimethylamine lactate.

[0167] Non-limiting examples of alkyl imidazoline surfactants include alkyl hydroxyethyl imidazoline, such as stearyl hydroxyethyl imidazoline, coco hydroxyethyl imidazoline, ethyl hydroxymethyl oleyl oxazoline, and the like.

[0168] Non-limiting examples of ethoxylated amines include PEG-cocopolyamine, PEG-15 tallow amine, quaternium-52, and the like.

[0169] Among the quaternary ammonium compounds useful as cationic surfactants, some correspond to the general formula: (R²⁰R²¹R²²R²³N⁺) E⁻, wherein R²⁰, R²¹, R²², and R²³ are independently selected from an aliphatic group having from 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having 1 to about 22 carbon atoms in the alkyl chain; and E⁻ is a salt-forming anion such as those selected from

halogen, (e.g., chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfate, and alkylsulfate. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, ester linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. In one aspect, the aryl groups are selected from phenyl and benzyl.

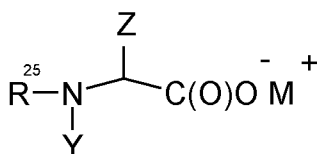
[0170] Exemplary quaternary ammonium surfactants include, but are not limited to cetyl trimethylammonium chloride, cetylpyridinium chloride, dicetyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, behenyl trimethyl ammonium chloride, benzalkonium chloride, benzethonium chloride, and di(coconutalkyl) dimethyl ammonium chloride, ditallowdimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, ditallowdimethyl ammonium methyl sulfate, ditallow dipropyl ammonium phosphate, and ditallow dimethyl ammonium nitrate.

[0171] At low pH, amine oxides can protonate and behave similarly to N-alkyl amines. Examples include, but are not limited to, dimethyl- dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyltetradecylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, dimethylhexadecylamine oxide, behenamine oxide, cocamine oxide, decyltetradecylamine oxide, dihydroxyethyl C₁₂-C₁₅ alkoxypropylamine oxide, dihydroxyethyl cocamine oxide, dihydroxyethyl lauramine oxide, dihydroxyethyl stearamine oxide, dihydroxyethyl tallowamine oxide, hydrogenated palm kernel amine oxide, hydrogenated tallowamine oxide, hydroxyethyl hydroxypropyl C₁₂-C₁₅ alkoxypropylamine oxide, lauramine oxide, myristamine oxide, cetylamine oxide, oleamidopropylamine oxide, oleamine oxide, palmitamine oxide, PEG-3 lauramine oxide, dimethyl lauramine oxide, potassium trisphosphonomethylamine oxide, soyamidopropylamine oxide, cocamidopropylamine oxide, stearamine oxide, tallowamine oxide, and mixtures thereof.

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[0172] The term “amphoteric surfactant” as used herein, is also intended to encompass zwitterionic surfactants, which are well known to formulators skilled in the art as a subset of amphoteric surfactants. Nonlimiting examples of amphoteric surfactants are disclosed *McCutcheon's Detergents and Emulsifiers*, North American Edition, supra, and *McCutcheon's, Functional Materials*, North American Edition, supra; both of which are incorporated by reference herein in their entirety. Suitable examples include but are not limited to amino acids (e.g., N-alkyl amino acids and N-acyl amino acids), betaines, sultaines, and alkyl amphocarboxylates.

[0173] Amino acid based surfactants suitable in the practice of the disclosed technology include surfactants represented by the formula:



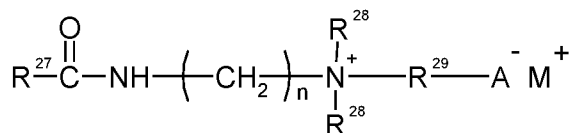
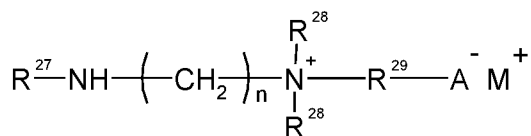
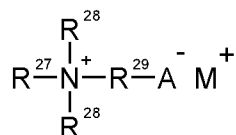
wherein R²⁵ represents a saturated or unsaturated hydrocarbon group having 10 to 22 carbon atoms or an acyl group containing a saturated or unsaturated hydrocarbon group having 9 to 22 carbon atoms, Y is hydrogen or methyl, Z is selected from hydrogen, -CH₃, -CH(CH₃)₂, -CH₂CH(CH₃)₂, -CH(CH₃)CH₂CH₃, -CH₂C₆H₅, -CH₂C₆H₄OH, -CH₂OH, -CH(OH)CH₃, -(CH₂)₄NH₂, -(CH₂)₃NHC(NH)NH₂, -CH₂C(O)O⁻M⁺, -(CH₂)₂C(O)O⁻M⁺. M is a salt forming cation. In one aspect, R²⁵ represents a radical selected from a linear or branched C₁₀ to C₂₂ alkyl group, a linear or branched C₁₀ to C₂₂ alkenyl group, an acyl group represented by R²⁶C(O)-, wherein R²⁶ is selected from a linear or branched C₉ to C₂₂ alkyl group, a linear or branched C₉ to C₂₂ alkenyl group. In one aspect, M⁺ is a cation selected from sodium, potassium, ammonium, and triethanolamine (TEA).

[0174] The amino acid surfactants can be derived from the alkylation and acylation of α-amino acids such as, for example, alanine, arginine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, lysine, phenylalanine, serine, tyrosine, and valine. Representative N-acyl amino acid surfactants are, but not limited to the mono- and di- carboxylate salts (e.g., sodium, potassium, ammonium and

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TEA) of N-acylated glutamic acid, for example, sodium cocoyl glutamate, sodium lauroyl glutamate, sodium myristoyl glutamate, sodium palmitoyl glutamate, sodium stearoyl glutamate, disodium cocoyl glutamate, disodium stearoyl glutamate, potassium cocoyl glutamate, potassium lauroyl glutamate, and potassium myristoyl glutamate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated alanine, for example, sodium cocoyl alaninate, and TEA lauroyl alaninate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated glycine, for example, sodium cocoyl glycinate, and potassium cocoyl glycinate; the carboxylate salts (e.g., sodium, potassium, ammonium and TEA) of N-acylated sarcosine, for example, sodium lauroyl sarcosinate, sodium cocoyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate, and ammonium lauroyl sarcosinate; and mixtures of the foregoing surfactants.

[0175] The betaines and sultaines useful in the disclosed technology are selected from alkyl betaines, alkylamino betaines, and alkylamido betaines, as well as the corresponding sulfobetaines (sultaines) represented by the formulas:



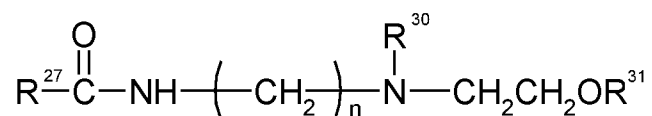
wherein R^{27} is a C_7 - C_{22} alkyl or alkenyl group, each R^{28} independently is a C_1 - C_4 alkyl group, R^{29} is a C_1 - C_5 alkylene group or a hydroxy substituted C_1 - C_5 alkylene

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group, n is an integer from 2 to 6, A is a carboxylate or sulfonate group, and M is a salt forming cation. In one aspect, R²⁷ is a C₁₁-C₁₈ alkyl group or a C₁₁-C₁₈ alkenyl group. In one aspect, R²⁸ is methyl. In one aspect, R²⁹ is methylene, ethylene or hydroxy propylene. In one aspect, n is 3. In a further aspect, M is selected from sodium, potassium, magnesium, ammonium, and mono-, di- and triethanolamine cations.

[0176] Examples of suitable betaines include, but are not limited to, lauryl betaine, coco betaine, oleyl betaine, cocohexadecyl dimethylbetaine, lauryl amidopropyl betaine, cocoamidopropyl betaine (CAPB), and cocamidopropyl hydroxysultaine.

[0177] The alkylamphocarboxylates such as the alkylamphoacetates and alkylamphopropionates (mono- and disubstituted carboxylates) can be represented by the formula:



wherein R²⁷ is a C₇-C₂₂ alkyl or alkenyl group, R³⁰ is -CH₂C(O)O⁻ M⁺, -CH₂CH₂C(O)O⁻ M⁺, or -CH₂CH(OH)CH₂SO₃⁻ M⁺, R³¹ is hydrogen or -CH₂C(O)O⁻ M⁺, and M is a cation selected from sodium, potassium, magnesium, ammonium, and mono-, di- and triethanolamine.

[0178] Exemplary alkylamphocarboxylates include, but are not limited to, sodium cocoamphoacetate, sodium lauroamphoacetate, sodium capryloamphoacetate, disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, and disodium capryloamphodipropionate.

[0179] Non-limiting examples of nonionic surfactants are disclosed in *McCutcheon's Detergents and Emulsifiers*, North American Edition, 1998, supra; and *McCutcheon's, Functional Materials*, North American, supra; both of which

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are incorporated by reference herein in their entirety. Additional Examples of nonionic surfactants are described in U.S. Patent No. 4,285,841, to Barrat et al., and U.S. Patent No. 4,284,532, to Leikhim et al., both of which are incorporated by reference herein in their entirety. Nonionic surfactants typically have a hydrophobic portion, such as a long chain alkyl group or an alkylated aryl group, and a hydrophilic portion containing various degrees of ethoxylation and/or propoxylation (e.g., 1 to about 50) ethoxy and/or propoxy moieties. Examples of some classes of nonionic surfactants that can be used include, but are not limited to, ethoxylated alkylphenols, ethoxylated and propoxylated fatty alcohols, polyethylene glycol ethers of methyl glucose, polyethylene glycol ethers of sorbitol, ethylene oxide-propylene oxide block copolymers, ethoxylated esters of fatty acids, condensation products of ethylene oxide with long chain amines or amides, condensation products of ethylene oxide with alcohols, and mixtures thereof.

[0180] Suitable nonionic surfactants include, for example, alkyl polysaccharides, alcohol ethoxylates, block copolymers, castor oil ethoxylates, ceto/oleyl alcohol ethoxylates, cetearyl alcohol ethoxylates, decyl alcohol ethoxylates, dinonyl phenol ethoxylates, dodecyl phenol ethoxylates, end-capped ethoxylates, ether amine derivatives, ethoxylated alkanolamides, ethylene glycol esters, fatty acid alkanolamides, fatty alcohol alkoxyates, lauryl alcohol ethoxylates, mono-branched alcohol ethoxylates, nonyl phenol ethoxylates, octyl phenol ethoxylates, oleyl amine ethoxylates, random copolymer alkoxyates, sorbitan ester ethoxylates, stearic acid ethoxylates, stearyl amine ethoxylates, tallow oil fatty acid ethoxylates, tallow amine ethoxylates, tridecanol ethoxylates, acetylenic diols, polyoxyethylene sorbitols, and mixtures thereof. Various specific examples of suitable nonionic surfactants include, but are not limited to, methyl gluceth-10, PEG-20 methyl glucose distearate, PEG-20 methyl glucose sesquistearate, ceteth-8, ceteth-12, dodoxynol-12, laureth-15, PEG-20 castor oil, polysorbate 20, steareth-20, polyoxyethylene-10 cetyl ether, polyoxyethylene-10 stearyl ether, polyoxyethylene-20 cetyl ether, polyoxyethylene-10 oleyl ether, polyoxyethylene-20 oleyl ether, an ethoxylated nonylphenol, ethoxylated octylphenol, ethoxylated dodecylphenol, or ethoxylated fatty (C₆-C₂₂) alcohol,

including 3 to 20 ethylene oxide moieties, polyoxyethylene-20 isohexadecyl ether, polyoxyethylene-23 glycerol laurate, polyoxyethylene-20 glyceryl stearate, PPG-10 methyl glucose ether, PPG-20 methyl glucose ether, polyoxyethylene-20 sorbitan monoesters, polyoxyethylene-80 castor oil, polyoxyethylene-15 tridecyl ether, polyoxyethylene-6 tridecyl ether, laureth-2, laureth-3, laureth-4, PEG-3 castor oil, PEG 600 dioleate, PEG 400 dioleate, poloxamers such as poloxamer 188, polysorbate 21, polysorbate 40, polysorbate 60, polysorbate 61, polysorbate 65, polysorbate 80, polysorbate 81, polysorbate 85, sorbitan caprylate, sorbitan cocoate, sorbitan diisostearate, sorbitan dioleate, sorbitan distearate, sorbitan fatty acid ester, sorbitan isostearate, sorbitan laurate, sorbitan oleate, sorbitan palmitate, sorbitan sesquiisostearate, sorbitan sesquioleate, sorbitan sesquistearate, sorbitan stearate, sorbitan triisostearate, sorbitan trioleate, sorbitan tristearate, sorbitan undecylenate, or mixtures thereof.

[0181] Alkyl glycoside nonionic surfactants can also be employed and are generally prepared by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide, with an alcohol such as a fatty alcohol in an acid medium. For example, U.S. Patent Nos. 5,527,892 and 5,770,543 describe alkyl glycosides and/or methods for their preparation. Suitable examples are commercially available under the names of Glucocon™ 220, 225, 425, 600 and 625, PLANTACARE®, and PLANTAPON®, all of which are available from Cognis Corporation of Ambler, Pennsylvania.

[0182] In another aspect, nonionic surfactants include, but are not limited to, alkoxyated methyl glucosides such as, for example, methyl gluceth-10, methyl gluceth-20, PPG-10 methyl glucose ether, and PPG-20 methyl glucose ether, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucam® E10, Glucam® E20, Glucam® P10, and Glucam® P20, respectively; and hydrophobically modified alkoxyated methyl glucosides, such as PEG 120 methyl glucose dioleate, PEG-120 methyl glucose trioleate, and PEG-20 methyl glucose sesquistearate, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucamate® DOE-120, Glucamate™ LT, and Glucamate™ SSE-20, respectively, are also suitable. Other exemplary hydrophobically modified alkoxyated methyl glucosides are disclosed in U.S. Patent Nos. 6,573,375 and

6,727,357, the disclosures of which are hereby incorporated by reference in their entirety.

