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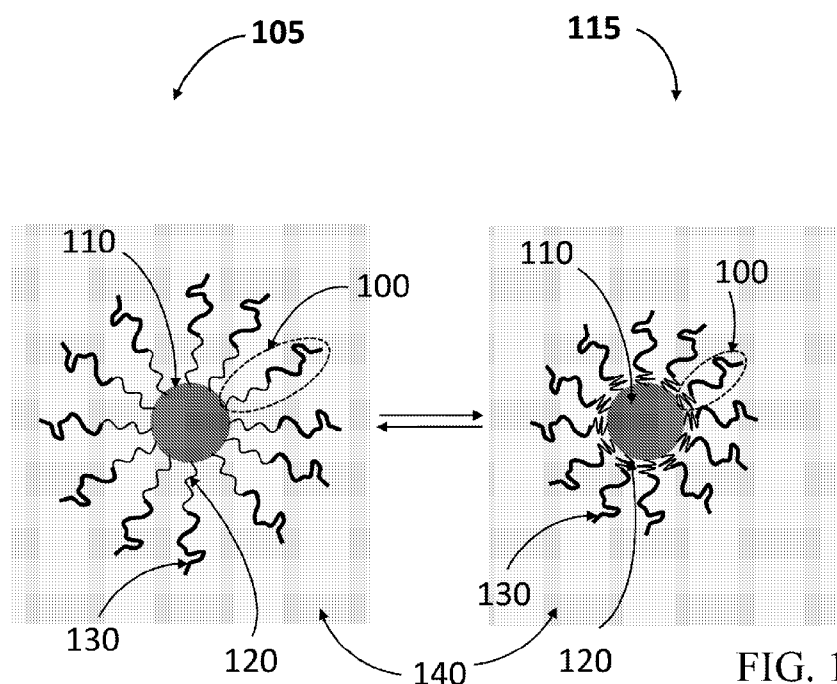


FIG. 1

(57) Abstract: Stimuli-responsive materials and associated compositions and methods are provided. In some embodiments, the material comprises polymers (e.g., block copolymers) attached to a particle (e.g., nanoparticle), wherein the polymers comprise a first portion and a second portion, wherein the first portion has a lower critical solution temperature in a first phase. In some embodiments, the second portion has an upper critical solution temperature in a first phase. In some cases, the material is used in a composition to stabilize an emulsion at a first temperature and destabilize the emulsion at a second temperature, wherein the first temperature exceeds the second temperature. In some embodiments, the material is soluble within a portion of the composition at the second temperature. In some embodiments, temperature-responsive emulsions comprising stimuli-responsive materials are provided for use in, e.g., enhanced oil recovery from oil and/or gas wells, catalysis (e.g. liquid phase heterogeneous catalysis), and emulsion polymerization.

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STIMULI-RESPONSIVE MATERIALS AND RELATED COMPOSITIONS AND METHODS

RELATED APPLICATIONS

5 This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Serial No. 62/510,250, filed May 23, 2017, and entitled “Stimuli-Responsive Materials and Related Compositions and Methods,” which is incorporated herein by reference in its entirety for all purposes.

FIELD OF INVENTION

10 Stimuli-responsive materials and related compositions, systems, and methods are generally described.

BACKGROUND

15 Stimuli-responsive (e.g., temperature-responsive) materials and related compositions (e.g., emulsions) have great potential utility in diverse fields such as enhanced oil recovery, catalysis (e.g. liquid phase heterogeneous catalysis), and emulsion polymerization. The utilization of temperature as a stimulus is of particular interest, for example, because temperature can be cycled readily as a practical matter, and temperature changes need not
20 result in changes to the material composition of a system. Previous efforts to develop stimuli-responsive emulsions using temperature as a stimulus have led to responsive systems that enable the formation of stable emulsions at room temperature, which can subsequently be triggered to destabilize with an increase in temperature. The development of a thermo-responsive system that exhibits the opposite response however, one that can be triggered to
25 form stable emulsions at elevated temperatures and subsequently be induced to phase separate into a destabilized state at lower temperatures, has so far been lacking.

 For example, it has been a challenge in the field of oil recovery to improve the de-emulsification of the oil-in-aqueous emulsions that result from utilizing materials (e.g., surfactants) to mobilize oil from an oil and/or gas well. The de-emulsification process is
30 often cost- and energy-intensive, requiring the use of de-emulsifiers and/or high temperatures to accomplish the macroscale phase separation of the oil from the aqueous phase.

 Accordingly, improvements in performance of such materials are needed.

SUMMARY

Stimuli-responsive materials and related compositions, components, systems, and methods associated therewith are provided.

5 In one set of embodiments, a material is provided. In some embodiments, the material comprises a particle and a plurality of polymers attached to the particle, wherein each of the plurality of polymers comprises a first portion having a lower critical solution temperature in a first phase and a second portion having an upper critical solution temperature in the first phase.

10 In another set of embodiments, an emulsion is provided. In some embodiments, the emulsion comprises a first phase, a second phase, and a stabilizing agent comprising a polymer attached to a particle, wherein the critical micelle temperature of the emulsion is greater than or equal to about 32 degrees Celsius.

15 In one set of embodiments, a method is provided. In one embodiment, the method comprises destabilizing an emulsion by changing the temperature of the emulsion from a first temperature to a second temperature, wherein the first temperature is greater than the second temperature.

In another embodiment, the method comprises exposing an emulsion to a first temperature to destabilize the emulsion, wherein the critical micelle temperature of the emulsion is greater than the first temperature.

20 In some embodiments, a method of enhanced oil recovery is provided. In one embodiment, the method of enhanced oil recovery comprises delivering a first composition comprising a material comprising a particle and a plurality of polymers attached to the particle, wherein each of the plurality of polymers comprises a first portion having a lower critical solution temperature in a first phase and a second portion having an upper critical solution temperature in the first phase, into an oil and/or gas well; and withdrawing a second composition comprising an aqueous phase, an oil phase, and the material from the oil and/or gas well.

25 In another set of embodiments, methods of making one or more of the embodiments are described herein. In still another set of embodiments, methods of using one or more of the embodiments are described herein.

Other advantages and novel features of the present embodiments will become apparent from the following detailed description of various non-limiting embodiments of the present disclosure when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting

and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

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BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present disclosure will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the disclosure shown where illustration is not necessary to allow those of ordinary skill in the art to understand the disclosure. In the figures:

FIG. 1 is a schematic diagram of non-limiting illustrative configurations 105 and 115 of a stimuli-responsive material comprising a first component 100 and a second component 110, according to certain embodiments;

FIG. 2 is a schematic diagram of non-limiting illustrative configurations 205 and 215 of a composition comprising a first phase 200, a second phase 210, and a material as in FIG. 1, according to one set of embodiments;

FIG. 3 is a schematic diagram of block copolymer-functionalized particles with reverse temperature-responsive oil-aqueous interface activity, according to certain embodiments;

FIG. 4 is a set of bright-field microscopy images of emulsions stabilized by block copolymer-functionalized silica nanoparticles, according to one set of embodiments;

FIG. 5 is a plot of separation time versus electrolyte concentration (fraction of API Brine) for various concentrations of block copolymer-functionalized silica nanoparticles in hexadecane-in-aqueous emulsions comprising the nanoparticles, according to certain embodiments;

FIG. 6A is a plot of normalized transmittance (%) versus cycle number for various concentrations of block copolymer-functionalized silica nanoparticles in hexadecane-in-aqueous emulsions comprising the nanoparticles, with electrolyte concentration fixed at API Brine conditions, according to one set of embodiments; and

FIG. 6B is a plot of normalized transmittance (%) versus cycle number for various electrolyte concentrations in hexadecane-in-aqueous emulsions comprising block copolymer-

functionalized silica nanoparticles, with the concentration of the nanoparticles fixed at 0.4 wt% particles, according to certain embodiments.

DETAILED DESCRIPTION

Stimuli-responsive materials and related compositions, systems, and methods are provided. In some embodiments, a material may comprise a first component (e.g., polymer) attached to a second component (e.g., particle). The first component may have one or more properties (e.g., solvation) that can be altered (e.g., reversibly) by exposure to certain conditions (e.g., temperatures). In such cases, the first component may impart stimuli responsivity to the material. The second component may stabilize and allow the material to assemble into desirable configurations (e.g., in the presence of a first phase and a second phase, assemble into e.g., micelles or emulsion droplets) under certain conditions. In some embodiments, the stimuli-responsive materials, described herein, may be used in the presence of a first phase and a second phase to form a stimuli-responsive emulsion. For example, the stimuli-responsive materials may be used to form an emulsion that is stable at relatively high temperatures (e.g., greater than or equal to about 50 degrees Celsius) and unstable at relatively low temperatures (e.g., less than or equal to about 30 degrees Celsius). The stimuli-responsive materials, described herein, may be used for a wide variety of applications, including enhanced oil recovery from oil and/or gas wells, catalysis (e.g. liquid phase heterogeneous catalysis), and emulsion polymerization.

As described herein, in some embodiments, a stimuli-responsive material may comprise a first component 100 and a second component 110 (see e.g., FIG. 1). In some embodiments, the first component may be a polymer and the second component may be a particle, as illustrated in FIG. 1. The polymer may be stimuli-responsive. For instance, the polymer may be temperature responsive. In certain embodiments, the first component (e.g., polymer) may have a first portion 120 and a second portion 130. In some embodiments, the polymer may be attached to the particle (e.g., covalently) by the first portion. In some embodiments, the solubility of the first portion in the first phase may decrease as the temperature increases. The first portion may have a lower critical solution temperature (LCST) with respect to a first phase 140 (e.g., a first fluid) to which the material is exposed. Above the lower critical solution temperature of the first portion in the first phase, the first portion may phase separate from the first phase, and the material may take on, as a non-limiting example, configuration 115. Below the lower critical solution temperature, the material may take on, as a non-limiting example, configuration 105. In some embodiments,

the solubility of the second portion may increase as the temperature increases. The second portion may have an upper critical solution temperature with respect to the first phase.

As described herein, in some embodiments, the material (e.g., 140 in FIG. 1) may be a component (e.g., a stabilizing agent) in a composition comprising a first phase 200 (e.g., a first fluid) and a second phase 210 (e.g., a second fluid; see e.g., FIG. 2). In some
5 embodiments, first phase 200 may be immiscible or otherwise have a relatively low solubility in second phase 210. Second phase 210 may be immiscible or otherwise have a relatively low solubility in first phase 200. In some such cases, first phase 200 and second phase 210 may tend to phase separate from one another under certain condition as shown in 205. In
10 some embodiments, material 212 may allow the first and second phases to form a stable emulsion under certain conditions (e.g., application of a stimulus). For instance, in some embodiments, the composition may take on one of the two configurations 205 (e.g., destabilized emulsion) and 215 (e.g., stable emulsion) as shown in FIG. 2.

In some embodiments, material 212 may allow a stable emulsion to form at relatively
15 high temperatures (e.g., greater than or equal to about 32 degrees Celsius). In some such embodiments, the composition may have a critical micelle temperature (e.g., a composition comprising the first phase, the second phase, and the material may have a critical micelle temperature). Above the critical micelle temperature, the composition may form, for example, a stabilized emulsion (e.g., an emulsion in a stabilized state), in which the second
20 phase is suspended in discrete droplets 220 within the continuous phase. The continuous phase may comprise the first phase and/or the material may be disposed at the interface between the first phase and the second phase. In some such embodiments, the composition may take on, as a non-limiting example, configuration 215. The term “critical micelle temperature” has its ordinary meaning in the art and may refer to the temperature at and
25 above which stable (e.g., persistent) micelles and emulsion droplets form for certain mole ratios of components in the composition. Below the critical micelle temperature, the composition may form, for example, a destabilized emulsion (e.g., an emulsion in a destabilized state), in which phase separation of the second phase and the first phase occurs to form two separate continuous phases. In some such embodiments, the composition may take
30 on, as a non-limiting example, configuration 205. In some embodiments in which the emulsion is destabilized (e.g., phase separation of the first phase and the second phase has occurred) the material is soluble in at least one of the first phase and the second phase (e.g., in the first phase, as shown in e.g. configuration 205). In some embodiments (e.g., in which the composition has a critical micelle temperature) the composition may be cycled between a

stable emulsion (e.g., 215) and a destabilized emulsion (e.g., 205) any suitable number of times as indicated by the arrows in FIG. 2.

In some embodiments, material 212 may be configured to facilitate the transition between the different configurations (e.g., 205, 215) of the composition. For example, material 212 may be configured to facilitate the transition from a stable emulsion (e.g., 215) to a destabilized emulsion (e.g., 205) and vice versa. In some embodiments, material 212 (e.g., one or more properties of the material) may be configured to allow for a relatively facile and/or rapid transition between different configurations (e.g., 205, 215). For instance, the elastic modulus of the second component (e.g., particle), the lower critical solution temperature of the first portion of the first component (e.g., polymer), the upper critical solution temperature of the second portion of the first component, the size of the first component, and/or the size of the second component, amongst other properties, may be configured to facilitate the transition between the different configurations (e.g., 205, 215) of the composition.

The term “phase” has its ordinary meaning in the art and may refer to a form of matter having relatively homogeneous chemical and physical properties (e.g., solid, liquid, gas). In some embodiments, a phase may be a fluid (e.g., a liquid, a gas). In some embodiments, a phase may be a solid. In some embodiments, a first phase may be a first fluid. In some embodiments, a second phase may be a second fluid.

In some embodiments, the elastic modulus of the second component (e.g., particle) of the material may be configured to facilitate the transition between different configurations (e.g., 205, 215). For instance, the elastic modulus of the second component (e.g., particle) of the material may be configured to allow the transition to occur over a relatively short period of time (e.g., less than or equal to about 100 minutes). For example, in some embodiments, the elastic modulus of the particle may be relatively large (e.g., greater than or equal to 1 GPa). In some such embodiments, configuration 215 may be rapidly destabilized to configuration 205 (e.g., in less than or equal to 100 minutes) once below the critical micelle temperature of the composition. In certain embodiments, the elastic modulus of the second component (e.g., particle) may dictate, at least in part, the configuration of the composition in certain conditions. Without being bound by theory, it is believed that, in some embodiments, the higher rate of phase separation for an emulsion comprising stimuli-responsive materials including particles having a relatively high elastic modulus (e.g., relatively stiff particles) may be caused by more steric stabilization, and a lesser extent of inter-particle polymer entanglement at the interface of an emulsion droplet (e.g., 220 in FIG. 2), compared to a

substantially similar emulsion that comprises stimuli-responsive materials including particles having a relatively low elastic modulus (e.g., relatively soft particles) instead of particles having a relatively high elastic modulus (e.g., relatively stiff particles).

In some embodiments, the lower critical solution temperature of the first portion of the first component in the a phase (e.g., first phase) may be configured to facilitate the transition between different configurations (e.g., 205, 215). For instance, the lower critical solution temperature of the first portion may be configured to allow the transition to occur over a relatively short period of time (e.g., less than or equal to about 100 minutes) and/or at certain temperatures. For instance, in some embodiments, the lower critical solution temperature of the first portion in the first phase may be high relative to a certain temperature (e.g., 25 degrees Celsius, room temperature, 20 degrees Celsius) such that configuration 215 may be rapidly destabilized to configuration 205 (e.g., in less than or equal to 100 minutes) below the critical micelle temperature of the composition. For example, the lower critical solution temperature of the first portion may be configured to be high relative to an ambient temperature in a process (e.g., above ground oil recovery, heterogeneous catalysis). The ambient temperature (e.g., 25 degrees Celsius, room temperature, 20 degrees Celsius) may be less than the critical micelle temperature, such that exposure to the ambient temperature of the process results in rapid destabilization of the emulsion. Without being bound by theory, it is believed that in some embodiments, the relatively high rate of phase separation for an emulsion comprising stimuli-responsive materials with a high lower critical solution temperature (e.g., greater than or equal to about 32 degrees Celsius) of the first portion in the first phase relative to a certain temperature may be caused by a higher driving force for solvating the first portion with the first phase 200, than in a substantially similar emulsion comprising stimuli-responsive materials with a lower lower critical solution temperature of the first portion in the first phase. Conversely, as another example, the lower critical solution temperature of the first portion may be configured to be low relative to an ambient temperature in a process (e.g., underground oil recovery). The ambient temperature (e.g., 65 degrees Celsius, greater than or equal to about 32 degrees Celsius) may be greater than the critical micelle temperature, such that exposure to the ambient temperature of the process results in rapid formation of a stable emulsion. In certain embodiments, the lower critical solution temperature of the first portion of the first component (e.g., polymer) in the first phase may contribute to the configuration of the composition in certain conditions.

In some embodiments, the size of the first component (e.g., polymer) may be configured to facilitate the transition between different configurations (e.g., 205, 215). For

instance, the size (e.g., length) of the first component may be configured to allow the transition to occur over a relatively short period of time (e.g., less than or equal to about 100 minutes). For example, in some embodiments, the size (e.g., length) of the polymer may be relatively small (e.g., short). In some such embodiments, configuration 215 may be rapidly destabilized to configuration 205 (e.g., in less than or equal to 100 minutes) below the critical micelle temperature of the composition. In certain embodiments, the size of the first component (e.g., polymer) may contribute to, at least in part, the configuration of the composition in certain conditions. Without being bound by theory, it is believed that in some embodiments, the relatively high rate of phase separation for an emulsion comprising stimuli-responsive materials with relatively small (e.g., short) polymers may be caused by a lesser extent of inter-particle polymer entanglements, at the interface of an emulsion droplet (e.g., 220), compared to a substantially similar emulsion comprising stimuli-responsive materials with larger (e.g., longer) polymers.

In some embodiments, the size of the second component (e.g., particle) may be configured to facilitate the transition between different configurations (e.g., 205, 215). For instance, the size (e.g., largest cross-sectional dimension) of the second component may be configured to allow the transition to occur over a relatively short period of time (e.g., less than or equal to about 100 minutes). In certain embodiments, the size of the second component (e.g., particle) may contribute to, at least in part, the configuration of the composition in certain conditions. For example, in some embodiments, the size (e.g., largest cross-sectional dimension) of the particle may be relatively small. In some such embodiments, configuration 215 may be rapidly destabilized to configuration 205 (e.g., in less than or equal to 100 minutes) below the critical micelle temperature of the composition. Without being bound by theory, it is believed that in some embodiments the relatively high rate of phase separation for an emulsion comprising stimuli-responsive materials with relatively small particles may be caused by weaker adsorption of relatively small particles, at the interface of an emulsion droplet 220, compared to larger particles in a substantially similar emulsion.

As noted above, in some embodiments, the stimuli-responsive material comprises polymers (e.g., block copolymers) attached to a particle (e.g., nanoparticle). The polymers may comprise a first portion and a second portion. In some embodiments, the first portion has a lower critical solution temperature in a first phase (e.g., a first fluid). In some embodiments, the second portion has an upper critical solution temperature in a first phase (e.g., the first phase in which the first portion has a lower critical solution temperature). In

some cases, the stimuli-responsive material may be used in a composition, e.g., as a stabilizing agent. In some such embodiments, the composition may comprise a first phase, a second phase, and the stabilizing agent. The stabilizing agent may stabilize an emulsion at a first temperature and/or allow for destabilization of the emulsion at a second temperature. In some such cases, the first temperature is greater than the second temperature. In some embodiments, the stimuli-responsive material is soluble within at least a portion of the composition at the second temperature. In some embodiments, temperature-responsive emulsions comprising the stimuli-responsive materials are provided for use in, for example, enhanced oil recovery from oil and/or gas wells, catalysis (e.g. liquid phase heterogeneous catalysis), and emulsion polymerization as described in more detail below.