[0183] Other useful nonionic surfactants include water soluble silicones such as PEG-10 Dimethicone, PEG-12 Dimethicone, PEG-14 Dimethicone, PEG-17 Dimethicone, PPG-12 Dimethicone, PPG-17 Dimethicone and derivatized/functionalized forms thereof such as Bis-PEG/PPG-20/20 Dimethicone Bis-PEG/PPG-16/16 PEG/PPG-16/16 Dimethicone, PEG/PPG-14/4 Dimethicone, PEG/PPG-20/20 Dimethicone, PEG/PPG-20/23 Dimethicone, and Perfluorononyl ethyl Carboxydecyl PEG-10 Dimethicone.

[0184] The amount of the at least one surfactant (active weight basis) utilized in formulating the yield stress fluid of the disclosed technology ranges from about 1 to about 70 wt.% based on the weight of the total yield stress fluid composition. In another aspect, the amount of the at least one surfactant utilized in the formulation ranges from about 2 to about 50 wt.% or from about 3 to about 25 wt.%. In still another aspect, the amount of the at least one surfactant employed in the yield stress fluid ranges from about 5 to about 22 wt.%. In a further aspect, the amount of the at least one surfactant utilized ranges from about 6 to about 20 wt.%. In still a further aspect, the amount of at least one surfactant is about 10, 12, 14, 16, and 18 wt.% based on the total weight yield of the stress fluid.

[0185] In one embodiment of the disclosed technology, the weight ratio (based on active material) of anionic surfactant (non-ethoxylated and/or ethoxylated) to amphoteric surfactant can range from about 10:1 to about 2:1 in one aspect, and can be 9:1, 8:1, 7:1 6:1, 5:1, 4.5:1, 4:1, or 3:1 in another aspect. When employing an ethoxylated anionic surfactant in combination with a non-ethoxylated anionic surfactant and an amphoteric surfactant, the weight ratio (based on active material) of ethoxylated anionic surfactant to non-ethoxylated anionic surfactant to amphoteric surfactant can range from about 3.5:3.5:1 in one aspect to about 1:1:1 in another aspect.

[0186] In one embodiment, the yield stress value of the fluid is at least about 1mPa, or 0.1 Pa in one aspect, about 0.5 Pa in one aspect, at least about 1 Pa in another aspect and at least about 1.5 Pa in a further aspect. In another

embodiment, the yield stress of the fluid ranges from about 0.1 to about 20 Pa in one aspect, from about 0.5 Pa to about 10 Pa in another aspect, from about 1 to about 3 Pa in a further aspect, and from about 1.5 to about 3.5 in a still further aspect.

[0187] Optionally, the yield stress fluids of the disclosed technology can contain an electrolyte. Suitable electrolytes are known compounds and include organic and inorganic salts of multivalent anions, such as potassium pyrophosphate, potassium tripolyphosphate, and sodium or potassium citrate, salts of multivalent cations, including alkaline earth metal salts such as calcium chloride and calcium bromide, as well as zinc halides, barium chloride and calcium nitrate, salts of monovalent cations with monovalent anions, including alkali metal or ammonium halides, such as potassium chloride, sodium chloride, potassium iodide, sodium bromide, and ammonium bromide, alkali metal or ammonium nitrates, and blends thereof.

[0188] The amount of the electrolyte used will generally depend on the amount of the amphiphilic polymer incorporated, but may be used at concentration levels of from about 0.1 to about 4 wt.% in one aspect and from about 0.2 to about 3 wt.% in another aspect, from about 0.5 to about 2.5 in a further aspect, and from about 0.75 to about 1.5 wt.% in a still further aspect, based on the weight of the total composition.

[0189] Optionally, the yield stress fluids of the disclosed technology can contain organic acid preservatives and salts thereof. Any acid based preservative that is useful in personal care, home care, health care, and institutional and industrial care products can be used in the compositions of the present invention. In one aspect the acid preservative is a carboxylic acid compound represented by the formula: $R^{40}C(O)OH$, wherein R^{40} represents hydrogen, a saturated and unsaturated hydrocarbyl group containing 1 to 8 carbon atoms or C_6 to C_{10} aryl. In another aspect, R^{40} is selected from a hydrogen, a C_1 to C_8 alkyl group, a C_2 to C_8 alkenyl group, or phenyl. Exemplary acids are, but are not limited to, formic acid, acetic acid, propionic acid, sorbic acid, caprylic acid, and benzoic acid, and mixtures thereof.

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[0190] In another aspect, suitable acids include but are not limited to, oxalic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, maleic acid, fumaric acid, lactic acid, glyceric acid, tartronic acid malic acid, tartaric acid, gluconic acid, citric acid, ascorbic acid, salicylic acid, phthalic acid, mandelic acid, benzilic acid, and mixtures thereof.

[0191] Salts of the foregoing acids are also useful as long as they retain efficacy at low pH values. Suitable salts include the alkali metal (e.g., sodium, potassium, calcium) and ammonium salts of the acids enumerated above.

[0192] The acid based preservatives and/or their salts can be used alone or in combination with non-acidic preservatives typically employed in personal care, homecare, health care, and institutional and industrial care products.

[0193] The preservatives typically comprise from about 0.01% to about 3.0% by weight in one aspect, from about 0.1% to about 1% by weight in another aspect, and from about 0.3% to about 1% by weight in a further aspect, of the total weight of the personal care compositions of the present invention.

[0194] The yield stress fluid must be easily pourable with a shear thinning index of less than 0.5 at shear rates between 0.1 and 1 reciprocal second. The yield stress fluid can have an optical transmission of at least 10%. In addition, or alternatively, the yield stress fluid can have a nephelometric turbidity unit (NTU) value of 50 or less, or 40 or less, or even 30 or 20 or less. The yield stress fluid of the disclosed technology can be utilized in combination with a rheology modifier (thickener) to enhance the yield value of a thickened liquid. In one aspect, the yield stress fluid of the disclosed technology can be combined with a nonionic rheology modifier which rheology modifier when utilized alone does not have a sufficient yield stress value. Any rheology modifier is suitable, so long as such is soluble in water, stable and contains no ionic or ionizable groups. Suitable rheology modifiers include, but are not limited to natural gums (e.g., polygalactomannan gums selected from fenugreek, cassia, locust bean, tara and guar), modified cellulose (e.g., ethylhexylethylcellulose (EHEC), hydroxybutylmethylcellulose (HBMC), hydroxyethylmethylcellulose (HEMC), hydroxypropylmethylcellulose (HPMC), methyl cellulose (MC), hydroxyethylcellulose (HEC), hydroxypropylcellulose (HPC) and cetyl

hydroxyethylcellulose); and mixtures thereof methylcellulose, polyethylene glycols (e.g., PEG 4000, PEG 6000, PEG 8000, PEG 10000, PEG 20000), polyvinyl alcohol, polyacrylamides (homopolymers and copolymers), and hydrophobically modified ethoxylated urethanes (HEUR). The rheology modifier can be utilized in an amount ranging from about 0.5 to about 25 wt.% in one aspect, from about 1 to about 15 wt.% in another aspect, and from about 2 to about 10 wt.% in a further aspect, based on the weight of the total weight of the composition.

[0195] The yield stress fluids of the disclosed technology can be used in any application requiring yield stress properties. The yield stress fluids can be used alone or in combination with other fluids to enhance the yield stress values thereof.

[0196] In one embodiment, the yield stress fluids of the disclosed technology can be utilized to suspend particulate materials and insoluble droplets within an aqueous composition. Such fluids are useful in the oil and gas, personal care, homecare, coatings and inks and adhesive/binder industries.

[0197] In the oil and gas industry, the yield stress fluids of the disclosed technology can be used to enhance the yield stress value of drilling and hydraulic fracturing fluids, and can be employed to suspend borehole cuttings and fracturing proppants such as, for example, sand, sintered bauxite, glass balls, ceramic materials, polystyrene beads, and the like.

[0198] In the personal and homecare industries, the yield stress fluids of the disclosed technology can be utilized to improve the yield stress properties of deterative compositions, hair and skin care compositions, as well as cosmetics, and can be utilized to suspend insoluble silicones, opacifiers and pearlescent agents (e.g., mica, coated mica), pigments, exfoliants, anti-dandruff agents, clay, swellable clay, laponite, gas bubbles, liposomes, microsponges, cosmetic beads, perfumes fragrance oils, fragrance microcapsules, fragrance particles, benefit agent containing microcapsules and particles, cosmetic microcapsules, and flakes. The yield stress fluids of the disclosed technology can stabilize these materials in suspension for at least one month at 23°C in one aspect, at least 6 months in another aspect, and at least one year in a further aspect.

[0199] Exemplary perfumes, fragrances and fragrance oils include but are not limited to allyl cyclohexane propionate, ambrettolide, Ambrox® DL

(dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1-b]furan), amyl benzoate, amyl cinnamate, amyl cinnamic aldehyde, amyl salicylate, anethol, aurantiol, benzophenone, benzyl butyrate, benzyl iso-valerate, benzyl salicylate, cadinene, campylcyclohexal, cedrol, cedryl acetate, cinnamyl cinnamate, citronellyl acetate, citronellyl isobutyrate, citronellyl propionate, cuminic aldehyde, cyclohexylsalicylate, cyclamen aldehyde, cyclomyral, dihydro isojasmonate, diphenyl methane, diphenyl oxide, dodecanal, dodecalactone, ethylene brassylate, ethylmethyl phenylglycidate, ethyl undecylenate, exaltolide, Galoxilide® (1,3,4,6,7,8-hexhydro,4,6,6,7,8,8-hexamethyl-cyclopenta- γ -2-benzopyran), geranyl acetate, geranyl isobutyrate, hexadecanolide, hexenyl salicylate, hexyl cinnamic aldehyde, hexyl salicylate, α -ionone, β -ionone, γ -ionone, α -irone, isobutyl benzoate, isobutyl quinoline, Iso E Super® (7-acetyl,1,2,3,4,5,6,7,8-octahydro,1,1,6,7-tetramethyl naphthalene), cis-jasmone, lillial, linalyl benzoate, 20 methoxy naphthaline, methyl cinnamate, methyl eugenol, γ -methylionone, methyl linolate, methyl linolenate, musk indanone, musk ketone, musk tibetine, myristicin, neryl acetate, δ -nonalactone, γ -nonalactone, patchouli alcohol, phantolide, phenylethyl benzoate, phenylethylphenylacetate, 2-phenylethanol, phenyl heptanol, phenyl hexanol, α -santalol, thibetolide, tonalid, δ -undecalactone, γ -undecalactone, vertenex, vetiveryl acetate, yara-yara, ylangene, allo-ocimene, allyl caproate, allyl heptoate, anisole, camphene, carvacrol, carvone, citral, citronellal, citronellol, citronellyl nitrile, coumarin, cyclohexyl ethylacetate, p-cymene, decanal, dihydromyrcenol, dihydromyrcenyl acetate, dimethyl octanol, ethyllinalool, ethylhexyl ketone, eucalyptol, fenchyl acetate, geraniol, gernyl formate, hexenyl isobutyrate, hexyl acetate, hexyl neopentanoate, heptanal, isobornyl acetate, isoeugenol, isomenthone, isononyl acetate, isononyl alcohol, isomenthol, isopulegol, limonene, linalool, linalyl acetate, menthyl acetate, methyl chavicol, methyl octyl acetaldehyde, myrcene, naphthalene, nerol, neral, nonanal, 2-nonanone, nonyl acetate, octanol, octanal, α -pinene, β -pinene, rose oxide, α -terpinene, γ -terpinene, α -terpinenol, terpinolene, terpinyl acetate, tetrahydrolinalool, tetrahydromyrcenol, undecenal, veratrol, verdox, acetanisol; amyl acetate; anisic aldehyde; anisylalcohol; benzaldehyde; benzyl acetate; benzyl acetone; benzyl alcohol; benzyl formate; hexenol; laevo-carveol; d-

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carvone; cinnamaldehyde; cinnamic alcohol; cinnamyl acetate; cinnamyl formate; cis-3-hexenyl acetate; Cyclal C (2,4-dimethyl-3-cyclohexen-1-carbaldehyde); dihydroxyindole; dimethyl benzyl carbinol; ethyl acetate; ethyl acetoacetate; ethyl butanoate; ethyl butyrate; ethyl vanillin; tricyclo decenyl propionate; furfural; hexanal; hexenol; hydratropic alcohol; hydroxycitronellal; indole; isoamyl alcohol; isopulegyl acetate; isoquinoline; ligustral; linalool oxide; methyl acetophenone; methyl amyl ketone; methyl anthranilate; methyl benzoate; methyl benzyl acetate; methyl heptenone; methyl heptyl ketone; methyl phenyl carbinyl acetate; methyl salicylate; octalactone; para-cresol; para-methoxy acetophenone; para-methyl acetophenone; phenethylalcohol; phenoxy ethanol; phenyl acetaldehyde; phenyl ethyl acetate; phenyl ethyl alcohol; prenyl acetate; propyl butyrate; safrole; vanillin and viridine.

[0200] In the coatings, inks, and adhesive/binder industries the yield stress fluids and non-ionic amphiphilic polymer composition with its at least one amphiphilic crosslinking agent can be utilized at a variety of different pH values and are useful to adjust viscosity of a fluid to: a) control or minimize settling or creaming of solid particles, dispersed liquids, trapped gases, and particulates (aid in suspension) that are more dense or less dense than the continuous media (often water based); b) to control application viscosity of continuous or discontinuous layers of a coating, ink, or adhesive to a substrate; c) to minimize movement or flow of coatings, inks, or adhesives immediately prior to application or in the time after application until the coating, ink, or adhesive forms a continuous gelled polymer; e) reduce splatter and misting in some application processes; f) etc., to facilitate optimal storage, application ease, and final surface finish in those applications. The coatings, inks and adhesives may comprise particulate or fibrous fillers, pigments, dyes, other polymers, surfactants and/or dispersants, coalescents, plasticizers, biocides and other conventional additives employed in coatings, inks, and adhesives. The coatings can be used on metals, plastics, wood, masonry, textiles, papers, etc. The inks can be used on any ink substrates such as paper, polymers, wovens, nonwovens, films, etc. The amphiphilic polymer can contribute to both viscosity control and optical clarity (helping color intensity of pigmented compositions) of the coating, ink, or adhesive.

[0201] The stable compositions maintain a smooth, acceptable rheology with good shear thinning properties without significant increases or decreases in viscosity, with no phase separation, e.g., settling or creaming out (rising to the surface), or loss of clarity over extended periods of time, such as for at least one month at 45°C.