A stimuli-responsive material generally comprises a particle and a plurality of polymers attached to the particle. In some embodiments, at least some (e.g., each) of the plurality of polymers may be covalently attached to the particle (e.g., by siloxane conjugation). In some embodiments, at least some (e.g., each) of the plurality of polymers may be covalently attached to the particle by means of a spacer (e.g., a polyethylene glycol spacer). In some embodiments, at least some of the plurality of polymers may be non-covalently attached to the particle (e.g., by electrostatic interactions, by hydrogen bonding interactions). In some embodiments, the plurality of polymers have been attached to the particle by means of grafting at least some (e.g., each) of the plurality of polymers to the particle, for example by siloxane conjugation. In other embodiments, the plurality of polymers have been attached to the particle by means of grafting at least some of the plurality of polymers from the particle, for example by surface-initiated atom transfer radical polymerization (ATRP) to grow polymer chains from the particle surface.

In some embodiments, at least some (e.g., each) of the plurality of polymers (e.g., copolymers) attached to the particle comprise a first portion and a second portion. In some embodiments, the first portion has a lower critical solution temperature in a first phase (e.g., a first fluid). The term “lower critical solution temperature” has its ordinary meaning in the art and may refer to the critical temperature below which the components of a composition (e.g., the first portion and a first phase to which the first portion is exposed) are miscible for certain mole ratios (e.g., all mole ratios) of components. The lower critical solution temperature may refer to the critical temperature below which a mixture (e.g., a composition comprising two or more components) is miscible. Upper and lower critical solution temperatures are further described in “Definition of Terms Related to Polymer Blends, Composites, and Multiphase Polymeric Materials,” Pure Appl. Chem., Vol. 76, No. 11, pp. 1985–2007, 2004. In some

embodiments, the lower critical solution temperature is the temperature above which the first portion of a polymer phase separates from an aqueous phase (e.g., water, brine, API Brine) for certain mole ratios of the first portion to the aqueous phase. In other embodiments, the lower critical solution temperature is the temperature above which the first portion of a polymer phase separates from a non-aqueous phase (e.g., cyclohexane, hexadecane, acetonitrile, n-hexane, mineral oil or a fraction of a mineral oil, fluorinated oils, ionic liquids) for certain mole ratios of the first portion to the non-aqueous phase. In some embodiments, the second portion has an upper critical solution temperature in a first phase (e.g., the first phase in which the first portion has a lower critical solution temperature).

The term “upper critical solution temperature” has its ordinary meaning in the art and may refer to the critical temperature above which the components of a composition (e.g., the second portion and a first phase to which the second portion is exposed) are miscible for all mole ratios of components. The upper critical solution temperature may refer to the critical temperature above which a mixture (e.g., a composition comprising two or more components) is miscible. In some embodiments, the upper critical solution temperature is the temperature below which the second portion of the polymer phase separates from an aqueous phase for certain mole ratios of the second portion to the aqueous phase. In other embodiments, the upper critical solution temperature is the temperature below which the second portion of the polymer phase separates from a non-aqueous phase for certain mole ratios of the second portion to the non-aqueous phase.

The first portion, in some embodiments, has a lower critical solution temperature in a first phase (e.g., a first fluid) of greater than or equal to about 32 degrees Celsius, greater than or equal to about 34 degrees Celsius, greater than or equal to about 37 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 42 degrees Celsius, greater than or equal to about 45 degrees Celsius, or greater than or equal to about 48 degrees Celsius. In some embodiments, the first portion has a lower critical solution temperature in a first phase (e.g., a first fluid) of less than or equal to about 50 degrees Celsius, less than or equal to about 48 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 42 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 37 degrees Celsius, or less than or equal to about 34 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 32 degrees Celsius and less than or equal to about 50 degrees Celsius, greater than or equal to about 40 degrees Celsius and less than or equal to about 44 degrees Celsius). In some cases, the first portion has a lower critical solution temperature in a first

phase (e.g., a first fluid) of about 42 degrees Celsius. In some embodiments, the lower critical solution temperature may be determined by light scattering. For instance, when the polymer is not attached to the particle, the lower critical solution temperature of the first portion in the first phase may be measured by dynamic light scattering, to determine the temperature at and above which micelles (e.g., micellar aggregates) form from the polymer. In some embodiments, the micelles formed from the polymer (unattached to a particle) as measured by dynamic light scattering may be for example greater than or equal to about 15 nm and less than or equal to about 40 nm in solvated (e.g., hydrodynamic) diameter.

The second portion, in some embodiments, has an upper critical solution temperature in a first phase (e.g., a first fluid) of less than or equal to about 20 degrees Celsius, less than or equal to about 18 degrees Celsius, less than or equal to about 16 degrees Celsius, less than or equal to about 14 degrees Celsius, less than or equal to about 12 degrees Celsius, less than or equal to about 10 degrees Celsius, less than or equal to about 8 degrees Celsius, or less than or equal to about 6 degrees Celsius. In some embodiments, the second portion has an upper critical solution temperature in a first phase (e.g., a first fluid) of greater than or equal to about 4 degrees Celsius, greater than or equal to about 6 degrees Celsius, greater than or equal to about 8 degrees Celsius, greater than or equal to about 10 degrees Celsius, greater than or equal to about 12 degrees Celsius, greater than or equal to about 14 degrees Celsius, greater than or equal to about 16 degrees Celsius, or greater than or equal to about 18 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 4 degrees Celsius and less than or equal to about 20 degrees Celsius, greater than or equal to about 14 degrees Celsius and less than or equal to about 18 degrees Celsius). In some cases, the second portion has an upper critical solution temperature in a first phase (e.g., a first fluid) of about 16 degrees Celsius. In some embodiments, the upper critical solution temperature may be determined by light scattering. For instance, when the polymer is not attached to the particle, the upper critical solution temperature of the second portion in the first phase may be measured by dynamic light scattering, to determine the temperature at and below which micelles (e.g., micellar aggregates) form from the polymer. In some embodiments, the micelles formed from the polymer (unattached to a particle) may be greater than or equal to about 15 nm and less than or equal to about 40 nm in solvated (e.g., hydrodynamic) diameter.

In some embodiments, the micelles formed from the polymer have a solvated (e.g., hydrodynamic) diameter in the first phase above the lower critical solution temperature and/or below the upper critical solution temperature of greater than or equal to about 10 nm,

greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 40 nm, greater than or equal to about 45 nm, greater than or equal to about 50 nm, greater than or equal to about 60 nm, greater than or equal to about 160 nm, or greater than or equal to about 200 nm. In some embodiments, the micelles formed from at least some (e.g., each) of the plurality of polymers have a solvated (e.g., hydrodynamic) diameter of less than or equal to about 300 nm, less than or equal to about 200 nm, less than or equal to about 160 nm, less than or equal to about 60 nm, less than or equal to about 40 nm, less than or equal to about 35 nm, less than or equal to about 30 nm, less than or equal to about 25 nm, less than or equal to about 20 nm, or less than or equal to about 15 nm in the first phase above the lower critical solution temperature and/or below the upper critical solution temperature. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 10 nm and less than or equal to about 300 nm, greater than or equal to about 15 nm and less than or equal to about 40 nm). The solvated (e.g., hydrodynamic) diameter of micelles formed from the polymer may be determined for example by dynamic light scattering. Methods of dynamic light scattering will be known to those of skill in the art.

Any suitable polymer (e.g., copolymer) having the properties described herein may be used. Non-limiting examples of suitable polymers include poly(N-alkyl methacrylamide), poly(N-alkyl acrylamide), polysilane, poly(ethylene glycol methacrylate), poly(2-(dimethylamino)ethyl methacrylate), hydroxypropylcellulose, poly(vinylcaprolactone), polysiloxane, and poly(vinyl methyl ether), and combinations thereof. In some embodiments, the first portion comprises a poly(N-alkyl methacrylamide). A non-limiting example of a suitable poly(N-alkyl methacrylamide) is poly(N-isopropyl methacrylamide). In some embodiments, the first portion comprises a poly(N-alkyl acrylamide). A non-limiting example of a suitable poly(N-alkyl acrylamide) is poly(N-isopropyl acrylamide). In some embodiments, the first portion comprises a polysilane. A non-limiting example of a suitable polysilane is poly(gamma-(trimethoxysilyl) propyl methacrylate). In some embodiments, the first portion comprises poly(ethylene glycol methacrylate). In some embodiments, the first portion comprises poly(2-(dimethylamino)ethyl methacrylate). In some embodiments, the first portion comprises at least two sub-portions. As a non-limiting example, the first portion may comprise poly(N-isopropyl methacrylamide) and poly(gamma-(trimethoxysilyl) propyl methacrylate). Other non-limiting examples of suitable polymer portions or sub-portions

having a lower critical solution temperature in aqueous solution include hydroxypropylcellulose, poly(vinylcaprolactone), and poly(vinyl methyl ether).

As used herein, “alkyl” refers to a radical of a straight-chain or branched saturated hydrocarbon group having from 1 to 10 carbon atoms (“C₁₋₁₀ alkyl”). In some embodiments, an alkyl group has 1 to 9 carbon atoms (“C₁₋₉ alkyl”). In some embodiments, an alkyl group has 1 to 8 carbon atoms (“C₁₋₈ alkyl”). In some embodiments, an alkyl group has 1 to 7 carbon atoms (“C₁₋₇ alkyl”). In some embodiments, an alkyl group has 1 to 6 carbon atoms (“C₁₋₆ alkyl”). In some embodiments, an alkyl group has 1 to 5 carbon atoms (“C₁₋₅ alkyl”). In some embodiments, an alkyl group has 1 to 4 carbon atoms (“C₁₋₄ alkyl”). In some embodiments, an alkyl group has 1 to 3 carbon atoms (“C₁₋₃ alkyl”). In some embodiments, an alkyl group has 1 to 2 carbon atoms (“C₁₋₂ alkyl”). In some embodiments, an alkyl group has 1 carbon atom (“C₁ alkyl”). In some embodiments, an alkyl group has 2 to 6 carbon atoms (“C₂₋₆ alkyl”). Examples of C₁₋₆ alkyl groups include methyl (C₁), ethyl (C₂), n-propyl (C₃), isopropyl (C₃), n-butyl (C₄), tert-butyl (C₄), sec-butyl (C₄), iso-butyl (C₄), n-pentyl (C₅), 3-pentanyl (C₅), amyl (C₅), neopentyl (C₅), 3-methyl-2-butanyl (C₅), tertiary amyl (C₅), and n-hexyl (C₆). Additional examples of alkyl groups include n-heptyl (C₇), n-octyl (C₈) and the like. Unless otherwise specified, each instance of an alkyl group is independently unsubstituted (an “unsubstituted alkyl”) or substituted (a “substituted alkyl”) with one or more substituents. In certain embodiments, the alkyl group is an unsubstituted C₁₋₁₀ alkyl (*e.g.*, -CH₃). In certain embodiments, the alkyl group is a substituted C₁₋₁₀ alkyl.

In some embodiments, the second portion is zwitterionic. In certain embodiments, the second portion comprises a polyzwitterion. A non-limiting example of a suitable polyzwitterion is poly(sulfobetaine methacrylamide). Other non-limiting examples of polyzwitterions include poly(2-methacryloyloxyethyl phosphorylcholine), n-butyl-substituted choline phosphate polymers, carboxybetaine polymers, phosphobetaine polymers, and sulfobetaine polymers. In some embodiments, the second portion comprises at least two sub-portions. Other non-limiting examples of suitable polymer portions or sub-portions having an upper critical solution temperature in aqueous solution include poly(N-acryloylglycinamide), ureido-functionalized polymers, copolymers of N-vinylimidazole and 1-vinyl-2-(hydroxymethyl)imidazole, and copolymers of acrylamide and acrylonitrile.

In some embodiments, at least some (*e.g.*, each) of the plurality of polymers attached to the particle comprise block copolymers. In some embodiments, the block copolymers comprise a first block comprising the first portion and a second block comprising the second portion. In some embodiments, at least some of the block copolymers are attached to the

particle by the first block (e.g., covalently attached, non-covalently attached). As a non-limiting example, the first block may be attached to the particle by siloxane conjugation.

In some embodiments, at least some (e.g., each) of the plurality of polymers attached to the particle comprise random copolymers. In a random copolymer comprising a first portion and a second portion; monomer units of the first portion and monomer units of the second portion are located along the copolymer chain in random order. In some embodiments, at least some (e.g., each) of the random copolymers are attached to the particle by the first portion. In some embodiments, at least some (e.g., each) of the plurality of polymers attached to the particle comprise gradient copolymers. In a gradient copolymer comprising a first portion and a second portion, there is a gradual change in the ratio of monomeric units (e.g., ratio of monomeric units of the first portion to monomeric units of the second portion) from one end of the polymer chain to the other, for example such that towards one end of the copolymer chain (e.g., one continuous half of the copolymer chain) is enriched in the first portion and towards the other end of the copolymer chain (e.g., the other continuous half of the copolymer chain) is enriched in the second portion. In some embodiments, at least some (e.g., each) of the gradient copolymers are attached to the particle by the first portion.

In some embodiments, the first portion comprises a polymer or an oligomer. In some embodiments, the second portion comprises a polymer or an oligomer. In some embodiments, the mole ratio of repeat units of the first portion (e.g., a polymer having a lower critical solution temperature in a first phase) to repeat units of the second portion (e.g., a polymer having an upper critical solution temperature in the first phase) is greater than or equal to about 1:5, greater than or equal to about 2:9, greater than or equal to about 1:4, greater than or equal to about 2:7, greater than or equal to about 1:3, or greater than or equal to about 2:5. In some embodiments, the mole ratio of repeat units of the first portion to repeat units of the second portion is less than or equal to about 1:2, less than or equal to about 2:5, less than or equal to about 1:3, less than or equal to about 2:7, less than or equal to about 1:4, or less than or equal to about 2:9. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 1:5 and less than or equal to about 1:2). The mole ratio of repeat units of the first portion to repeat units of the second portion may be determined in some embodiments by nuclear magnetic resonance spectroscopy. Methods of nuclear magnetic resonance spectroscopy will be known to those of skill in the art. In some embodiments, nuclear magnetic resonance spectroscopy may be carried out on the polymer unattached to the particle.

In some embodiments, the plurality of polymers attached to the particle have a number average molecular weight of greater than or equal to about 1000 Da, greater than or equal to about 2000 Da, greater than or equal to about 5000 Da, greater than or equal to about 10,000 Da, greater than or equal to about 15,000 Da, greater than or equal to about 20,000 Da, greater than or equal to about 25,000 Da, greater than or equal to about 50,000 Da, or greater than or equal to about 100,000 Da. In some embodiments, the plurality of polymers attached to the particle have a number average molecular weight of less than or equal to about 500,000 Da, less than or equal to about 100,000 Da, less than or equal to about 50,000 Da, less than or equal to about 25,000 Da, less than or equal to about 20,000 Da, less than or equal to about 15,000 Da, less than or equal to about 10,000 Da, less than or equal to about 5000 Da, or less than or equal to about 2000 Da. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 1000 Da and less than or equal to about 500,000 Da, greater than or equal to about 2000 Da and less than or equal to about 25,000 Da). In embodiments in which the polymer is unattached to the particle, number average molecular weight may be measured for example by gel permeation chromatography coupled with light-scattering detection. Methods of gel permeation chromatography coupled with light-scattering detection will be known to those of skill in the art. In embodiments wherein the polymer is attached to a particle, the number average molecular weight may be determined for example by small angle neutron scattering, and by fitting the scattering data to a hard solid spherical core, hairy particle model. Methods of small angle neutron scattering will be known to those of skill in the art.

In some embodiments, at least some (e.g., each) of the plurality of polymers has a solvated (e.g., hydrodynamic) length in the first phase below the critical micelle temperature, below the lower critical solution temperature of the first portion, and/or above the upper critical solution temperature of the second portion of greater than or equal to about 1 nm, greater than or equal to about 5 nm, greater than or equal to about 10 nm, greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 40 nm, greater than or equal to about 60 nm, greater than or equal to about 160 nm, greater than or equal to about 200 nm, greater than or equal to about 300 nm, or greater than or equal to about 400 nm. In some embodiments, at least some (e.g., each) of the plurality of polymers has a solvated (e.g., hydrodynamic) length of less than or equal to about 500 nm, less than or equal to about 400 nm, less than or equal to about 300 nm, less than or equal to about 200 nm, less than or equal to about 160 nm, less than or equal to about 60 nm,

less than or equal to about 40 nm, less than or equal to about 35 nm, less than or equal to about 30 nm, less than or equal to about 25 nm, less than or equal to about 20 nm, less than or equal to about 15 nm, less than or equal to about 10 nm, or less than or equal to about 5 nm.

Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 1 nm and less than or equal to about 40 nm, greater than or equal to about 10 nm and less than or equal to about 25 nm). In embodiments in which the polymer is attached to a particle, the solvated (e.g., hydrodynamic) length may be determined for example by small angle neutron scattering, and by fitting the scattering data to a hard solid spherical core, hairy particle model. Methods of small angle neutron scattering will be known to those of skill in the art. In embodiments wherein the polymer is unattached to a particle, the solvated (e.g., hydrodynamic) length (e.g., diameter) may be determined for example by dynamic light scattering. Methods of dynamic light scattering will be known to those of skill in the art.

In some embodiments, the material has a solvated (e.g., hydrodynamic) diameter in the first phase below the critical micelle temperature, below the lower critical solution temperature of the first portion, and/or above the upper critical solution temperature of the second portion of greater than or equal to about 10 nm, greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 40 nm, greater than or equal to about 45 nm, greater than or equal to about 50 nm, greater than or equal to about 60 nm, greater than or equal to about 160 nm, greater than or equal to about 200 nm, greater than or equal to about 300 nm, greater than or equal to about 400 nm, greater than or equal to about 500 nm, or greater than or equal to about 600 nm. In some embodiments, at least some (e.g., each) of the plurality of polymers has a solvated (e.g., hydrodynamic) length of less than or equal to about 700 nm, less than or equal to about 600 nm, less than or equal to about 500 nm, less than or equal to about 400 nm, less than or equal to about 300 nm, less than or equal to about 200 nm, less than or equal to about 160 nm, less than or equal to about 60 nm, less than or equal to about 40 nm, less than or equal to about 35 nm, less than or equal to about 30 nm, less than or equal to about 25 nm, less than or equal to about 20 nm, or less than or equal to about 15 nm in the first phase below the critical micelle temperature. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 10 nm and less than or equal to about 700 nm, greater than or equal to about 25 nm and less than or equal to about 40 nm). The solvated (e.g., hydrodynamic) diameter of the material may be determined for example by dynamic light scattering. Methods of dynamic light scattering will be known to those of skill in the art.

In some embodiments, the plurality of polymers have a grafting density on the particle of greater than or equal to about 0.05 chains/nm², greater than or equal to about 0.07 chains/nm², greater than or equal to about 0.08 chains/nm², greater than or equal to about 0.1 chains/nm², greater than or equal to about 0.2 chains/nm², greater than or equal to about 0.3 chains/nm², greater than or equal to about 0.4 chains/nm², greater than or equal to about 0.5 chains/nm², greater than or equal to about 0.6 chains/nm², greater than or equal to about 0.7 chains/nm², greater than or equal to about 0.8 chains/nm², greater than or equal to about 0.9 chains/nm², greater than or equal to about 1.0 chains/nm², greater than or equal to about 1.1 chains/nm², greater than or equal to about 1.2 chains/nm², or greater than or equal to about 1.3 chains/nm². In some embodiments, the plurality of polymers have a grafting density on the particle of less than or equal to about 1.5 chains/nm², less than or equal to about 1.4 chains/nm², less than or equal to about 1.3 chains/nm², less than or equal to about 1.2 chains/nm², less than or equal to about 1.1 chains/nm², less than or equal to about 1.0 chains/nm², less than or equal to about 0.9 chains/nm², less than or equal to about 0.8 chains/nm², less than or equal to about 0.7 chains/nm², less than or equal to about 0.6 chains/nm², less than or equal to about 0.5 chains/nm², less than or equal to about 0.4 chains/nm², less than or equal to about 0.3 chains/nm², less than or equal to about 0.2 chains/nm², less than or equal to about 0.1 chains/nm², less than or equal to about 0.08 chains/nm², or less than or equal to about 0.07 chains/nm². Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0.05 chains/nm² and less than or equal to about 1.5 chains/nm², greater than or equal to about 0.5 chains/nm² and less than or equal to about 1.5 chains/nm²). In embodiments in which the particle is unattached to the polymer in one sample, attached to the polymer in another sample, and the material is soluble in aqueous solution, acid-base titration in aqueous solution may be used to determine the grafting density of polymers on the particle by comparison with acid-base titration in aqueous solution of the particle unattached to the polymer. Methods of acid-base titration will be known to those of skill in the art.