[0202] Exemplary bead components include, but are not limited to, agar beads, alginate beads, jojoba beads, gelatin beads, Styrofoam™ beads, polyacrylate, polymethylmethacrylate (PMMA), polyethylene beads, Unispheres™ and Unipearls™ cosmetic beads (Induchem USA, Inc., New York, NY), Lipocapsule™, Liposphere™, and Lipopearl™ microcapsules (Lipo Technologies Inc., Vandalia, OH), and Confetti II™ dermal delivery flakes (United-Guardian, Inc., Hauppauge, NY). Beads can be utilized as aesthetic materials or can be used to encapsulate benefit agents to protect them from the deteriorating effects of the environment or for optimal delivery, release and performance in the final product.

[0203] In one aspect, the cosmetic beads range in size from about 0.5 to about 1.5 mm. In another aspect, the difference in specific gravity of the bead and water is between about +/- 0.01 and 0.5 in one aspect and from about +/- 0.2 to 0.3 g/ml in another aspect.

[0204] In one aspect, the microcapsules range in size from about 0.5 to about 300 µm. In another aspect, the difference in specific gravity between the microcapsules and water is from about +/- 0.01 to 0.5. Non-limiting examples of microcapsule beads are disclosed in U.S. Patent No. 7,786,027, the disclosure of which is herein incorporated by reference.

[0205] In one aspect of the disclosed technology, the amount of particulate component and/or insoluble droplets can range from about 0.1% to about 10% by weight based on the total weight of the composition.

[0206] While overlapping weight ranges for the various components and ingredients that can be contained in the yield stress fluids of the disclosed technology have been expressed for selected embodiments and aspects of the disclosed technology, it should be readily apparent that the specific amount of each component in the compositions will be selected from its disclosed range such

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that the amount of each component is adjusted so that the sum of all components in the composition will total 100 weight percent. The amounts employed will vary with the purpose and character of the desired product and can be readily determined by one skilled in the formulation art and from the literature.

[0207] The disclosed technology is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the disclosed technology or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Test Methodology

Yield Stress

[0208] The yield stress values of these polymers are determined by oscillatory and steady shear measurements on a controlled stress rheometer (TA Instruments AR1000N rheometer, New Castle, DE) utilizing parallel plate geometry (60 mm 2° cone-plate geometry) at 25°C. The oscillatory measurements are performed at a fixed frequency of 1 rad/sec. The elastic and viscous moduli (G' and G'' respectively) are obtained as a function of increasing stress amplitude. The stress corresponding to the crossover of G' and G'' is noted as the yield stress.

Brookfield Viscosity

[0209] Brookfield rotating spindle method (all viscosity measurements reported herein are conducted by the Brookfield method whether mentioned or not): The viscosity measurements are calculated in mPa·s, employing a Brookfield rotating spindle viscometer, Model RVT (Brookfield Engineering Laboratories, Inc.), at about 20 revolutions per minute (rpm), at ambient room temperature of about 20 to 25°C (BV viscosity). Spindle sizes are selected in accordance with the standard operating recommendations from the manufacturer. Generally, spindle sizes are selected as follows:

Spindle Size No.	Viscosity Range (mPa·s)
1	1 - 50
2	500 - 1,000
3	1,000 - 5,000

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4	5,000 – 10,000
5	10,000 – 20,000
6	20,000 – 50,000
7	>50,000

[0210] The spindle size recommendations are for illustrative purposes only. The artisan of ordinary skill in the art will select a spindle size appropriate for the system to be measured. A no. 5 spindle was utilized for the viscosity measurements herein.

Bead Suspension Test

[0211] The ability of a polymer system to suspend active and/or aesthetically pleasing insoluble oily and particulate materials is important from the standpoint of product efficacy and appeal. A six dram vial (approximately 70 mm high x 25 mm in diameter) is filled to the 50 mm point with the test formulation. Each sample vial is centrifuged to remove any trapped air bubbles contained in the formulation. Approximately 0.1 to 0.2g of mixed Unispheres™ NTL-32120C, NTL-2412 and NTL-2512 beads, commercially available from InduChem AG, are stirred gently with a wooden stick until they are uniformly dispersed throughout the sample. The position of the beads within each sample vial is noted by taking a photograph immediately after preparation to establish the initial position of the beads within the formulation. The vials are placed in a 45°C to age for a 12 week period. The bead suspension properties of each sample are visually evaluated at the conclusion of the 12 week test period. If the initial position of the beads is unchanged following the conclusion of the test period the sample passes. If the initial position of one or more of the beads changes (or the beads settle to the bottom of the vial) following the conclusion of the test period the sample fails.

Light Transmittance (optical clarity)

[0212] The optical clarity (expressed as percent transmittance or %T) of the composition is measured in % T (transmittance) by Brinkmann PC 920 calorimeter with a 640 nm filter. Clarity measurements are taken against deionized water (clarity rating of 100%). Compositions having a clarity value of about 60% (T) or more are substantially clear. Compositions having a clarity value in the range of

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about 45 to 59% (T) are substantially translucent. Compositions having a clarity value of 80% and above are considered clear.

Turbidity

[0213] The clarity (turbidity) of a composition is determined in Nephelometric Turbidity Units (NTU) employing a nephelometric turbidity meter (Micro 100 Turbidimeter, HF Scientific, Inc.) at ambient room temperature of about 20 to 25°C. Distilled water (NTU = 0) is utilized as a standard. Six dram screw cap vials (70 mm x 25 mm) are filled almost to the top with test sample and centrifuged at 100 rpm until all bubbles are removed. Upon centrifugation, each sample vial is wiped with tissue paper to remove any smudges before placement in the turbidity meter. The sample is placed in the turbidity meter and a reading is taken. Once the reading stabilizes the NTU value is recorded. The vial is given one-quarter turn and another reading is taken and recorded. This is repeated until four readings are taken. The lowest of the four readings is reported as the turbidity value. Lower turbidity values indicate clearer (less turbid) compositions.

[0214] The following abbreviations and trade names are utilized in the examples.

Abbreviations

AA	Acrylic Acid
AM (E-Sperse® RS-1617)	Amphiphilic crosslinker with two polymerizable reactive groups from Ethox Chemical, LLC
AM (E-Sperse® RS-1618)	Amphiphilic crosslinker with two polymerizable reactive groups from Ethox Chemical, LLC
AM (E-Sperse® RS-1684)	Amphiphilic crosslinker with two polymerizable reactive groups from Ethox Chemical, LLC
AMD	Acrylamide
AOS	Sodium C ₁₄ -C ₁₆ alpha olefin sulfonate (≈ 40% active), Bio-Terge® AS-40K surfactant, Stepan Company
APE	Allyl Pentaerythritol
BEM	Sipomer® Polyethoxylated (25 moles) Behenyl Methacrylate (66.67% BEM/33.33% MAA by wt.), Rhodia
CAPB	Chembetaine™ CAD, Cocamidopropyl Betaine (amphoteric surfactant), Lubrizol Advanced Materials, Inc. (35% active)
CSEM	Cetearyl Polyethoxylated (25 moles) methacrylate (75% active), Bimax Chemicals LTD

DI Water	Deionized Water
EA	Ethyl Acrylate
E-Sperse® RS-1596	Reactive surfactant with one polymerizable reactive group from Ethox Chemical, LLC
E-Sperse® RS-1616	Reactive surfactant with one polymerizable reactive group from Ethox Chemical, LLC
HEMA	2-Hydroxyethyl Methacrylate
MAA	Methacrylic Acid
MAMD	Methacrylamide
n-BA	n-Butyl Acrylate
n-VP	n-Vinyl Pyrrolidone
Polystep® TSP-16S	Nonionic Surfactant (Tristyrylphenol Ethoxylate-16) without reactive group, Stepan Company
Selvol® 502 and 205 PVA	Polyvinyl Alcohol (hydrolysis % = 87-89%), Sekisui Corporation
SLES-2	Sulfochem™ ES-2, Sodium Laureth Sulfate - 2 moles of ethoxylation (anionic surfactant), Lubrizol Advanced Materials, Inc. (27-28% active)
SLES-3	Sulfochem™ ES-3, Sodium Laureth Sulfate - 3 moles of ethoxylation (anionic surfactant, Lubrizol Advanced Materials, Inc. (27.5-29.5% active)
SLS	Sulfochem™ Sodium Lauryl Sulfate (anionic surfactant), Lubrizol Advanced Materials, Inc. (30% active)
TBHP	t-butyl hydroperoxide (70%), Alfa Aesar
VA-086	Azo VA-086 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide], Wako
VAc	Vinyl Acetate

[0215] The following examples illustrate the technology disclosed herein.

Example 1 (comparative)

Monomer composition = EA/n-BA/HEMA/BEM (35/15/45/5) (wt.% total monomers)

[0216] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 12.5 grams of AOS, 175 grams of (EA), 75 grams of (n-BA), 225 grams of (HEMA) and 33.3 grams of (BEM) (as supplied). Initiator A was made by mixing 3.57 grams of TBHP in 40 grams of DI water. Reductant A was prepared by dissolving 0.13 grams of erythorbic acid in 5 grams of DI water. Reductant B was prepared by dissolving 2.5 grams of erythorbic acid in 100 grams of DI water. A 3-liter reactor was charged with 825 grams of DI water, 7.5 grams of AOS and 15 grams of Selvol® 502 PVA, and then

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the contents were heated to 70°C under a nitrogen blanket with agitation. After holding the reactor contents at 70°C for one hour, the contents of the reactor were cooled down to 65°C, and then initiator A was then added to the reactor followed by addition of reductant A. After about 1 minute, the monomer premix was metered into the reaction vessel over a period of 180 minutes. About 3 minutes after the start of monomer premix introduction, reductant B was metered into the reactor over a period of 210 minutes. After completion of the reductant B feed, the temperature of the reaction vessel contents was maintained at 65°C for 60 minutes. The reactor contents were then cooled to 60°C. A solution of 1.96 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.27 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C. After 30 minutes, a solution of 1.96 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.27 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C for about 30 minutes. Then, the reactor contents were cooled to room temperature (22°C) and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4.5 with ammonium hydroxide. The polymer product had a solids content of 29%, a viscosity of 14 cps, and particle size of 111 nm.

Example 2 (comparative)

Monomer composition = EA/n-BA/HEMA/BEM/APE (35/14.91/45/5/0.09) (wt.% total monomers including APE)

[0217] An emulsion polymer employing APE crosslinker was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 3.75 grams of AOS, 175 grams of (EA), 70.6 grams of (n-BA), 225 grams of (HEMA) and 33.3 grams of (BEM) (as supplied) . Initiator A was made by mixing 3.57 grams of TBHP in 40 grams of DI water. Reductant A was prepared by dissolving 0.13 grams of erythorbic acid in 5 grams of DI water. Reductant B was prepared by dissolving 2.5 grams of erythorbic acid in 100 grams of DI water. A 3-liter reactor was charged with 800 grams of DI water, 10 grams of AOS and 25 grams

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of Selvol® 502 PVA and then was heated to 70°C under a nitrogen blanket with proper agitation. After holding the reactor at 70°C for one hour, initiator A was added to the reactor and followed by addition of reductant A. After about 1 minute, the monomer premix was metered to the reaction vessel over a period of 180 minutes. About 3 minutes after the start of monomer premix introduction, reductant B was metered to the reactor over a period of 210 minutes. The reaction temperature was kept at 65°C. At about 115 minutes after the monomer premix introduction, the premix metering was stopped for 10 minutes, and then 0.44 grams of 70% APE in 3.94 grams of n-BA was added to the monomer premix. After the 10 minute period, the premix metering was resumed. After completion of reductant B feed, the temperature of the reaction vessel contents was maintained at 65°C for 60 minutes. The reactor contents were then cooled to 60°C. A solution of 1.96 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.27 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C. After 30 minutes, a solution of 1.96 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.27 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C for about 30 minutes. Then, the reactor contents were cooled to room temperature and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4.5 with ammonium hydroxide. The polymer product had a solids content of 31.5%, a viscosity of 20 cps, and a particle size of 145 nm.

Example 3 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (35/15/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0218] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 175 grams of (EA), 75 grams of (n-BA), 225 grams of (HEMA) and 33.3 grams of (BEM) (as supplied). Initiator A was made by mixing 2.86 grams of TBHP in 40 grams of DI water. Reductant A was prepared by

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dissolving 0.13 grams of erythorbic acid in 5 grams of DI water. Reductant B was prepared by dissolving 2.0 grams of erythorbic acid in 100 grams of DI water. A 3-liter reactor was charged with 800 grams of DI water, 10 grams of AOS and 25 grams of Selvol® 502 PVA. The contents of the reactor were heated to 70°C under a nitrogen blanket with agitation. After holding the reactor contents at 70°C for one hour, initiator A was added to the reactor followed by addition of reductant A. After about 1 minute, the monomer premix was metered into the reaction vessel over a period of 180 minutes. About 3 minutes after the start of monomer premix introduction, reductant B was metered to the reactor over a period of 210 minutes. The reaction temperature was kept at 65°C. After completion of reductant B feed, the temperature of the reaction vessel contents was maintained at 65°C for 60 minutes. The reactor contents were then cooled to 60°C. A solution of 1.79 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.05 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C. After 30 minutes, a solution of 1.79 grams of TBHP and 0.13 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 1.05 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 60°C for about 30 minutes. Then, the reactor was cooled to room temperature and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4.5 with ammonium hydroxide. The polymer product had a solids content of 30.4%, a viscosity of 21 cps, and a particle size of 119 nm.

Example 4 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (35/15/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0219] An emulsion polymer was prepared in a similar method as Comparative Example 1 except 12.5 grams of AOS in the monomer mix was replaced by 5 grams of E-Sperse® RS-1618 amphiphilic crosslinker. The polymer product had a solids content of 30.85%, a viscosity of 19 cps, and a particle size of 99 nm.

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Example 5 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/APE/AM* (35/14.91/45/5/0.09/1*)
(wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0220] An emulsion polymer employing APE crosslinker was prepared in a similar method as Comparative Example 2 except 3.75 grams of AOS in the monomer mix was replaced by 5 grams of E-Sperse® RS-1618 amphiphilic crosslinker. The polymer product had a solids content of 30.8%, a viscosity of 24 cps and a particle size of 110 nm.