The particle in some embodiments may be a spherical particle. In some embodiments, the particle has a density of greater than or equal to about 1.0 g/cm³, greater than or equal to about 1.01 g/cm³, greater than or equal to about 1.04 g/cm³, greater than or equal to about 1.5 g/cm³, greater than or equal to about 2.0 g/cm³, greater than or equal to about 2.6 g/cm³, greater than or equal to about 2.65 g/cm³, greater than or equal to about 3 g/cm³, greater than or equal to about 4 g/cm³, greater than or equal to about 5.1 g/cm³, greater than or equal to about 5.2 g/cm³, greater than or equal to about 5.24 g/cm³, greater than or equal to about 10

g/cm³, greater than or equal to about 15 g/cm³, greater than or equal to about 19 g/cm³, greater than or equal to about 19.32 g/cm³, or greater than or equal to about 20 g/cm³.

In some embodiments, the particle has an elastic modulus of greater than or equal to about 1 GPa, greater than or equal to about 1.5 GPa, greater than or equal to about 1.9 GPa, greater than or equal to about 2.0 GPa, greater than or equal to about 2.5 GPa, greater than or equal to about 2.9 GPa, greater than or equal to about 3 GPa, greater than or equal to about 3.5 GPa, greater than or equal to about 4 GPa, greater than or equal to about 6 GPa, greater than or equal to about 8 GPa, greater than or equal to about 10 GPa, greater than or equal to about 25 GPa, greater than or equal to about 40 GPa, greater than or equal to about 55 GPa, greater than or equal to about 70 GPa, greater than or equal to about 79 GPa, greater than or equal to about 100 GPa, greater than or equal to about 125 GPa, greater than or equal to about 151 GPa, greater than or equal to about 175 GPa, greater than or equal to about 192 GPa, greater than or equal to about 250 GPa, greater than or equal to about 500 GPa, greater than or equal to about 750 GPa, or greater than or equal to about 1 TPa. The elastic modulus of the particle may be measured by atomic force microscopy (e.g., nanoindentation) on the particle. In embodiments in which the particle is attached to polymer, this may be carried out by first removing the polymer from the particle (e.g., by heating, e.g., by thermogravimetric analysis) and then using atomic force microscopy on the particle that remains. In some embodiments, the particle comprises a stiff material. Non-limiting examples of suitable stiff materials include silica, iron oxide, graphene, magnetite, gold, and polystyrene.

In some embodiments, the particle comprises a material having a contact angle with an aqueous phase of less than or equal to about 45 degrees, less than or equal to about 40 degrees, less than or equal to about 35 degrees, less than or equal to about 30 degrees, less than or equal to about 25 degrees, less than or equal to about 20 degrees, less than or equal to about 15 degrees, less than or equal to about 10 degrees, or less than or equal to about 5 degrees. In some embodiments, the particle comprises a material having a contact angle with a non-aqueous phase of less than or equal to about 45 degrees, less than or equal to about 40 degrees, less than or equal to about 35 degrees, less than or equal to about 30 degrees, less than or equal to about 25 degrees, less than or equal to about 20 degrees, less than or equal to about 15 degrees, less than or equal to about 10 degrees, or less than or equal to about 5 degrees. The contact angle of the same material with water may be measured by a method known to those of skill in the art. The material composition of the particle may be determined by, as a non-limiting example, energy dispersive x-ray spectroscopy.

In some embodiments, the stimuli-responsive materials comprise particles having a largest cross-sectional dimension of less than or equal to about 500 nm, less than or equal to about 400 nm, less than or equal to about 300 nm, less than or equal to about 200 nm, less than or equal to about 160 nm, less than or equal to about 60 nm, less than or equal to about 40 nm, less than or equal to about 35 nm, less than or equal to about 30 nm, less than or equal to about 25 nm, less than or equal to about 20 nm, less than or equal to about 15 nm, less than or equal to about 10 nm, or less than or equal to about 5 nm. In some embodiments, the stimuli-responsive materials comprise particles having a largest cross-sectional dimension of greater than or equal to about 1 nm, greater than or equal to about 5 nm, greater than or equal to about 10 nm, greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 40 nm, greater than or equal to about 60 nm, greater than or equal to about 160 nm, greater than or equal to about 200 nm, greater than or equal to about 300 nm, or greater than or equal to about 400 nm. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 1 nm and less than or equal to about 1 micron, greater than or equal to about 1 nm and less than or equal to about 40 nm, greater than or equal to about 10 nm and less than or equal to about 25 nm). In some cases, the stimuli-responsive materials comprise particles having a largest cross-sectional dimension of about 20 nm. The cross-sectional dimension of the particles may be measured by scanning electron microscopy.

In some embodiments, a stimuli-responsive material comprises a plurality of polymers attached to the particle, wherein the length of at least some of the plurality of polymers (e.g., of each polymer) is of the same order of magnitude as the largest dimension of the particle. In some embodiments, at least some (e.g., each) of the plurality of polymers has a length, relative to the largest cross-sectional dimension of the particle, of greater than or equal to about 0.5 times, greater than or equal to about 0.6 times, greater than or equal to about 0.7 times, greater than or equal to about 0.8 times, greater than or equal to about 0.9 times, greater than or equal to about 1 times, greater than or equal to about 1.1 times, greater than or equal to about 1.2 times, greater than or equal to about 1.3 times, or greater than or equal to about 1.4 times the largest cross-sectional dimension of the particle. In some embodiments, at least some (e.g., each) of the plurality of polymers has a length, relative to the largest cross-sectional dimension of the particle, of less than or equal to about 1.5 times, less than or equal to about 1.4 times, less than or equal to about 1.3 times, less than or equal to about 1.2 times, less than or equal to about 1.1 times, less than or equal to about 1.0 times,

less than or equal to about 0.9 times, less than or equal to about 0.8 times, less than or equal to about 0.7 times, or less than or equal to about 0.6 times the largest cross-sectional dimension of the particle. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0.5 times and less than or equal to about 1.5 times).

5 In some embodiments, at least some (e.g., each) of the plurality of polymers attached to the particle have an overall number average degree of polymerization of less than or equal to about 400, less than or equal to about 350, less than or equal to about 300, less than or equal to about 250, less than or equal to about 200, less than or equal to about 150, less than or equal to about 100, less than or equal to about 50, less than or equal to about 20, or less
10 than or equal to about 10. In some embodiments, at least some (e.g., each) of the plurality of polymers attached to the particle have an overall degree of polymerization of greater than or equal to about 5, greater than or equal to about 10, greater than or equal to about 20, greater than or equal to about 50, greater than or equal to about 100, greater than or equal to about 150, greater than or equal to about 200, greater than or equal to about 250, greater than or
15 equal to about 300, or greater than or equal to about 350. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 5 and less than or equal to about 400, greater than or equal to about 10 and less than or equal to about 300). In some cases, at least some (e.g., each) of the plurality of polymers attached to the particle have an overall degree of polymerization of about 250.

20 Some embodiments of the present disclosure are generally directed to compositions comprising an emulsion. In some embodiments, the emulsion comprises a first phase (e.g., a liquid comprising ions) and a second phase (e.g., an oil). In some embodiments, the emulsion comprises an aqueous phase and a non-aqueous phase. Non-limiting examples of substances the aqueous phase may comprise include water, brine, and API Brine. API Brine has its
25 ordinary meaning in the art and may refer to 8 wt% NaCl and 2 wt% CaCl₂ in water. Non-limiting examples of substances the non-aqueous phase may comprise include cyclohexane, hexadecane, silicone oil, xylene, mineral oil or a fraction of a mineral oil, ionic liquids, and fluorinated oils. In some embodiments, the emulsion comprises a stabilizing agent (e.g., a surfactant) comprising a polymer attached to a particle. The stabilizing agent may be a
30 stimuli-responsive material, as described in the present disclosure. In a non-limiting set of embodiments, the polymer comprises a first portion and a second portion. For instance, the stabilizing agent may comprise a plurality of polymers attached to a particle. The polymers may comprise a first portion and a second portion as described herein. In some embodiments, the first portion has a lower critical solution temperature in a first phase (e.g., a

first fluid) as described herein. In some embodiments, the second portion has an upper critical solution temperature in a first phase (e.g., a first fluid). In some embodiments, the emulsion has a critical micelle temperature.

In some embodiments, below the critical micelle temperature, the stabilizing agent is soluble in at least one of the first phase (e.g., a aqueous phase) and the second phase (e.g., a non-aqueous phase). For instance, in some embodiments, the stabilizing agent may have a solubility of greater than or equal to about 0.005 wt%, greater than or equal to about 0.010 wt%, greater than or equal to about 0.1 wt%, greater than or equal to about 0.2 wt%, greater than or equal to about 0.5 wt%, greater than or equal to about 1 wt%, or greater than or equal to about 5 wt%, at a temperature below the critical micelle temperature (e.g., 25 degrees Celsius) in at least one of the first phase and the second phase. In some embodiments, the stabilizing agent may have a solubility of less than or equal to about 10 wt%, less than or equal to about 5 wt%, less than or equal to about 1 wt%, less than or equal to about 0.5 wt%, or less than or equal to about 0.2 wt% at a temperature below the critical micelle temperature (e.g., 25 degrees Celsius) in at least one of the first phase and the second phase.

Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0.005 wt% and less than or equal to about 10 wt%, greater than or equal to about 0.005 wt% and less than or equal to about 1 wt%). Solubility of the material in the first phase and/or the second phase may be measured by starting with a homogeneous first phase comprising the solubilized (e.g., dispersed) material as measured by dynamic light scattering, centrifuging the composition, decanting the supernatant so that only the material remains, drying the material, and weighing the material.