Example 6 (comparative)

Monomer composition = EA/n-BA/HEMA/BEM (35/15/45/5) (wt.% total monomers)

[0221] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution, 175 grams of (EA), 75 grams of (n-BA), 225 grams of (HEMA) and 33.3 grams of (BEM) (as supplied). Initiator A was made by dissolving 5 grams of Azo VA-086 in 40 grams of DI water. Initiator B was prepared by dissolving 2.5 grams of Azo VA-086 in 100 grams of DI water. A 3-liter reactor was charged with 800 grams of DI water, 5 grams of AOS and 10 grams of Selvol® 203 PVA. The contents of the reactor were heated to 87°C under a nitrogen blanket with agitation. After holding the reactor contents at 87°C for one hour, initiator A was added to the reactor. After about 1 minute, the monomer premix was metered to the reaction vessel over a period of 120 minutes. About 3 minutes after the start of monomer premix introduction, initiator B was metered to the reactor over a period of 150 minutes. The reaction temperature was maintained at 87°C. After completion of the initiator B feed, the temperature of the reaction vessel contents were maintained at 87°C for 60 minutes. The reactor contents were then cooled to 49°C. A solution of 0.61 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C. After 30 minutes, a

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solution of 0.69 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C for about 30 minutes. The reactor was cooled to the room temperature and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4.5 with ammonium hydroxide. The polymer had a solids content of 29.8%, a viscosity of 18 cps, and a particle size of 84 nm.

Example 7 (comparative)

Monomer composition = EA/n-BA/HEMA/BEM/RS-1596* (35/15/45/5/1*) (wt.% total monomers) (*RS-1596 = 1 wt.% based on total monomer wt. of EA, n-BA, HEMA, BEM)

[0222] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 5.56 grams of 90% E-Sperse® RS-1596 reactive surfactant which is monounsaturated. The polymer product had a solids content of 30.7%, a viscosity of 28 cps and a particle size of 87 nm.

Example 8 (comparative)

Monomer composition = EA/n-BA/HEMA/BEM/RS-1616* (35/15/45/5/1*) (wt.% total monomers) (*RS-1616 = 1 wt.% based on total monomer wt. of EA, n-BA, HEMA, BEM)

[0223] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 16.67 grams of 30% E-Sperse® RS-1616 reactive surfactant which is monounsaturated. The polymer product had a solids content of 31.7%, a viscosity of 14 cps and a particle size of 107 nm.

Example 9 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (35/15/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

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[0224] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 5 grams of 100% E-Sperse® RS-1617 amphiphilic crosslinker. The polymer product had a solids content of 31.4%, a viscosity of 14 cps and a particle size of 105 nm.

Example 10 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (35/15/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0225] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 10 grams of 50% E-Sperse® RS-1684 amphiphilic crosslinker. The polymer product had a solids content of 30%, a viscosity of 29 cps and a particle size of 93 nm.

Example 11 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (30/20/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0226] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 5 grams of 100% E-Sperse® RS-1618 amphiphilic crosslinker and monomer compositions were changed to 30 wt.% (EA), 20 wt.% (n-BA), 45 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) instead of 35 wt.% (EA), 15 wt.% (n-BA), 45 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) . The polymer product had a solids content of 30.8%, a viscosity of 26 cps and a particle size of 83 nm.

Example 12 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (25/25/45/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0227] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous

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surfactant solution in the monomer mix was replaced by 5 grams of 100% E-Sperse® RS-1618 amphiphilic crosslinker and the monomer compositions were changed to 25 wt.% (EA), 25 wt.% (n-BA), 45 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) instead of 35 wt.% (EA), 15 wt.% (n-BA), 45 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) . The polymer product had a solids content of 30.9%, a viscosity of 39 cps and a particle size of 78 nm.

Example 13 (Illustrative)

Monomer composition = EA/n-BA/HEMA/BEM/AM* (35/20/40/5/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0228] An emulsion polymer was prepared in the same manner as Comparative Example 6 except 16.67 grams of 30% Polystep TSP-16S aqueous surfactant solution in the monomer mix was replaced by 5 grams of 100% E-Sperse® RS-1618 amphiphilic crosslinker and monomer compositions were changed to 35 wt.% (EA), 20 wt.% (n-BA), 40 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) instead of 35 wt.% (EA), 15 wt.% (n-BA), 45 wt.% (HEMA) and 5 wt.% (BEM) (as supplied) . The polymer product had a solids content of 31.4%, a viscosity of 42 cps and a particle size of 87 nm.

Example 14 (Illustrative)

Monomer composition = EA/n-BA/BEM/HEMA/AA/AM* (35/15/5/43/2/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0229] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 70 grams of DI water, 2.5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 87.5 grams of (EA), 37.5 grams of (n-BA), 16.67 grams of (BEM) (as supplied) , 107.5 grams of (HEMA), and 5 grams of (AA). Initiator No. 1 was made by dispersing 2.5 grams of VA-086 in 20 grams of DI water. Initiator No. 2 was prepared by dissolving 1.25 grams of VA-086 in 50 grams of DI water. A 1-liter reactor vessel was charged with 400 grams of DI water, 2.5 grams of AOS and 5 grams of Selvol® 203 PVA and then the contents were heated to 87°C under a nitrogen blanket and agitation. Initiator No. 1 was added to the reaction vessel. The monomer premix was then metered into the reaction vessel over a period of

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120 minutes; while at the same time, initiator No. 2 was metered to the reaction vessel over a period of 150 minutes. After the completion of monomer premix feed, 16.5 grams of DI water was added to the dropping funnel which held the monomer premix to flush out the residual monomers into the reaction mixture. After the completion of initiator No. 2 feed, the temperature of the reaction vessel contents was maintained at 87°C for 60 minutes. The reaction vessel contents were then cooled to 49°C. A solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. After 5 minutes, a solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel. After 30 minutes, another solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. A solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was then added to the reaction vessel after 5 minutes. The reaction vessel contents were maintained at 60°C for another 30 minutes. The reaction vessel contents were then cooled to room temperature (23°C) and filtered through a 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 3.5 to 4.5 with 28% ammonium hydroxide in DI water. The resulting polymer latex had a solids level of 30.7%, and a particle size of 113 nm.

Example 15 (Illustrative)

Monomer composition = EA/n-BA/BEM/HEMA/AMD/AM* (35/15/5/43/2/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0230] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 70 grams of DI water, 2.5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 87.5 grams of (EA), 37.5 grams of (n-BA), 16.67 grams of (BEM) (as supplied), 107.5 grams of 2-hydroxyl ethyl methacrylate (HEMA), and 10 grams 50% acrylamide (AMD). Initiator No. 1 was made by dispersing 2.5 grams of VA-086 in 20 grams of DI water. Initiator No. 2 was prepared by dissolving 1.25 grams of VA-086 in 50 grams of DI water. A 1-liter reactor vessel was charged with 400 grams of DI water, 2.5 grams of AOS and 5 grams of Selvol® 203 PVA. The contents of the vessel was heated to 87°C under a nitrogen blanket and agitation. Initiator No. 1 was added to the reaction vessel. The monomer

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premix was then metered to the reaction vessel over a period of 120 minutes; while at the same time, initiator No. 2 was metered to the reaction vessel over a period of 150 minutes. After the completion of monomer premix feed, 16.5 grams of DI water was added to the dropping funnel which held the monomer premix to flush out the residual monomers. After the completion of initiator No. 2 feed, the temperature of the reaction vessel contents was maintained at 87°C for 60 minutes. The reaction vessel contents were then cooled to 49°C. A solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. After 5 minutes, a solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel. After 30 minutes, another solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. A solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was then added to the reaction vessel after 5 minutes. The reaction vessel contents were maintained at 60°C for another 30 minutes. Then, the reaction vessel contents were cooled to room temperature and filtered through a 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 3.5-4.5 with 28% ammonium hydroxide solution. The resulting polymer latex had a solid level of 30.4%, and a particle size of 90.4 nm.

Example 16 (Illustrative)

Monomer composition = EA/n-BA/BEM/HEMA/MAMD/AM* (35/15/5/43/2/1*)
(wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0231] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 70 grams of DI water, 2.5 grams of E-Sperse[®] RS-1618 amphiphilic crosslinker, 87.5 grams of (EA), 37.5 grams of (n-BA), 16.67 grams of (BEM) (as supplied), 107.5 grams of (HEMA), and 20 grams 25% (MAMD). Initiator No. 1 was made by dispersing 2.5 grams of VA-086 in 20 grams of DI water. Initiator No. 2 was prepared by dissolving 1.25 grams of VA-086 in 50 grams of DI water. A 1-liter reactor vessel was charged with 400 grams of DI water, 2.5 grams of AOS and 5 grams of Selvol[®] 203 PVA, and then the contents heated to 87°C under a nitrogen blanket and agitation. Initiator No. 1 was added

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to the reaction vessel. The monomer premix was then metered to the reaction vessel over a period of 120 minutes; while at the same time, initiator No. 2 was metered to the reaction vessel over a period of 150 minutes. After the completion of monomer premix feed, 16.5 grams of DI water was added to the dropping funnel which held the monomer premix to flush out the residual monomers. After the completion of initiator No. 2 feed, the temperature of the reaction vessel was maintained at 87°C for 60 minutes. The reaction vessel was then cooled to 49°C. A solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. After 5 minutes, a solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel. After 30 minutes, another solution of 0.3 grams of TBHP and 0.14 grams of AOS in 7.5 grams of DI water was added to the reaction vessel. A solution of 0.3 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel after 5 minutes. The reaction vessel contents were maintained at 60°C for another 30 minutes. The reaction vessel contents were cooled to room temperature and filtered through a 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 3.5-4.5 with a 28% ammonium hydroxide solution. The resulting polymer latex had a solid level of 26.2%, and a particle size of 100 nm.

Example 17 (Illustrative)

Monomer composition = EA/n-BA/BEM/HEMA/BEM/AM* (20.5/27.5/45/7/1*)
(wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0232] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 102.5 grams of (EA), 137.5 grams of (n-BA), 175 grams of (HEMA), 46.67 grams of (BEM) (as supplied). Initiator A was made by dissolving 5 grams of Azo VA-086 in 40 grams of DI water. Initiator B was prepared by dissolving 2.5 grams of Azo VA-086 in 100 grams of DI water. A 3-liter reactor was charged with 800 grams of DI water, 5 grams of AOS and 10 grams of Selvol® 203 PVA, and then the contents were heated to 87°C under a nitrogen blanket with agitation. After holding the reactor contents at 87°C for one

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hour, initiator A was then added to the reactor. After about 2 to 3 minutes, the monomer premix was metered into the reaction vessel over a period of 120 minutes. About 1 minute after the start of monomer premix metering, Initiator B was metered into the reactor over a period of 150 minutes. The reaction temperature was kept at 87°C. After completion of initiator B feed, the temperature of the reaction vessel contents were maintained at 87°C for 60 minutes. The reactor contents were then cooled to 49°C. A solution of 0.61 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C. After 30 minutes, a solution of 0.69 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C for about 30 minutes. The contents of the reactor were cooled to room temperature and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4 to 5 with a 28% ammonium hydroxide solution. The polymer was diluted with 340 grams of DI water to attain a solids 25.1%, a viscosity 13 cps, and particle size 82 nm.

Example 17A (Illustrative) Monomer composition = EA/n-BA/HEMA/BEM/AM* (15/25/45/15/0.08*) (wt.% total monomers) (*AM = 0.8 wt.% based on total monounsaturated monomer wt.)

[0233] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 4 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 75 grams of (EA), 125 grams of (n-BA), 225 grams of (HEMA), 100 grams of (BEM) (as supplied). Initiator A was made by dissolving 5 grams of Azo VA-086 in 40 grams of DI water. Initiator B was prepared by dissolving 2.5 grams of Azo VA-086 in 100 grams of DI water. A 3-liter reactor was charged with 770 grams of DI water, 6.67 grams of SLS and 10 grams of Selvol® 203 PVA, and then the contents were heated to 87°C under a nitrogen blanket with agitation. After holding the reactor contents at 87°C for one hour, initiator A was then added to the reactor. After about 2 to 3 minutes, the monomer

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premix was metered into the reaction vessel over a period of 120 minutes. About 1 minute after the start of monomer premix metering, Initiator B was metered into the reactor over a period of 150 minutes. The reaction temperature was kept at 87°C. After completion of initiator B feed, the temperature of the reaction vessel contents was maintained at 85°C for 60 minutes. The reactor contents were then cooled to 49°C. A solution of 0.61 grams of TBHP and 0.38 grams of SLS in 16.8 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 16.8 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C. After 30 minutes, a solution of 0.64 grams of TBHP and 0.38 grams of SLS in 16.8 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 16.8 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C for about 30 minutes. The contents of the reactor were cooled to room temperature and filtered through 100 micron filter cloth. The polymer was diluted with 340 grams of DI water to attain a solids about 25.1%, a viscosity of 13 cps, and particle size about 80 nm.

Example 18 (Illustrative)

Monomer composition = n-VP/EA/BA/VAc/HEMA/AM* (20/15/20/20/25/1*) (wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0234] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 70 grams of DI water, 2.5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 50 grams of (n-VP), 37.5 grams of (EA), 50 grams of (n-BA), 50 grams of vinyl acetate (VAc), and 62.5 grams of (HEMA). Initiator 1 was made by mixing 1.07 grams of TBHP in 20 grams of DI water. Reductant 2 was prepared by dissolving 0.83 grams of erythorbic acid in 50 grams of DI water. A 1 liter reactor vessel was charged with 400 grams of DI water, 2.5 grams of AOS and 12.5 grams of Selvol® 502 PVA, and then the contents were heated to 65°C under a nitrogen blanket and agitation. Initiator 1 was added to the reaction vessel. After about 1 minute, the monomer premix was metered into the reaction vessel over a period of 120 minutes; while at the same time Reductant 2 was metered to the reaction vessel for over a period of 150 minutes. After the

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completion of monomer premix feed, 16.5 grams of DI water was added to flush the residual monomers from the premix vessel into the reaction vessel. After the completion of Reductant 2 feed, the temperature of the reaction vessel contents were maintained at 65°C for 60 minutes. The reaction vessel contents were then cooled to 50°C. A solution of 0.3 grams of TBHP and 7.5 grams of DI water was added to the reaction vessel. After 5 minutes, a solution of 0.29 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel. After 30 minutes, a solution of 0.32 grams of TBHP and 7.5 grams of DI water was added to the reaction vessel. After 5 minutes, a solution of 0.29 grams of erythorbic acid in 7.5 grams of DI water was added to the reaction vessel. The reaction vessel contents were maintained at 50°C for about 30 minutes. Then, the reaction vessel was cooled to room temperature (22°C) and filtered through 100 micron filter cloth. The resulting polymer latex had a solids level 30.8%, and particle size 100 nm.

Example 19 (Illustrative)

Monomer composition = EA/n-BA/HEMA/n-VP/CSEM/AM* (23/20/35/20/2/1*)
(wt.% total monomers) (*AM = 1 wt.% based on total monounsaturated monomer wt.)

[0235] An emulsion polymer was prepared as follows. A monomer premix was made by mixing 140 grams of DI water, 5 grams of E-Sperse® RS-1618 amphiphilic crosslinker, 115 grams of (EA), 100 grams of (n-BA), 175 grams of (HEMA), 12.5 grams (CSEM), and 100 grams of (n-VP). Initiator A was made by dissolving 4 grams Azo VA-086 in 40 grams of DI water. Initiator B was prepared by dissolving 0.75 grams of Azo VA-086 in 100 grams of DI water. A 3-liter reactor was charged with 800 grams of DI water, 5 grams of AOS and 20 grams of Selvol® 203 PVA, and then the contents were heated to 87°C under a nitrogen blanket with mild agitation. After holding the reactor contents at 87°C for one hour Initiator A was then added to the reactor. After about 1 minute, the monomer premix was metered into the reaction vessel for over a period of 120 minutes. About 3 minutes after the start of monomer premix introduction, Initiator B was metered into the reactor over a period of 150 minutes. The reaction temperature was maintained

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at 87°C. After completion of the Initiator B feed, the temperature of the reaction vessel contents were maintained at 87°C for an additional 60 minutes. The reactor contents were then cooled to 49°C. A solution of 0.61 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C. After 30 minutes, a solution of 0.69 grams of TBHP and 0.29 grams of AOS in 15 grams of DI water was added to the reactor. After 5 minutes, a solution of 0.59 grams of erythorbic acid in 15 grams of DI water was added to the reactor. The reactor contents were maintained at 49°C for about 30 minutes. The reactor contents were then cooled to the room temperature (23°C) and filtered through 100 micron filter cloth. The pH of the resulting emulsion was adjusted to 4.5 with 10% ammonium hydroxide in water. The polymer emulsion had a solids content of 30.9%, a Brookfield viscosity of 36 cps, and particle size 113 nm.

Examples 20 and 21

[0236] The following two Examples (20 and 21) compare the effectiveness of a polymer prepared according to the present technology using a reactive surfactant containing two allyl groups versus a polymer containing no crosslinker in creating yield stress fluids with high optical clarity in surfactant media.

[0237] Samples containing 2.5wt% polymer solids, 14 wt.% SLES-2 and 3 wt.% CAPB in DI water were prepared using each of the polymers in Examples 1 and 4. The yield stress of these samples was determined by oscillatory shear measurements on a controlled stress rheometer (TA instruments AR2000EX rheometer, New Castle, DE) with cone and plate geometry (60 mm cone with a cone angle of 2 degrees and 56 μm gap) at 25°C. The oscillatory measurements are performed at a frequency of 1Hz. The elastic and viscous moduli (G' and G'' respectively) are obtained as a function of increasing stress amplitude. In cases where the swollen polymer particles created a jammed network, G' is larger than G'' at low stress amplitudes but decreases at higher amplitudes crossing G'' because of rupture of the network. The stress corresponding to the crossover of G' and G'' is noted as the yield stress. The optical clarity of the samples (expressed

in terms of the nephelometric turbidity unit (NTU)) was measured using a laboratory turbidimeter (HF Scientific Micro 100 Laboratory Turbidimeter, Fort Myers, FL). The results of these measurements are shown in Table 1.

TABLE 1

Example No.	Polymer No.	Yield Stress (Pa)	Optical Clarity (NTU)
20 (Illustrative)	4	6.4	15.8
21 (comparative)	1	0	6.1

[0238] The technology provides a sample with improved yield stress and acceptable optical clarity. The sample prepared using the comparative polymer (no crosslinking) has high optical clarity but does not have a yield stress.

Examples 22 to 24

[0239] The following Examples (22 to 24) compare the effectiveness of polymers prepared according to the present technology that use either an amphiphilic crosslinking agent containing two allyl groups or a combination of an amphiphilic crosslinking agent containing two allyl groups and a conventional crosslinking agent versus a polymer prepared using a conventional crosslinking agent only in terms of creating yield stress fluids with high optical clarity in surfactant media.

[0240] Samples containing 2.5wt% polymer solids, 14 wt.% SLES-2 and 3 wt.% CAPB in DI water were prepared using each of the polymers in Examples 2, 3 and 5. The yield stress and optical clarity of these samples were measured using the same procedures as described in examples 20 and 21. The results are shown in Table 2.

TABLE 2

Example No.	Polymer No.	Yields Stress (Pa)	Optical Clarity (NTU)
22 (Illustrative)	3	8.4	32.2
23 (Illustrative)	5	8.7	45.5
24 (comparative)	2	7	55.3

[0241] The technology provides a desirable combination of yield stress and optical clarity (lower NTU) relative to the comparative example.

Examples 25 to 32

[0242] The following Examples (25 to 32) compare the effectiveness of polymers prepared according to the present technology that use an amphiphilic crosslinking agent containing two allyl groups versus polymers prepared using amphiphilic crosslinking agents containing either only one allyl group or amphiphilic agents with no crosslinking groups. Samples containing 2.5% wt% polymer, 14% SELS2 and 3% CAPB in DI water were prepared and the yield stress and optical clarity were determined using the techniques described in examples 20 and 21.

TABLE 3

Example No.	Polymer No.	Yield Stress (Pa)	Optical Clarity (NTU)
25 (Illustrative)	9	9.9	40.5
26 (Illustrative)	10	12.8	19.2
27 (Illustrative)	11	11.1	11.1
28 (Illustrative)	12	10.5	8.0
29 (Illustrative)	13	10.7	10.5
30 (comparative)	6	0	2.4
31 (comparative)	7	0	2.9
32 (comparative)	8	0	4.8

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[0243] The present technology provides samples that show both yield stress and optical clarity. In contrast, the control samples have optical clarity (low NTU) but do not display a yield stress.

Examples 33 to 35

[0244] Additional samples containing 2.5 wt% polymer, 14 wt.% SLES-2 and 3 wt.% CAPB were prepared (Examples 33 to 35) and the yield stress and optical clarity were determined by the methods outlined earlier. The results are shown in Table 4.

TABLE 4

Example No.	Polymer No.	Yield Stress (Pa)	Optical Clarity (NTU)
33 (Illustrative)	14	13.0	43.1
34 (Illustrative)	15	13.6	16.0
35 (Illustrative)	16	11.1	18.0

[0245] Once again, the present technology provides compositions that exhibit the combined properties of yield stress and good optical clarity.

Example 36

[0246] Surfactant formulations containing the amphiphilic polymer of comparative Example 2 were compared to identical formulations containing the amphiphilic polymer of Example 17 for salt tolerance. Stock surfactant formulations containing the amphiphilic polymers of Example 2 (comparative) and Example 17 (illustrative) were prepared with the components set forth in Table 5 below.

TABLE 5

PART	Component	Active %
A	DI Water	q.s. to 100
	Amphiphilic Polymer (25% solids)	2
B	SLES-3	4.7
	SLS	3.5
	CAPB	1.8
C	Fragrance Oil	1
D	Sodium Chloride	0-3.5
	Citric Acid	pH 4.8 to 5.0

The formulations were prepared as follows:

[0247] 1) The Part A component was prepared by adding the amphiphilic polymer to the DI water and mixed via a magnetic stir bar at 180 rpm for 2 minutes.

[0248] 2) The Part B components were added to Part A and stirred with a magnetic stir bar at 180 rpm for 5 minutes or until the Part AB mixture became transparent.

[0249] 3) The Part C fragrance oil (without solubilizer) was added drop-wise to the PART AB mixture, whereupon the mixture immediately became translucent. The mixture was stirred at 180 rpm with a magnetic stir bar until the fragrance oil was well dispersed and the mixture turned back to the transparent state (about 5 minutes).

[0250] 4) Aliquots of the PART ABC mixture were prepared from the stock formulations. To each aliquot sodium chloride (5 wt.% aqueous solution) was added in the amounts indicated in TABLE 6. The pH of each sample was adjusted to about 4.8 to 5. Each sample was stirred at 180 rpm with a magnetic stirrer for about 12 hours.

[0251] Each sample was then centrifuged to remove air bubbles and any undissolved solids before measuring Brookfield viscosity, optical clarity and yield stress (YS) values. The results are reported in Table 6.

TABLE 6

No Polymer				Polymer of Example 2				Polymer of Example 17			
NaCl (wt.%)	B.V. (cps)	Optical Clarity (%T)	Y.S. (Pa)	NaCl (wt.%)	B.V. (cps)	Optical Clarity (%T)	Y.S. (Pa)	NaCl (wt.%)	B.V. (cps)	Optical Clarity (%T)	Y.S. (Pa)
0	10	100	0	0	880	94.6	1.1	0	1900	98.7	2.5
0.5	80	100	0	0.25	160	94.6	1.6	0.25	3940	98.4	4.2
1	680	100	0	0.5	254	93.1	2.2	0.5	5800	98.2	5.5
1.5	6620	100	0	1	364	83.3	2.5	1	1042	97.5	9.1
2	10720	100	0	1.5	350	69.8	1.6	1.5	1238	96.5	11.2
2.5	8920	100	0	2	260	43.3	0	2	1302	95.4	11.4
3	2060	100	0	--	--	--	--	--	--	--	--
3.5	480	100	0	--	--	--	--	--	--	--	--
0	10	100	0	0	880	94.6	1.1	0	1900	98.7	2.5
0.5	80	100	0	0.25	160	94.6	1.6	0.25	3940	98.4	4.2

[0252] In the presence of an electrolyte the results demonstrate that surfactant systems containing an amphiphilic polymer crosslinked with an amphiphilic crosslinker of the disclosed technology exhibit a synergistic improvement in viscosity and yield value while maintaining clarity compared to surfactant systems containing no amphiphilic polymer and surfactant systems containing an amphiphilic polymer crosslinked with APE.

[0253] The control formulation failed the bead suspension test for all salt concentrations tested. The formulation containing the polymer of comparative Example 2 passed at salt concentrations of 0, 0.25, 0.5, 1, 1.5 wt.%, but failed at a salt concentration of 2 wt.%. The formulation containing the polymer of illustrative Example 17 passed at salt concentrations of 0, 0.25, 0.5, 1, 1.5 and 2 wt.%. The results for Brookfield viscosity, yield stress, and optical clarity are plotted in Figs. 1, 2 and 3, respectively.

Example 37

[0254] Surfactant formulations containing the amphiphilic polymer of comparative Example 2 were compared to identical formulations containing the

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amphiphilic polymer of Example 17 for tolerance to organic acid preservatives. Stock surfactant formulations containing the amphiphilic polymers of Example 2 (comparative) and Example 17 (illustrative) were prepared with the components set forth in Table 7 below.

Table 7

PART	Component	Active %
A	DI Water	q.s. to 100
	Amphiphilic Polymer (25% solids)	2.5
B	SLES-2	9
	CAPB	3
C	Fragrance Oil	1
D	Sodium Benzoate	0-0.5
	Citric Acid	pH 4.8 to 5

[0255] The formulations were prepared as follows:

[0256] 1) The Part A component was prepared by adding the amphiphilic polymer to the DI water and mixed via a magnetic stir bar at 180 rpm for 2 minutes.

[0257] 2) The Part B components were added to Part A and stirred with a magnetic stir bar at 180 rpm until the Part AB mixture became transparent (approximately 5 minutes).

[0258] 3) The Part C fragrance oil (without solubilizer) was added drop-wise to the PART AB mixture, whereupon the mixture immediately became translucent. The mixture was stirred at 180 rpm with a magnetic stir bar until the fragrance oil was well dispersed and the mixture turned back to the transparent state (about 5 minutes).

[0259] 4) Aliquots of the PART ABC mixture were prepared from the stock formulations. To each aliquot sodium benzoate was added in the amounts indicated in TABLE 8. The pH of each sample was adjusted to about 4.8 to 5. Each sample was stirred at 180 rpm with a magnetic stirrer for about 12 hours.

[0260] Each sample was then centrifuged to remove air bubbles and any undissolved solids before measuring Brookfield viscosity, optical clarity and yield stress (YS) values. The results are reported in Table 8.

TABLE 8

Polymer of Example 2				Polymer of Example 17			
NaCl (wt.%)	B.V. (cps)	Optical Clarity (%T)	Y.S. (Pa)	NaCl (wt.%)	B.V. (cps)	Optical Clarity (%T)	Y.S. (Pa)
0	2060	67.3	0.8	0	10580	97.4	9.5
0.25	1100	43.1	0	0.25	11800	97.1	10.1
0.5	480	22.6	0	0.5	12520	96.2	10.4

[0261] In the presence of sodium benzoate (an organic acid preservative) the results demonstrate that surfactant systems containing an amphiphilic polymer crosslinked with an amphiphilic crosslinker of the disclosed technology exhibit an improvement in viscosity, yield value and clarity compared to surfactant systems containing an amphiphilic polymer crosslinked with APE.

[0262] In the bead suspension test, the surfactant formulation containing the polymer of comparative Example 2 failed at all concentrations of sodium benzoate (i.e., at 0.25 and 0.5 wt.%) while the formulation containing the polymer of illustrative Example 17 passed at all sodium benzoate concentrations (i.e., at 0.25 and 0.5 wt.%). The control sample containing no sodium benzoate (0 wt.%) passed the bead suspension test. The results for Brookfield viscosity and yield stress are plotted in Fig 4.