In some embodiments, the critical micelle temperature of the emulsion is greater than or equal to about 32 degrees Celsius, greater than or equal to about 35 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 50 degrees Celsius, greater than or equal to about 55 degrees Celsius, greater than or equal to about 60 degrees Celsius, greater than or equal to about 65 degrees Celsius, greater than or equal to about 70 degrees Celsius, or greater than or equal to about 75 degrees Celsius. In some embodiments, the critical micelle temperature of the emulsion is less than or equal to about 80 degrees Celsius, less than or equal to about 75 degrees Celsius, less than or equal to about 70 degrees Celsius, less than or equal to about 65 degrees Celsius, less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 40 degrees Celsius, or less than or equal to about

35 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 32 degrees Celsius and less than or equal to about 80 degrees Celsius, greater than or equal to about 32 degrees Celsius and less than or equal to about 50 degrees Celsius). The critical micelle temperature may be measured by spectrophotometry, as the temperature at which the transmittance of the composition decreases by at least 50% relative to the starting transmittance at a starting temperature below the critical micelle temperature. The critical micelle temperature may be confirmed by optical microscopy on the emulsion to detect the presence of emulsion droplets at the temperature at or above which the composition has a transmittance of 50% or less of the starting transmittance.

In some embodiments, the emulsion has a concentration of stimuli-responsive materials of greater than or equal to about 0.05 wt%, greater than or equal to about 0.1 wt%, greater than or equal to about 0.2 wt%, greater than or equal to about 0.3 wt%, greater than or equal to about 0.4 wt%, greater than or equal to about 0.5 wt%, greater than or equal to about 0.6 wt%, greater than or equal to about 0.7 wt%, greater than or equal to about 0.8 wt%, greater than or equal to about 0.9 wt%, greater than or equal to about 1.0 wt%, or greater than or equal to about 1.1 wt%. In some embodiments, the emulsion has a concentration of stimuli-responsive materials of less than or equal to about 1.2 wt%, less than or equal to about 1.1 wt%, less than or equal to about 1.0 wt%, less than or equal to about 0.9 wt%, less than or equal to about 0.8 wt%, less than or equal to about 0.7 wt%, less than or equal to about 0.6 wt%, less than or equal to about 0.5 wt%, less than or equal to about 0.4 wt%, less than or equal to about 0.3 wt%, less than or equal to about 0.2 wt%, or less than or equal to about 0.1 wt%. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0.05 wt% and less than or equal to about 1.2 wt%, or greater than or equal to about 0.3 wt% and less than or equal to about 1.2 wt%, or greater than or equal to about 0.3 wt% and less than or equal to about 0.5 wt%). In some cases, the emulsion has a particle concentration of about 0.4 wt%.

In some embodiments, the emulsion has a concentration of ionic species in the aqueous phase of greater than or equal to about 0 M, greater than or equal to about 0.2 M, greater than or equal to about 0.4 M, greater than or equal to about 0.6 M, greater than or equal to about 0.8 M, greater than or equal to about 1 M, greater than or equal to about 1.2 M, greater than or equal to about 1.4 M, greater than or equal to about 1.6 M, or greater than or equal to about 1.8 M. In some embodiments, the emulsion has a concentration of ionic species in the aqueous phase of less than or equal to about 2 M, less than or equal to about 1.8 M, less than or equal to about 1.6 M, less than or equal to about 1.4 M, less than or equal to

about 1.2 M, less than or equal to about 1.0 M, less than or equal to about 0.8 M, less than or equal to about 0.6 M, less than or equal to about 0.4 M, or less than or equal to about 0.2 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0 M and less than or equal to about 2 M, greater than or equal to about 0.2 M and less than or equal to about 2 M, or greater than or equal to about 1.4 M and less than or equal to about 2 M). In some cases, the emulsion has a concentration of ionic species in the aqueous phase of about 1.8 M.

In some embodiments, the emulsion has a concentration of ionic species in the aqueous phase of greater than or equal to about 0 API Brine (API Brine is defined as 8 wt% NaCl and 2 wt% CaCl₂), greater than or equal to about 0.1 API Brine, greater than or equal to about 0.2 API Brine, greater than or equal to about 0.3 API Brine, greater than or equal to about 0.4 API Brine, greater than or equal to about 0.5 API Brine, greater than or equal to about 0.6 API Brine, greater than or equal to about 0.7 API Brine, greater than or equal to about 0.8 API Brine, or greater than or equal to about 0.9 API Brine. In some embodiments, the emulsion has an electrolyte concentration in the aqueous phase of less than or equal to about 1 API Brine, less than or equal to about 0.9 API Brine, less than or equal to about 0.8 API Brine, less than or equal to about 0.7 API Brine, less than or equal to about 0.6 API Brine, less than or equal to about 0.5 API Brine, less than or equal to about 0.4 API Brine, less than or equal to about 0.3 API Brine, less than or equal to about 0.2 API Brine, or less than or equal to about 0.1 API Brine. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 0 API Brine and less than or equal to about 1 API Brine, greater than or equal to about 0.1 API Brine and less than or equal to about 1 API Brine, greater than or equal to about 0.9 API Brine and less than or equal to about 1.1 API Brine). In some cases, the emulsion has a concentration of ionic species in the aqueous phase of about 1 API Brine.

Some embodiments of the present disclosure are generally directed to methods involving destabilizing an emulsion (e.g., a stable emulsion) by changing the temperature of the emulsion from a first temperature to a second temperature. In some embodiments, the first temperature is greater than the second temperature. In such embodiments, the emulsion may be referred to as a reverse temperature-responsive emulsion. In some embodiments, the emulsion may be further described by any embodiment of emulsions in the present disclosure.

The first temperature, in some embodiments, is greater than or equal to about 32 degrees Celsius, greater than or equal to about 34 degrees Celsius, greater than or equal to

about 37 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 42 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 48 degrees Celsius, greater than or equal to about 50 degrees Celsius, greater than or equal to about 55 degrees Celsius, greater than or equal to about 60 degrees Celsius, greater than or equal to about 65 degrees Celsius, greater than or equal to about 70 degrees Celsius, or greater than or equal to about 75 degrees Celsius. In some embodiments, the first temperature is less than or equal to about 80 degrees Celsius, less than or equal to about 75 degrees Celsius, less than or equal to about 70 degrees Celsius, less than or equal to about 65 degrees Celsius, less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 48 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 42 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 37 degrees Celsius, or less than or equal to about 34 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 32 degrees Celsius and less than or equal to about 80 degrees Celsius, greater than or equal to about 50 degrees Celsius and less than or equal to about 80 degrees Celsius, greater than or equal to about 60 degrees Celsius and less than or equal to about 70 degrees Celsius). In some cases, the first temperature is about 65 degrees Celsius.

The second temperature, in some embodiments, is less than or equal to about 30 degrees Celsius, less than or equal to about 28 degrees Celsius, less than or equal to about 25 degrees Celsius, less than or equal to about 24 degrees Celsius, less than or equal to about 22 degrees Celsius, less than or equal to about 20 degrees Celsius, less than or equal to about 18 degrees Celsius, less than or equal to about 16 degrees Celsius, less than or equal to about 14 degrees Celsius, or less than or equal to about 12 degrees Celsius. In some embodiments, the second temperature is greater than or equal to about 10 degrees Celsius, greater than or equal to about 12 degrees Celsius, greater than or equal to about 14 degrees Celsius, greater than or equal to about 16 degrees Celsius, greater than or equal to about 18 degrees Celsius, greater than or equal to about 20 degrees Celsius, greater than or equal to about 22 degrees Celsius, greater than or equal to about 24 degrees Celsius, greater than or equal to about 25 degrees Celsius, or greater than or equal to about 28 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 10 degrees Celsius and less than or equal to about 30 degrees Celsius, greater than or equal to about 10 degrees Celsius and less than or equal to about 25 degrees Celsius, greater than or equal to about 20

degrees Celsius and less than or equal to about 25 degrees Celsius). In some cases, the second temperature is about 25 degrees Celsius.

The first temperature, in some embodiments, is greater than the second temperature by a difference of greater than or equal to about 10 degrees Celsius, greater than or equal to about 20 degrees Celsius, greater than or equal to about 25 degrees Celsius, greater than or equal to about 30 degrees Celsius, greater than or equal to about 35 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 50 degrees Celsius, or greater than or equal to about 55 degrees Celsius. In some embodiments, the first temperature is greater than the second temperature by less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 35 degrees Celsius, less than or equal to about 30 degrees Celsius, less than or equal to about 25 degrees Celsius, less than or equal to about 20 degrees Celsius, or less than or equal to about 15 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 10 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 30 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 35 degrees Celsius and less than or equal to about 45 degrees Celsius). In some cases, the first temperature is greater than the second temperature by about 40 degrees Celsius.

In some embodiments, an emulsion that is stable (e.g., in a stabilized state) at the first temperature is exposed to the second temperature, causing the emulsion to destabilize (e.g., phase separate into a destabilized state, de-emulsify). In some embodiments, the emulsion phase separates into a destabilized state at the second temperature in less than or equal to about 230 minutes, in less than or equal to about 220 minutes, in less than or equal to about 190 minutes, in less than or equal to about 180 minutes, in less than or equal to about 120 minutes, in less than or equal to about 110 minutes, in less than or equal to about 100 minutes, in less than or equal to about 90 minutes, in less than or equal to about 80 minutes, in less than or equal to about 70 minutes, in less than or equal to about 60 minutes, in less than or equal to about 50 minutes, in less than or equal to about 40 minutes, in less than or equal to about 30 minutes, or in less than or equal to about 20 minutes.

In some embodiments, the separation time for the emulsion to phase separate into a destabilized state at the second temperature decreases as the electrolyte concentration in the aqueous phase of the emulsion increases. In some embodiments, the separation time for the

emulsion to phase separate into a destabilized state at the second temperature increases as the particle concentration in the emulsion increases. In some embodiments, the separation time for the emulsion to phase separate into a destabilized state at the second temperature is lower for an emulsion comprising particles to which a plurality of block copolymers are attached by the first block than for an emulsion comprising particles to which a plurality of randomly oriented copolymers are attached.