Examples 38-39

[0263] The polymer of comparative Example 2 and the polymer of illustrative Example 17A were formulated into identical surfactant formulations containing acid preservatives and selected perfumes. The formulation components are set forth in Table 9.

TABLE 9

	Ex. 38	Ex. 39
Component	Active wt.%	Active wt.%
Polymer No. 2 (comparative)	2.5	--
Polymer No. 17A		2.5
SLES-2	9	9
CAPB	3	3
Perfume (see Table 9)	1	1
Citric Acid	q.s. to pH 4.4-4.6	q.s. to pH 4.4-4.6
DI Water	q.s. to 100	q.s. to 100

[0264] Formulation protocol:

1. Add polymer to DI water and disperse.
2. Add SLES-2 surfactant to (1) with gentle mixing.
3. Add CAPB surfactant to (2) with continued mixing.
4. Add perfume component to (3) with continued mixing.
5. Add sodium benzoate to (4) with continued mixing.
6. Add citric acid to adjust pH with continued mixing until homogeneous.

[0265] Each perfume containing formulation was evaluated for rheological and turbidity properties. The results are set forth in Table 10.

TABLE 10

Fragrance	Ex. 38 (comparative)		Ex. 39	
	Viscosity ¹ (mPa·s)	Turbidity (NTU)	Viscosity (mPa·s)	Turbidity (NTU)
Pinene	1920	92.8	11880	17.5
Limonene	3080	91.2	8670	16.1
2-Phenylethanol	40	861	7580	17.2

¹Spindle No. 5

[0266] Nonionic polymers prepared from the amphiphilic crosslinker of the disclosed technology are more tolerant of the deleterious effects that perfumes and fragrances have on rheological and clarity properties of surfactant containing compositions as evidenced by the enhanced viscosity and turbidity values.

[0267] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the disclosed technology can be used together with ranges or amounts for any of the other elements.

[0268] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

[0269] While certain representative embodiments and details have been shown for the purpose of illustrating the subject technology, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject disclosed technology. In this regard, the scope of the disclosed technology is to be limited only by the following claims.

WHAT IS CLAIMED IS:

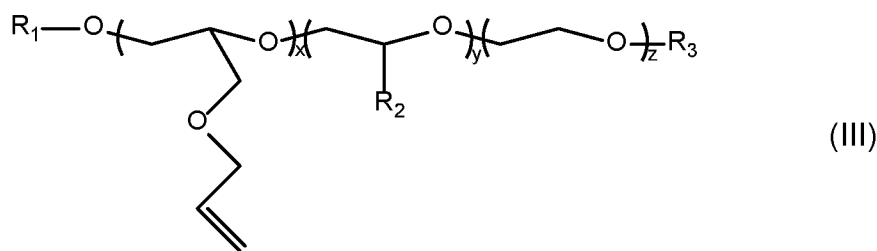
1. A nonionic amphiphilic polymer composition polymerized from a monomer composition comprising:

- (i) at least one hydrophilic monomer,
- (ii) at least one hydrophobic monomer, and
- (iii) about 0.01 to about 5 wt. % of at least one amphiphilic crosslinking agent containing more than one unsaturated moiety (based on the total weight of the monounsaturated monomers utilized to prepare the polymer).

2. The polymer composition of claim 1, wherein the more than one reactive moieties of said at least one amphiphilic crosslinking agent comprise at least one allyl group.

3. The polymer composition according to claim 1 wherein the more than one reactive moieties of said at least one amphiphilic crosslinking agent comprise at least two allyl groups.

4. The polymer composition according to claim 1 wherein the amphiphilic crosslinking agent is a compound of formula (III):



where:

R1 is a C₁₀₋₂₄ alkyl, alkaryl, alkenyl, or cycloalkyl;

R2 is CH₃, CH₂CH₃, C₆H₅, or C₁₄H₂₉;

R3 is H or Z⁻ M⁺

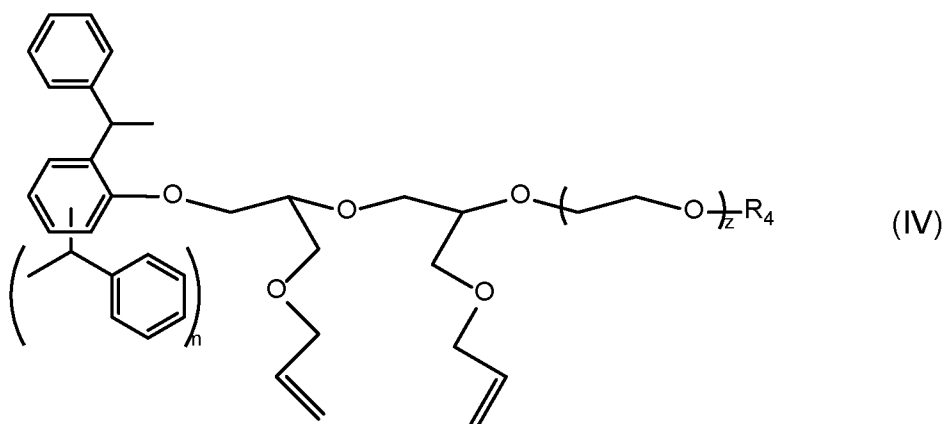
Z⁻ is SO₃⁻, or PO₃²⁻;

M⁺ is Na⁺, K⁺, NH₄⁺, or an alkanolamine;

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x is 2-10;
 y is 0-200; and
 z is 4-200.

5. The polymer composition according to claim 1 wherein the amphiphilic crosslinking agent is a compound of formula (IV):



where:

n is 1 or 2;

z is 4 to 40 in one aspect, 5 to 38 in another aspect, and 10 to 20 in a further aspect; and

R₄ is H, SO₃⁻M⁺ or PO₃⁻M⁺, and M is selected from Na⁺, K⁺, NH₄⁺ or an alkanolamine.

6. The polymer composition according to any previous claim, wherein the composition additionally comprises a steric stabilizer.

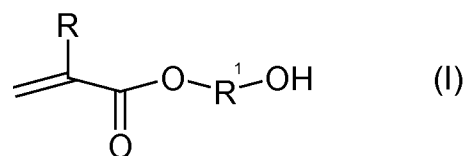
7. The polymer composition according to claim 6, wherein the steric stabilizer is a partially hydrolyzed polyvinyl alcohol.

8. The polymer composition according to any previous claim wherein:
 said hydrophilic monomer is selected from hydroxy(C₁-C₅)alkyl (meth)acrylates, N-vinyl amides, amino group containing monomers, or mixtures

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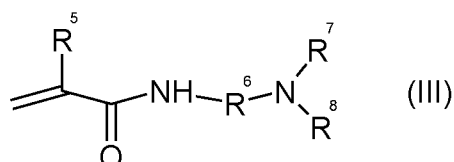
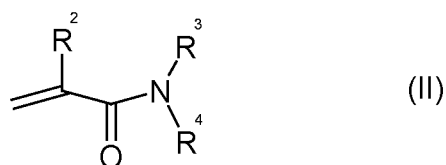
thereof; and said hydrophobic monomer is selected from esters of (meth)acrylic acid with alcohols containing 1 to 30 carbon atoms, vinyl esters of aliphatic carboxylic acids containing 1 to 22 carbon atoms, vinyl ethers of alcohols containing 1 to 22 carbon atoms, vinyl aromatic monomers, vinyl halides, vinylidene halides, associative monomers, semi-hydrophobic monomers, or mixtures thereof.

9. The polymer composition according to any previous claim wherein said hydroxy(C₁-C₅)alkyl (meth)acrylate is selected from at least one compound represented by the formula:



wherein R is hydrogen or methyl and R¹ is a divalent alkylene moiety containing 1 to 5 carbon atoms, wherein the alkylene moiety optionally can be substituted by one or more methyl groups.

10. The polymer composition according to any previous claim wherein said amino group containing monomer is selected from (meth)acrylamide, diacetone acrylamide and at least one monomer structurally represented by the following formulas:

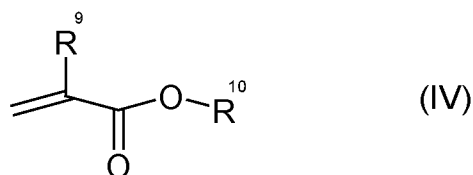


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wherein R² is hydrogen or methyl, R³ independently is selected from hydrogen, C₁ to C₅ alkyl and C₁ to C₅ hydroxyalkyl, and R⁴ independently is selected from is C₁ to C₅ alkyl or C₁ to C₅ hydroxyalkyl, R⁵ is hydrogen or methyl, R⁶ is C₁ to C₅ alkylene, R⁷ independently is selected from hydrogen or C₁ to C₅ alkyl, and R⁸ independently is selected from C₁ to C₅ alkyl; or mixtures thereof.

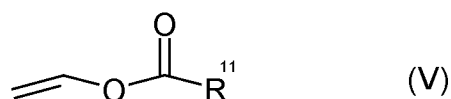
11. The polymer composition according to any previous claim wherein said N-vinyl amide is selected from a N-vinyl lactam containing 4 to 9 atoms in the lactam ring moiety, wherein the ring carbon atoms, optionally, can be substituted by one or more C₁-C₃ lower alkyl group.

12. The polymer composition according to any previous claim wherein said ester of (meth)acrylic acid with alcohols containing 1 to 30 carbon is selected from at least one compound represented by the formula:



wherein R⁹ is hydrogen or methyl and R¹⁰ is C₁ to C₂₂ alkyl.

13. The polymer composition according to any previous claim wherein said vinyl ester of aliphatic carboxylic acids containing 1 to 22 carbon atoms is selected from at least one compound represented by the formula:



wherein R¹¹ is a C₁ to C₂₂ aliphatic group which can be an alkyl or alkenyl.

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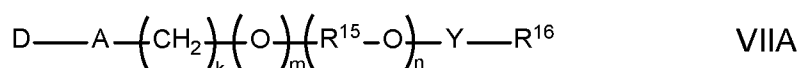
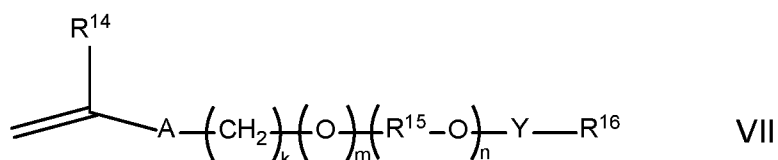
14. The polymer composition according to any previous claim wherein said vinyl ether of alcohols containing 1 to 22 carbon atoms is selected from at least one compound represented by the formula:



wherein R¹³ is a C₁ to C₂₂ alkyl.

15. The polymer composition according to any previous claim wherein said associative monomer comprises (i) an ethylenically unsaturated end group portion; (ii) a polyoxyalkylene mid-section portion, and (iii) a hydrophobic end group portion containing 8 to 30 carbon atoms.

16. The polymer composition according to any previous claim wherein said associative monomer is represented by formulas VII and/or VIIA:

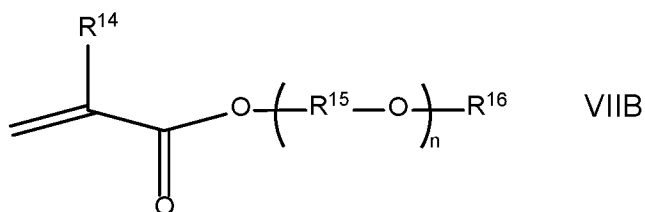


wherein R¹⁴ is hydrogen or methyl; A is -CH₂C(O)O-, -C(O)O-, -O-, -CH₂O-, -NHC(O)NH-, -C(O)NH-, -Ar-(CE₂)_z-NHC(O)O-, -Ar-(CE₂)_z-NHC(O)NH-, or -CH₂CH₂NHC(O)-; Ar is a divalent arylene (e.g., phenylene); E is H or methyl; z is 0 or 1; k is an integer ranging from about 0 to about 30, and m is 0 or 1, with the proviso that when k is 0, m is 0, and when k is in the range of 1 to about 30, m is 1; D represents a vinyl

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or an allyl moiety; $(R^{15}-O)_n$ is a polyoxyalkylene moiety, which can be a homopolymer, a random copolymer, or a block copolymer of C_2 - C_4 oxyalkylene units, R^{15} is a divalent alkylene moiety selected from C_2H_4 , C_3H_6 , or C_4H_8 , and combinations thereof; and n is an integer in the range of about 2 to about 150 in one aspect, from about 10 to about 120 in another aspect, and from about 15 to about 60 in a further aspect; Y is $-R^{15}O-$, $-R^{15}NH-$, $-C(O)-$, $-C(O)NH-$, $-R^{15}NHC(O)NH-$, or $-C(O)NHC(O)-$; R^{16} is a substituted or unsubstituted alkyl selected from a C_8 - C_{30} linear alkyl, a C_8 - C_{30} branched alkyl, a C_8 - C_{30} carbocyclic alkyl, a C_2 - C_{30} alkyl-substituted phenyl, an araalkyl substituted phenyl, and an aryl-substituted C_2 - C_{30} alkyl; wherein the R^{16} alkyl group, aryl group, phenyl group optionally comprises one or more substituents selected from the group consisting of a hydroxyl group, an alkoxy group, benzyl group styryl group, and a halogen group.

17. The polymer composition according to any previous claim wherein said associative monomer is represented by formula VIIB:

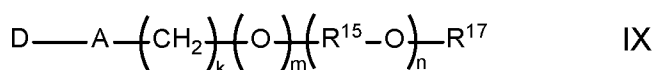
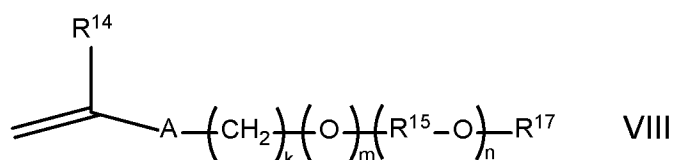


wherein R^{14} is hydrogen or methyl; R^{15} is a divalent alkylene moiety independently selected from C_2H_4 , C_3H_6 , and C_4H_8 , and n represents an integer ranging from about 10 to about 60, $(R^{15}-O)$ can be arranged in a random or a block configuration; R^{16} is a substituted or unsubstituted alkyl selected from a C_8 - C_{30} linear alkyl, a C_8 - C_{30} branched alkyl, a C_8 - C_{30} carbocyclic alkyl, a C_2 - C_{30} alkyl-substituted phenyl, an araalkyl substituted phenyl, and an aryl-substituted C_2 - C_{30} alkyl, wherein the R^{16} alkyl group, aryl group, phenyl group optionally comprises one or more substituents selected from the group consisting of a hydroxyl group, an alkoxy group, benzyl group styryl group, and a halogen group.