The emulsion in a stabilized state may have a transmittance of less than or equal to about 0.5, less than or equal to about 0.4, less than or equal to about 0.3, less than or equal to about 0.2, less than or equal to about 0.1, less than or equal to about 0.05, or less than or equal to about 0.01 at a wavelength of for example 750 nm; and the transmittance may persist for greater than or equal to about 0.5 hours, greater than or equal to about 1 hour, greater than or equal to about 2 hours, greater than or equal to about 12 hours, or greater than or equal to about 24 hours. Transmittance may be measured by absorption spectroscopy at a wavelength or wavelengths at which the components of the emulsion do not significantly absorb, which in some embodiments is/are greater than or equal to about 250 nm and less than or equal to about 750 nm.

The first phase and/or second phase of the emulsion in a destabilized state may have a transmittance of greater than or equal to about 0.5, greater than or equal to about 0.6, greater than or equal to about 0.7, greater than or equal to about 0.8, greater than or equal to about 0.9, or greater than or equal to about 0.99 at a wavelength of, for example, 750 nm; and the transmittance may persist for greater than or equal to about 0.5 hours, greater than or equal to about 1 hour, greater than or equal to about 2 hours, greater than or equal to about 12 hours, or greater than or equal to about 24 hours. Transmittance may be measured by absorption spectroscopy at a wavelength or wavelengths at which the components of the emulsion do not significantly absorb, which in some embodiments is/are greater than or equal to about 250 nm and less than or equal to about 750 nm.

In some embodiments, the emulsion may be cycled between the first temperature and the second temperature, and thereby between a stabilized state (e.g., a stable emulsion) and a destabilized state (e.g., a phase separated system), greater than or equal to about one time, greater than or equal to about 2 times, greater than or equal to about 3 times, or greater than or equal to about 4 times, and substantially maintain the transmittance of the first phase and/or second phase of the emulsion in a destabilized state with each cycle. The extent to which the transmittance of the first phase and/or second phase of the emulsion in a destabilized state at the second temperature is maintained with each cycle can be determined

by calculating the normalized transmittance. The term “normalized transmittance” is given its ordinary meaning in the art and may refer to for example the ratio of the measured transmittance of the first phase and/or second phase in the destabilized state at the second temperature before cycling the emulsion, to the measured transmittance of the first phase and/or second phase in the destabilized state at the second temperature after cycling the emulsion a given number of times, multiplied by one hundred, to give the normalized transmittance as a percentage.

In some embodiments, the normalized transmittance of the first phase and/or the second phase of the emulsion in a destabilized state at the second temperature after cycling the emulsion (e.g., greater than or equal to about one time, or greater than or equal to about 4 times) is greater than or equal to about 80%, greater than or equal to about 82%, greater than or equal to about 85%, greater than or equal to about 87%, greater than or equal to about 90%, greater than or equal to about 92%, greater than or equal to about 95%, greater than or equal to about 96%, greater than or equal to about 97%, greater than or equal to about 98%, greater than or equal to about 99%. Transmittance may be measured by absorption spectroscopy.

Some embodiments of the present disclosure are generally directed to methods involving exposing an emulsion (e.g., a stable emulsion) to a first temperature to destabilize (e.g., phase separate into a destabilized state) the emulsion, wherein the critical micelle temperature of the emulsion is greater than the first temperature. In some embodiments, the method comprises exposing the emulsion to a second temperature before exposing the emulsion to the first temperature. In some embodiments, the second temperature is greater than the critical micelle temperature of the emulsion.

The first temperature, in some embodiments, is less than or equal to about 30 degrees Celsius, less than or equal to about 28 degrees Celsius, less than or equal to about 25 degrees Celsius, less than or equal to about 24 degrees Celsius, less than or equal to about 22 degrees Celsius, less than or equal to about 20 degrees Celsius, less than or equal to about 18 degrees Celsius, less than or equal to about 16 degrees Celsius, less than or equal to about 14 degrees Celsius, or less than or equal to about 12 degrees Celsius. In some embodiments, the first temperature is greater than or equal to about 10 degrees Celsius, greater than or equal to about 12 degrees Celsius, greater than or equal to about 14 degrees Celsius, greater than or equal to about 16 degrees Celsius, greater than or equal to about 18 degrees Celsius, greater than or equal to about 20 degrees Celsius, greater than or equal to about 22 degrees Celsius, greater than or equal to about 24 degrees Celsius, greater than or equal to about 25 degrees

Celsius, or greater than or equal to about 28 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 10 degrees Celsius and less than or equal to about 30 degrees Celsius, greater than or equal to about 10 degrees Celsius and less than or equal to about 25 degrees Celsius, greater than or equal to about 20 degrees Celsius and less than or equal to about 25 degrees Celsius). In some cases, the first temperature is about 25 degrees Celsius.

The second temperature, in some embodiments, is greater than or equal to about 32 degrees Celsius, greater than or equal to about 34 degrees Celsius, greater than or equal to about 37 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 42 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 48 degrees Celsius, greater than or equal to about 50 degrees Celsius, greater than or equal to about 55 degrees Celsius, greater than or equal to about 60 degrees Celsius, greater than or equal to about 65 degrees Celsius, greater than or equal to about 70 degrees Celsius, or greater than or equal to about 75 degrees Celsius. In some embodiments, the second temperature is less than or equal to about 80 degrees Celsius, less than or equal to about 75 degrees Celsius, less than or equal to about 70 degrees Celsius, less than or equal to about 65 degrees Celsius, less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 48 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 42 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 37 degrees Celsius, or less than or equal to about 34 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 32 degrees Celsius and less than or equal to about 80 degrees Celsius, greater than or equal to about 50 degrees Celsius and less than or equal to about 80 degrees Celsius, greater than or equal to about 60 degrees Celsius and less than or equal to about 70 degrees Celsius). In some cases, the second temperature is about 65 degrees Celsius.

The second temperature, in some embodiments, is greater than the critical micelle temperature by a difference greater than or equal to about 5 degrees Celsius, greater than or equal to about 10 degrees Celsius, greater than or equal to about 15 degrees Celsius, greater than or equal to about 20 degrees Celsius, greater than or equal to about 25 degrees Celsius, greater than or equal to about 30 degrees Celsius, greater than or equal to about 35 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 50 degrees Celsius, or greater than or equal to about 55 degrees Celsius. In some embodiments, the second temperature is greater than the

critical micelle temperature by less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 35 degrees Celsius, less than or equal to about 30 degrees Celsius, less than or equal to about 25 degrees Celsius, less than or equal to about 20 degrees Celsius, less than or equal to about 15 degrees Celsius, or less than or equal to about 10 degrees Celsius.

Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 5 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 10 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 15 degrees Celsius and less than or equal to about 45 degrees Celsius). In some cases, the second temperature is greater than the critical micelle temperature by about 15 degrees Celsius.

The first temperature, in some embodiments, is less than the critical micelle temperature by a difference greater than or equal to about 5 degrees Celsius, greater than or equal to about 10 degrees Celsius, greater than or equal to about 15 degrees Celsius, greater than or equal to about 20 degrees Celsius, greater than or equal to about 25 degrees Celsius, greater than or equal to about 30 degrees Celsius, greater than or equal to about 35 degrees Celsius, greater than or equal to about 40 degrees Celsius, greater than or equal to about 45 degrees Celsius, greater than or equal to about 50 degrees Celsius, or greater than or equal to about 55 degrees Celsius. In some embodiments, the first temperature is less than the critical micelle temperature by less than or equal to about 60 degrees Celsius, less than or equal to about 55 degrees Celsius, less than or equal to about 50 degrees Celsius, less than or equal to about 45 degrees Celsius, less than or equal to about 40 degrees Celsius, less than or equal to about 35 degrees Celsius, less than or equal to about 30 degrees Celsius, less than or equal to about 25 degrees Celsius, less than or equal to about 20 degrees Celsius, less than or equal to about 15 degrees Celsius, or less than or equal to about 10 degrees Celsius. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to about 5 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 10 degrees Celsius and less than or equal to about 60 degrees Celsius, greater than or equal to about 15 degrees Celsius and less than or equal to about 45 degrees Celsius). In some cases, the first temperature is less than the critical micelle temperature by about 25 degrees Celsius.

In some embodiments, an emulsion that is stable at the second temperature is exposed to the first temperature, causing the emulsion to destabilize (e.g., phase separate into a destabilized state, de-emulsify). In some embodiments, the emulsion phase separates into a

destabilized state at the first temperature in less than or equal to about 230 minutes, in less than or equal to about 220 minutes, in less than or equal to about 190 minutes, in less than or equal to about 180 minutes, in less than or equal to about 120 minutes, in less than or equal to about 110 minutes, in less than or equal to about 100 minutes, in less than or equal to about 90 minutes, in less than or equal to about 80 minutes, in less than or equal to about 70 minutes, in less than or equal to about 60 minutes, in less than or equal to about 50 minutes, in less than or equal to about 40 minutes, in less than or equal to about 30 minutes, or in less than or equal to about 20 minutes.

The emulsion in a stabilized state may have a transmittance of less than or equal to about 0.5, less than or equal to about 0.4, less than or equal to about 0.3, less than or equal to about 0.2, less than or equal to about 0.1, less than or equal to about 0.05, or less than or equal to about 0.01 at a wavelength of for example 750 nm; and the transmittance may persist for greater than or equal to about 0.5 hours, greater than or equal to about 1 hour, greater than or equal to about 2 hours, greater than or equal to about 12 hours, or greater than or equal to about 24 hours. Transmittance may be measured by absorption spectroscopy at a wavelength or wavelengths at which the components of the emulsion do not significantly absorb, which in some embodiments is/are greater than or equal to about 250 nm and less than or equal to about 750 nm.

The first phase and/or second phase of the emulsion in a destabilized state may have a transmittance of greater than or equal to about 0.5, greater than or equal to about 0.6, greater than or equal to about 0.7, greater than or equal to about 0.8, greater than or equal to about 0.9, or greater than or equal to about 0.99 at a wavelength of for example 750 nm; and the transmittance may persist for greater than or equal to about 0.5 hours, greater than or equal to about 1 hour, greater than or equal to about 2 hours, greater than or equal to about 12 hours, or greater than or equal to about 24 hours. Transmittance may be measured by absorption spectroscopy at a wavelength or wavelengths at which the components of the emulsion do not significantly absorb, which in some embodiments is/are greater than or equal to about 250 nm and less than or equal to about 750 nm.