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18. The polymer composition according to any previous claim wherein said semi-hydrophobic monomer comprises (i) an ethylenically unsaturated end group portion; (ii) a polyoxyalkylene mid-section portion, and (iii) an end group portion selected from hydrogen or an alkyl group containing 1 to 4 carbon atoms.

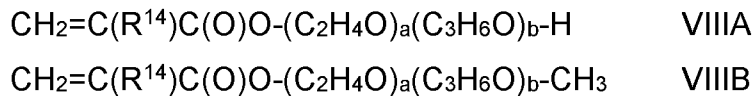
19. The polymer composition according to any previous claim wherein said semi-hydrophobic monomer is selected from at least one monomer represented by formulas VIII and IX:



wherein R^{14} is hydrogen or methyl; A is $-\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{O}-$, $-\text{O}-$, $-\text{CH}_2\text{O}-$, $-\text{NHC}(\text{O})\text{NH}-$, $-\text{C}(\text{O})\text{NH}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{O}-$, $-\text{Ar}-(\text{CE}_2)_z-\text{NHC}(\text{O})\text{NH}-$, or $-\text{CH}_2\text{CH}_2\text{NHC}(\text{O})-$; Ar is a divalent arylene (e.g., phenylene); E is H or methyl; z is 0 or 1; k is an integer ranging from about 0 to about 30, and m is 0 or 1, with the proviso that when k is 0, m is 0, and when k is in the range of 1 to about 30, m is 1; $(\text{R}^{15}-\text{O})_n$ is a polyoxyalkylene moiety, which can be a homopolymer, a random copolymer, or a block copolymer of C₂-C₄ oxyalkylene units, R^{15} is a divalent alkylene moiety selected from C₂H₄, C₃H₆, or C₄H₈, and combinations thereof; and n is an integer in the range of about 2 to about 150 in one aspect, from about 5 to about 120 in another aspect, and from about 10 to about 60 in a further aspect; R^{17} is selected from hydrogen and a linear or branched C₁-C₄ alkyl group; and D represents a vinyl or an allyl moiety.

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20. The polymer composition according to any previous claim wherein said semi-hydrophobic monomer is selected from at least one monomer represented by formulas VIIIA and VIIIB:



wherein R^{14} is hydrogen or methyl, and "a" is an integer ranging from 0 or 2 to about 120 in one aspect, from about 5 to about 45 in another aspect, and from about 10 to about .25 in a further aspect, and "b" is an integer ranging from about 0 or 2 to about 120 in one aspect, from about 5 to about 45 in another aspect, and from about 10 to about .25 in a further aspect, subject to the proviso that "a" and "b" cannot be 0 at the same time.

21. The polymer composition according to claim 20 wherein b is 0.

22. The polymer composition according to any previous claim wherein said polymer is polymerized from a monomer mixture comprising at least 30 wt.% of said hydrophilic monomer(s) and at least 5 wt.% of said hydrophobic monomers.

23. A polymer composition according to any of the preceding claims wherein said amphiphilic polymer comprises a conventional crosslinking agent which is present in an amount sufficient to be incorporated into said polymer from about 0.01 to about 1 wt.% (based on the total weight of the monounsaturated monomers utilized to prepare the polymer).

24. A polymer composition according to any of the preceding claims wherein said conventional crosslinking agent contains an average of about 3 crosslinkable unsaturated moieties.

25. A polymer composition according to any of the preceding claims wherein said monomer mixture comprises a conventional crosslinking agent which is

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present in an amount sufficient to be incorporated into said polymer from about 0.01 to about 0.3 wt.% (based on the total weight of the monounsaturated monomers utilized to prepare the polymer).

26. A polymer composition according to any of the preceding claims wherein the at least one conventional crosslinking agent is selected from polyallyl ethers of trimethylolpropane, polyallyl ethers of pentaerythritol, polyallyl ethers of sucrose, or mixtures thereof.

27. A polymer composition according to any of the preceding claims wherein the at least one conventional crosslinking agent is selected from pentaerythritol diallyl ether, pentaerythritol triallyl ether, pentaerythritol tetraallyl ether; or mixtures thereof.

28. A polymer composition according to any of the preceding claims wherein said polymer is an emulsion polymer.

29. A polymer composition according to claim 28 prepared in the presence of a stabilizing surfactant or a reactive derivative thereof.

30. A polymer composition according to any previous claim wherein said monomer mixture is polymerized in the presence of a protective colloid.

31. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

a) from about 20 to about 60 wt.% of at least one C₁-C₄ hydroxyalkyl (meth)acrylate;

b) from about 10 to about 70 wt.% of at least one C₁-C₁₂ alkyl (meth)acrylate or from about 10 to about 70 wt.% of at least one C₁-C₅ alkyl (meth)acrylate;

c) from about 0, 1, 5 or 15 to about 40 wt.% of at least one vinyl ester of a C₁-C₁₀ carboxylic acid;

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d) from about 0, 1, 5 or 15 to about 30 wt.% of a vinyl lactam (e.g., vinyl pyrrolidone);

e) from about 0, 0.1, 1, 5, or 7 to about 15 wt.% of at least one associative and/or a semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and

f) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

32. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

a) from about 20 to about 60 wt.% of at least one C₁-C₄ hydroxyalkyl (meth)acrylate;

b) from about 10 to about 30 wt.% ethyl acrylate;

c) from about 10 to about 35 wt.% butyl acrylate;

d) from about 0, 1, 5 or 15 to about 25 wt.% of a vinyl ester of a carboxylic acid selected from vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, and vinyl valerate;

e) from about 0, 1 or 15 to about 30 wt.% of vinyl pyrrolidone;

f) from about 0, 0.1, 1, 5 or 7 to about 15 wt.% of at least one associative monomer and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and

g) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

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33. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

- a) from about 20 to about 50 wt.% of hydroxyethyl methacrylate;
 - b) from about 10 to about 30 wt.% ethyl acrylate;
 - c) from about 10 to about 30 wt.% butyl acrylate;
 - d) from about 0, 1, or 15 to about 25 wt.% of vinyl pyrrolidone;
 - e) from about 0 or 15 to about 25 wt.% of vinyl acetate;
 - f) from about 0, 0.1, 1, 5 or 7 to about 10 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and
- g) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

34. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

- a) from about 20 to about 50 wt.% of hydroxyethyl methacrylate;
 - b) from about 10 to about 40 wt.% ethyl acrylate;
 - c) from about 10 to about 20 wt.% butyl acrylate;
 - d) from about 0.1 to about 10 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and
- e) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

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35. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

- a) from about 20 to about 50 wt.% of hydroxyethyl methacrylate;
- b) from about 10 to about 30 wt.% ethyl acrylate;
- c) from about 10 to about 30 wt.% butyl acrylate;
- d) from about 1 to about 15 wt.% of at least one associative and/or semi-hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and
- e) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

36. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

- a) from about 20 to about 35 wt.% of hydroxyethyl methacrylate;
- b) from about 10 to about 30 wt.% ethyl acrylate;
- c) from about 10 to about 30 wt.% butyl acrylate;
- d) from about 15 to about 25 wt.% of vinyl pyrrolidone,
- e) from about 15 to about 25 wt.% of vinyl acetate (wherein all monomer weight percentages are based on the weight of the total monomers); and
- f) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

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37. A polymer composition according to any previous claim wherein said polymer is polymerized from a monomer composition comprising:

- a) from about 20 to about 40 wt.% of hydroxyethyl methacrylate;
- b) from about 10 to about 30 wt.% ethyl acrylate;
- c) from about 10 to about 30 wt.% butyl acrylate;
- d) from about 15 to about 25 wt.% of vinyl pyrrolidone;
- e) from about 1 to about 5 wt.% of at least one associative and/or semi-

hydrophobic monomer (wherein all monomer weight percentages are based on the weight of the total monomers); and

e) from about 0.01 to about 5 wt.% in one aspect, from about 0.1 to about 3 wt.% in another aspect, and from about 0.5 to about 1 wt.% in a further aspect of at least one crosslinker (based on the total weight of the monounsaturated monomers utilized to prepare the polymer) selected from an amphiphilic crosslinking agent or a combination of an amphiphilic crosslinking agent and said conventional crosslinking agent.

38. A polymer composition according to any previous claim wherein said associative monomer in said monomer composition is selected from lauryl polyethoxylated (meth)acrylate, cetyl polyethoxylated (meth)acrylate, cetearyl polyethoxylated (meth)acrylate, stearyl polyethoxylated (meth)acrylate, arachidyl polyethoxylated (meth)acrylate, behenyl polyethoxylated (meth)acrylate, cerotyl polyethoxylated (meth)acrylate, montanyl polyethoxylated (meth)acrylate, melissyl polyethoxylated (meth)acrylate, where the polyethoxylated portion of the monomer contains about 2 to about 50 ethylene oxide units in one aspect, from about 10 to 40 ethylene oxide units in another aspect, from about 15 to 30 units in still another aspect.

39. A polymer composition according to any previous claim where said monomer is prepared from a monomer composition further comprising 0 to 5 wt.% of an ionizable and/or ionized monomer, based on the weight of the total monomers.

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40. A polymer composition according to any previous claim where said polymer is prepared from a monomer composition containing less than 5 wt.% in one aspect, less than 3 wt.% in another aspect, less than 1 wt.% in a further aspect, less than 0.5 wt.% in a still further aspect, less than 0.1 wt.% in an additional aspect, less than 0.05 wt.% in a further aspect, and 0 wt.% in a still further of an ionizable and/or an ionized monomer.

41. A polymer composition according to any previous claim where said polymer is prepared from a monomer composition containing less than 5 wt.% in one aspect, less than 3 wt.% in another aspect, less than 1 wt.% in a further aspect, less than 0.5 wt.% in a still further aspect, less than 0.1 wt.% in an additional aspect, less than 0.05 wt.% in a further aspect, and 0 wt.% in a still further of acrylic acid, methacrylic acid and mixtures thereof.

42. A yield stress fluid composition comprising:

(A) water;

(B) about 0.1 to about 5 wt.% of at least one nonionic amphiphilic polymer according to any of claims 1 to 38; and

(C) from about 1 to about 70 wt% based on the total weight of the yield stress fluid of at least one surfactant.

43. 40. A composition according to claim 42 39 wherein the concentration of said polymer ranges from about 0.5 to about 3 wt.%.

44. The yield stress composition of any of claims 42 or 43 wherein the at least one surfactant is selected from an anionic, cationic, amphoteric, nonionic, or mixtures thereof.

45. A composition according to any of claims 42 to 44 wherein the at least one surfactant is selected from an anionic surfactant.

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46. A composition according to any of claims 42 to 45 wherein the at least one surfactant is selected from an anionic surfactant and an amphoteric surfactant.

47. A composition according to any of claims 42 to 46 wherein the at least one anionic surfactant is ethoxylated.

48. A composition according to any of claims 39 to 44 wherein the at least one anionic surfactant contains an average of 1 to 3 moles of ethoxylation.

49. A composition according to any of claims 42 to 48 wherein the at least one anionic surfactant contains an average of 1 to 2 moles of ethoxylation.

50. A composition according to any of claims 42 to 49 wherein the at least one anionic surfactant is selected from sodium dodecyl sulfate, sodium lauryl sulfate, sodium laureth sulfate, or mixtures thereof.

51. A composition according to any of claims 42 to 50 wherein the at least one amphoteric surfactant is cocamidopropyl betaine.

52. A composition according to any of claims 42 to 51 wherein the at least polymer and the at least one surfactant are substantially free of ethylene oxide moieties.

53. A composition according to any of claims 42 to 52 wherein the concentration of surfactant is less than 25 wt. % (active), based on the weight of the yield stress fluid.

54. A composition according to any of claims 42 to 53 wherein the concentration of surfactant ranges from about 6 to about 20 wt. % (active material), based on the weight of the total composition.

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55. A composition according to any of claims 30 to 54 wherein the ratio of anionic surfactant to amphoteric surfactant (active material) is 10:1 to about 2:1 in one aspect, and 9:1, 8:1, 7:1 6:1, 5:1, 4.5:1, 4:1, or 3:1 in another aspect.

56. A composition according to any of claims 30 to 55 wherein the amount of polymer solids ranges from about 1 to about 3 wt.%, based on the weight of the total composition.

57. A composition according to any of claims 42 to 56 wherein said yield stress of said yield stress fluid is at least 1 mPa.

58. A composition according to any of claims 42 to 57 wherein said yield stress of said yield stress fluid is at least 0.5 Pa.

59. A composition according to any of claims 42 to 58 wherein said yield stress of said yield stress fluid is at least 1 Pa.

60. A composition according to any of claims 42 to 59 wherein said yield stress is measured at a fixed frequency selected from a frequency range of 1Hz to 0.001Hz.

61. A composition according to any of claims 42 to 60 wherein said yield stress fluid is able to suspend beads of a size between 0.5 and 1.5 mm for at least one month at 23°C wherein the difference in specific gravity between the bead material and water is between +/- 0.01 and 0.5.

62. A composition according to any of claims 42 to 61 wherein said composition is able to suspend microcapsules of a size between 0.5 and 300 μm for at least one month at 23°C wherein the difference in specific gravity between the microcapsule beads and water is between +/- 0.2 and 0.5.

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63. A composition according to any of claims 42 to 62 wherein said yield stress is substantially independent of pH in the pH range 2 to 14.
64. A composition according to any of claims 42 to 63 wherein said yield stress is substantially independent of pH in the pH range 3 to 10.
65. A yield stress composition according to any of claims 42 to 64 having a nephelometric turbidity unit (NTU) value of 50 or less.
66. A composition of any of claims 42 to 65 wherein said polymer is in the form of particles that exhibit plateau swelling of at least a factor of 2.5 in linear dimension in the presence of sodium lauryl sulfate and 0.1 wt.% sodium chloride.
67. A composition according to any of claims 42 to 66 wherein the percent optical transmission is at least 10%.
68. A composition according to any of claims 42 to 67 wherein the percent optical transmission is at least 20%.
69. A composition according to any of claims 42 to 68 further comprising mica particles.
70. A composition according to any of claims 42 to 69 that is pearlescent in appearance.
71. A composition according to any of claims 42 to 70 wherein the viscosity is less than 2 Pa·s at a shear rate of 3 reciprocal seconds.
72. A composition according to any of claims 42 to 71 that has a shear thinning index less than 0.5 at shear rates between 0.1 and 1 reciprocal second.

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73. A composition according to any of claims 42 to 72 wherein the elastic modulus is greater than the viscous modulus at oscillatory stress below a critical stress at a fixed frequency.

74. A composition in any of claims 42 to 73 further comprising an electrolyte.

75. A composition according to claim 65 wherein said electrolyte is selected from potassium pyrophosphate, potassium tripolyphosphate, sodium or potassium citrate, calcium chloride and calcium bromide, zinc halides, barium chloride calcium nitrate, potassium chloride, sodium chloride, potassium iodide, sodium bromide, and ammonium bromide, alkali metal or ammonium nitrates, and mixtures thereof.

76. A composition according to claim 65 wherein the amount of the electrolyte ranges from about 0.1 to about 4 wt.%, based on the weight of the total composition.

77. A composition according to any of claims 42 to 76 further comprising a preservative selected from an organic acid and salts thereof.

78. A composition according to claim 77 wherein said organic acid is selected from a carboxylic acid compound represented by the formula: $R^{40}C(O)OH$ and a salt thereof, wherein R^{40} represents hydrogen, a saturated and unsaturated hydrocarbyl group containing 1 to 8 carbon atoms or a C_6 to C_{10} aryl group.

79. A composition according to claim 77 to 78 wherein said organic acid is selected from formic acid, acetic acid, propionic acid, sorbic acid, caprylic acid, and benzoic acid; and salts thereof; and mixtures thereof.

80. A composition according to claim 77 wherein said organic acid is selected from oxalic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, maleic acid, fumaric acid, lactic acid, glyceric acid, tartronic acid malic acid, tartaric acid,

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gluconic acid, citric acid, ascorbic acid, salicylic acid, phthalic acid, mandelic acid, benzoic acid; and salts thereof; and mixtures thereof.

81. A composition according to any of claims 77 to 80 wherein said salt is selected from the alkali metal and ammonium salts of said acids.

82. A composition according to any of claims 42 to 81 further comprising an insoluble material, a particulate material, or combinations thereof.

83. A composition according to claim 82 wherein said particulate material is selected from mica, coated mica, pigments, exfoliants, anti-dandruff agents, clay, swellable clay, laponite, microsponges, cosmetic beads, cosmetic microcapsules, flakes, fragrance microcapsules, fragrance particles, and mixtures thereof.

84. A composition according to any of claims claim 74 to 83 further comprising perfumes, fragrances, fragrance oils, and mixtures thereof.

85. A composition according to claim 82 wherein said particulate material is selected from sand, sintered bauxite, glass balls, ceramic materials, polystyrene beads, or mixtures thereof.

86. A composition according to claim 82 wherein said insoluble material is selected from gas bubbles, liposomes, silicones, or mixtures thereof.

87. A drilling fluid for use in drilling subterranean formations comprising a yield stress fluid according to any of claims 42 to 82 or 85.

88. A hydraulic fracturing fluid for use in fracturing subterranean formations comprising a yield stress fluid according to any of claims 42 to 82 or 85.

89. A hydraulic fracturing fluid according to claim 87 further comprising a proppant.

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90 A method for synergistically enhancing the viscosity and yield stress of a surfactant composition according to any of claims 42 to 89 comprising adding an electrolyte to said composition in an amount ranging from about 0.1 to about 4 wt.%, based on the weight of the total composition.

91. A method according to claim 90 wherein said electrolyte is selected from an inorganic salt.

92. A method according to claim 91 wherein said electrolyte is selected from potassium pyrophosphate, potassium tripolyphosphate, sodium or potassium citrate, calcium chloride and calcium bromide, zinc halides, barium chloride calcium nitrate, potassium chloride, sodium chloride, potassium iodide, sodium bromide, and ammonium bromide, alkali metal or ammonium nitrates, and mixtures thereof.

93. A method for synergistically enhancing the viscosity of a surfactant composition comprising the polymer of any of claims 31 to 42 comprising adding an electrolyte to said composition in an amount ranging from about 0.1 to about 4 wt.%, based on the weight of the total composition.

94. A method of claim 93 wherein said surfactant composition further comprises an organic acid preservative and salts thereof.

95. A method of claim 94 wherein said surfactant composition further comprises a perfume, a fragrance, a fragrance oil, and mixtures thereof.

97. A method of any of claims 93 to 94 wherein said surfactant composition comprises an anionic surfactant, an amphoteric surfactant, and mixtures thereof.

Fig. 1

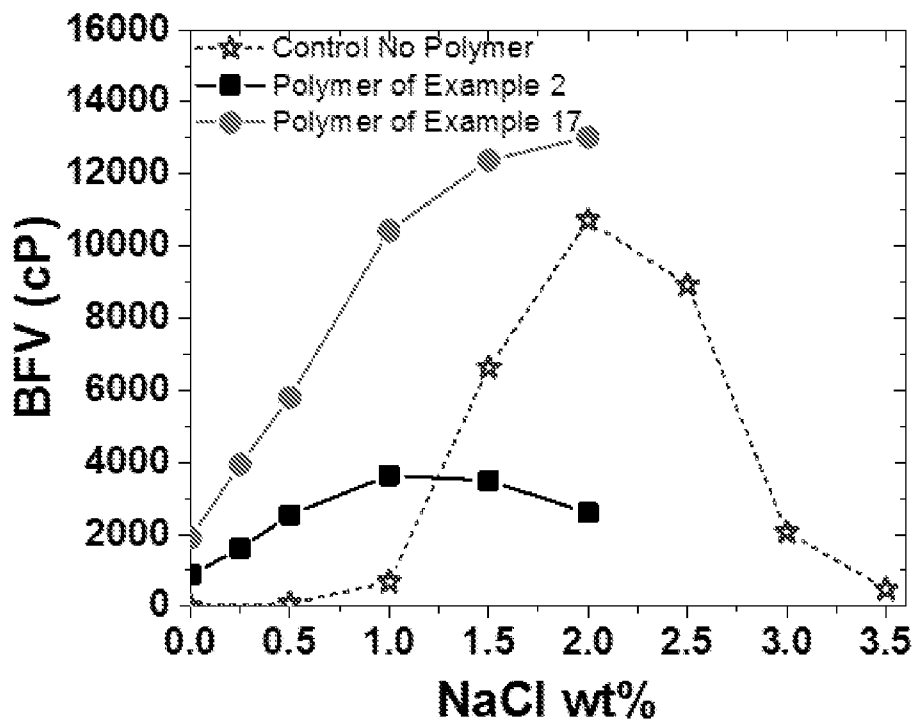


Fig. 2

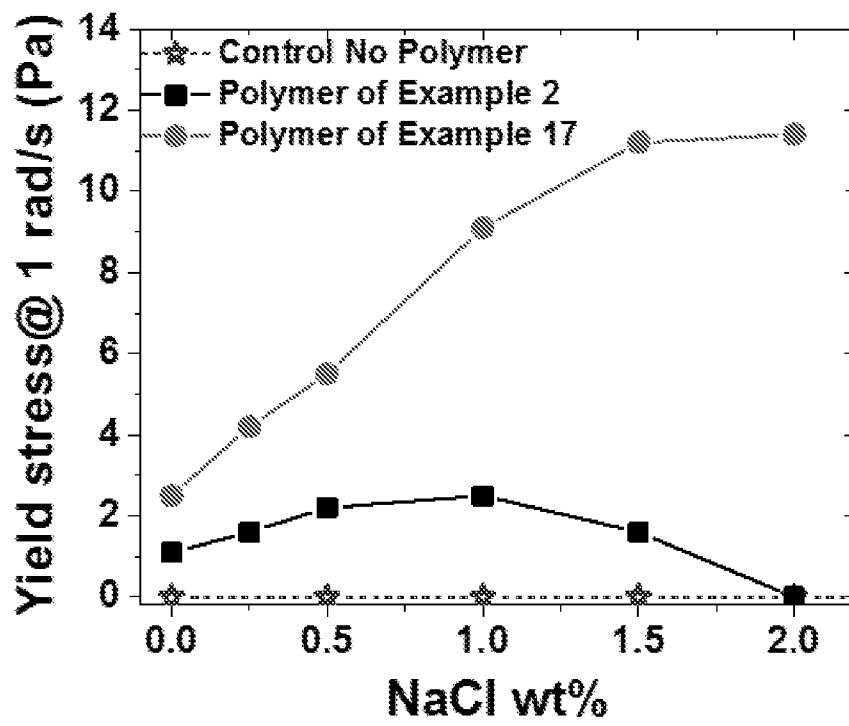


Fig. 3

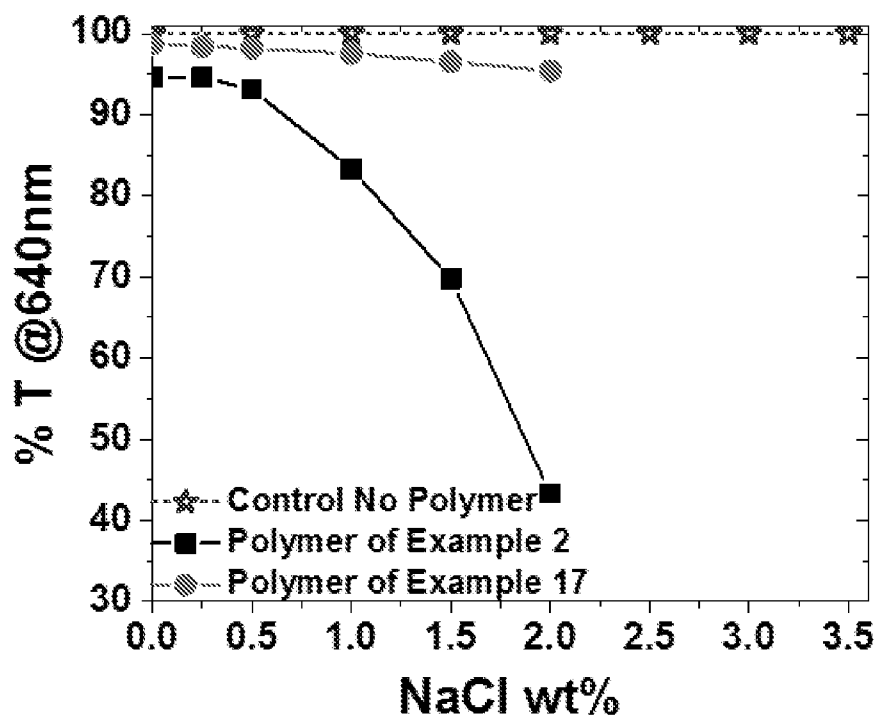
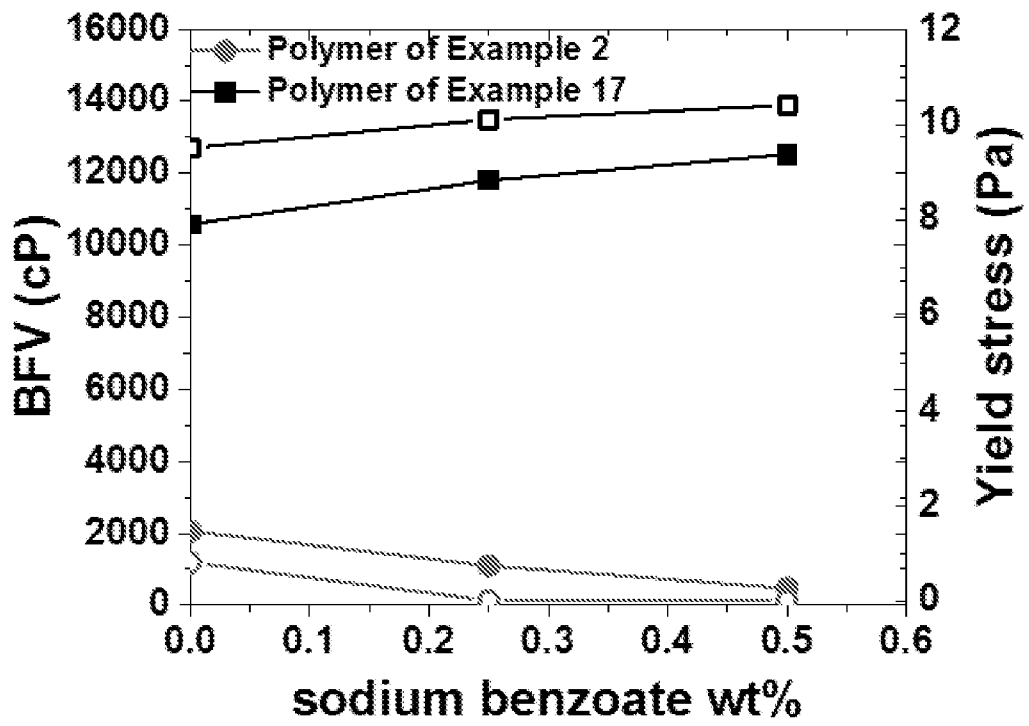


Fig. 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/065495

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F216/12 C08F220/18
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2015/095286 A1 (LUBRIZOL ADVANCED MAT INC [US]) 25 June 2015 (2015-06-25) claims 1-80 examples 1-33 paragraph [0084] paragraph [0114] paragraph [0116]	1-89
X	WO 2013/059765 A1 (ETHOX CHEMICALS LLC [US]) 25 April 2013 (2013-04-25) example 1 table 1 run 14-19; table 2	1-6,23, 28,29, 39-41
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 22 March 2016	Date of mailing of the international search report 31/03/2016
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fischer, Brigitte
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/065495

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/040178 A1 (LUBRIZOL ADVANCED MAT INC [US]; YANG WEI-YEIH [US]; CHARI KRISHNAN [US) 21 March 2013 (2013-03-21) claims 1,12	42
A	----- WO 2014/164092 A1 (LUBRIZOL ADVANCED MAT INC [US]) 9 October 2014 (2014-10-09) the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2015/065495

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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