In some embodiments, the emulsion may be cycled between the second temperature and the first temperature, and thereby between a stabilized state (e.g., a stable emulsion) and a destabilized state (e.g., a phase separated system), greater than or equal to about one time, greater than or equal to about 2 times, greater than or equal to about 3 times, or greater than or equal to about 4 times, and substantially maintain the transmittance of the first phase and/or second phase of the emulsion in a destabilized state with each cycle. The extent to

which the transmittance of the first phase and/or second phase of the emulsion in a destabilized state at the first temperature is maintained with each cycle can be determined by calculating the normalized transmittance. The normalized transmittance is given its ordinary meaning in the art and may refer to for example the ratio of the measured transmittance of the first phase and/or second phase in the destabilized state at the first temperature before cycling the emulsion, to the measured transmittance of the first phase and/or second phase in the destabilized state at the first temperature after cycling the emulsion a given number of times, multiplied by one hundred, to give the normalized transmittance as a percentage.

In some embodiments, the normalized transmittance of the first phase and/or the second phase of the emulsion in a destabilized state at the first temperature after cycling the emulsion (e.g., greater than or equal to about one time, or greater than or equal to about 4 times) is greater than or equal to about 80%, greater than or equal to about 82%, greater than or equal to about 85%, greater than or equal to about 87%, greater than or equal to about 90%, greater than or equal to about 92%, greater than or equal to about 95%, greater than or equal to about 96%, greater than or equal to about 97%, greater than or equal to about 98%, or greater than or equal to about 99%. Transmittance may be measured by absorption spectroscopy.

In some embodiments, the stimuli-responsive materials are surface-active at a first temperature or set of temperatures, and the particles lose their activity at a second temperature or second set of temperatures. In some embodiments, the stimuli-responsive materials may be used to form a stable emulsion at a first temperature or range of temperatures, and to cause the emulsion to spontaneously phase separate into a destabilized state at a second temperature or range of temperatures. In some embodiments, the first temperature (e.g., about 65 degrees Celsius) or range of temperatures is greater than the second temperature (e.g., about 25 degrees Celsius) or range of temperatures. In such embodiments, the emulsion may be referred to as a reverse temperature-responsive emulsion. In some embodiments, the stimuli-responsive materials may be utilized in for example enhanced oil recovery, wherein a stable emulsion is formed in a first temperature range within an oil and/or gas well, and the oil spontaneously separates from the aqueous phase in a second lower temperature range outside of the oil and/or gas well.

In some embodiments, the stimuli-responsive materials are used in for example enhanced oil recovery, liquid-phase heterogeneous catalysis, emulsion polymerization, or any other application where stable emulsions are only desired at elevated temperatures (e.g., greater than about 30 degrees Celsius). In some embodiments, a method of enhanced oil

recovery is provided, wherein the method comprises delivering a first composition comprising a stimuli-responsive material into an oil and/or gas well; and withdrawing a second composition comprising an aqueous phase, an oil phase, and the stimuli-responsive material from the oil and/or gas well. In enhanced oil recovery, as a non-limiting example, the stimuli-responsive materials can be used to emulsify underground oil pockets (e.g., at elevated temperatures relative to 25 degrees Celsius), which once recovered above ground (e.g., at about 25 degrees Celsius) can be readily destabilized and phase separated into extracted oil and aqueous phase.

In some embodiments, a method of enhanced oil recovery comprises injecting into an oil and/or gas well a first composition comprising a stimuli-responsive material dissolved in an aqueous medium in which the stimuli-responsive material is soluble or substantially soluble below its LCST, at an injection temperature between 0 degrees Celsius and 40 degrees Celsius, in some cases preferably between 10 degrees Celsius and 30 degrees Celsius, wherein the stimuli-responsive material has a lower critical solution temperature higher than the injection temperature by from 5 degrees Celsius to 30 degrees Celsius.

As another non-limiting example, in liquid-phase heterogeneous catalysis, a biphasic reaction system can be stably emulsified (e.g., for enhanced reaction surface area) at an elevated reaction temperature relative to 25 degrees Celsius, and subsequently restored to a phase separated destabilized state when cooled (e.g., at about 25 degrees Celsius).

The following examples are intended to illustrate certain embodiments described herein, but do not exemplify the full scope of embodiments.

EXAMPLES

EXAMPLE 1

This example describes the synthesis of block copolymer-functionalized nanoparticles and the reverse temperature-responsive performance of emulsions comprising these nanoparticles.

Reversible addition-fragmentation chain transfer (RAFT) polymerization was utilized to synthesize a low-polydispersity block copolymer comprising: a first block comprising a poly(N-alkyl methacrylamide), specifically poly(N-isopropyl methacrylamide) (polyNIPMAM), having a lower critical solution temperature (LCST) of 42 degrees Celsius in aqueous solution; and a second block comprising a polyzwitterion, specifically poly(sulfobetaine methacrylamide) (polySBMA), having an upper critical solution temperature (UCST) of 16 degrees Celsius in aqueous solution. The block copolymer was

subsequently conjugated to 20 nm diameter silica nanoparticles via siloxane conjugation. At an ambient temperature of 25 degrees Celsius, both the first block and the second block were hydrophilic and aqueous soluble, such that the functionalized nanoparticles lacked surface (e.g., aqueous-non-aqueous interface) activity and partitioned into the aqueous phase. On the other hand, at an elevated temperature of 65 degrees Celsius, the dehydration of the poly(N-alkyl methacrylamide) block competed with the hydration of the polyzwitterion block, at least for this reason resulting in interfacially-active nanoparticles that stabilized an oil-in-aqueous emulsion at elevated temperatures, as shown in a non-limiting illustrative schematic in FIG. 3.

Synthesis Scheme: A synthetic scheme for developing polymer-functionalized nanoparticles began with the synthesis of a low-polydispersity block copolymer, wherein a reversible chain transfer agent 4-Cyano-4(phenylcarbonothioylthio)pentanoic acid was used to conduct a sequential one-pot reversible addition-fragmentation chain transfer (RAFT) polymerization. The polymerization was conducted in trifluoroethanol (TFE), and block lengths of 200 for the poly(SBMA) block and 50 for poly(NIPMAM) respectively were targeted. 10 mol % of a silane, specifically gamma-(trimethoxysilyl) propyl methacrylate, was also copolymerized in the poly(NIPMAM) block to enable permanent immobilization of the polymer layer to the nanoparticles via siloxane conjugation. This siloxane conjugation prevented desorption of the polymer layer, and increased the stability of the particles such that for example the particles did not lose function after a one-time exposure to elevated temperatures.

Block Copolymer Synthesis: The sulfobetaine methacrylamide (SBMA) block (the second block) was synthesized first, and utilized as a macromolecular chain transfer agent for the subsequent polymerization of the next block (the first block). To synthesize the SBMA block: 20mM sulfobetaine methacrylamide, 0.1mM 4-Cyano-4 (phenylcarbonothioylthio) pentanoic acid, and 0.035 mM 4,4'-Azobis(4-cyanovaleric acid) were dissolved in trifluoroethanol to a volume of 13 mL in a round bottom flask. Nitrogen was bubbled through the solution for 30 minutes, and the reactor was heated to 65 degrees Celsius. The polymerization was terminated after 12 hours by exposure to atmospheric oxygen. To synthesize the N-isopropyl methacrylamide (NIPMAM) block: 5mM NIPMAM, 2.5 mM gamma-(trimethoxysilyl) propyl methacrylate, 0.035mM 4,4'-Azobis(4-cyanovaleric acid) and 3 mL trifluoroethanol were dissolved in the polySBMA block solution. Nitrogen was bubbled through the solution for 30 minutes, and the reactor was heated to 70 degrees

Celsius. The polymerization was terminated after 8 hours by exposure to atmospheric oxygen.

The ability to synthesize di-block, tri-block, or higher-order block architectures is in some cases limited by the availability of a common solvent for all relevant monomers. TFE as a solvent was found to be suitable in this respect, since it provided simultaneously polar (due to fluorine groups) and hydrophobic (due to ethanolic backbone) properties as a solvent, and therefore at least for these reasons enabled successful solvation of all three monomers: SBMA, NIPMAM, and gamma-(trimethoxysilyl) propyl methacrylate. By selective copolymerization of the silane monomer within the first block only, the grafted polymer was always oriented to position the LCST block toward the particle core (see, e.g., FIG. 3). Such segregation played a role in maintaining cyclability of an emulsion comprising the polymer-functionalized nanoparticles. The effects of polymer architecture are discussed further below.

Preparation of Block Copolymer Conjugated Nanoparticles: 500 microliters of Ludox TM-40 was dissolved in a 50/50 (v/v) mixture of trifluoroethanol and aqueous phase. 2.5 grams of block copolymer solution was slowly added to the dispersion, and the reaction mixture was subsequently heated at 75 degrees Celsius for 10 hours. Next, the reaction mixture was diluted with 15 mL of 0.5M NaCl solution, and the polymer-functionalized nanoparticles were separated from free polymer via three 90-minute centrifugation cycles at 16,128 RCF. The particles were finally dispersed in 0.5M NaCl solution to a concentration of 50mg/mL.

The ability of the nanoparticles to stabilize and/or destabilize emulsions was characterized in terms of at least two parameters: (1) separation time to attain oil-aqueous phase separation, and (2) system cyclability (the ability of the particles to stabilize/destabilize emulsions repeatedly). Particle concentration, electrolyte concentration, and polymer architecture were studied as factors affecting the two parameters. Oil-in-aqueous emulsions (20/80 (v/v)) were prepared with three different oils of varying viscosity to demonstrate the ability of the particles to stabilize the emulsions under different conditions. FIG. 4 shows optical microscopy images of (polymer-functionalized particle)-stabilized emulsion droplets at 65 degrees Celsius for three different oil phases (hexadecane, cyclohexane, and silicone oil), demonstrating the broad ability of the particles to stabilize oil phases with different properties. The emulsions in FIG. 4 were maintained at 65 degrees Celsius, with 20% (v/v) oil volume fraction and a particle concentration of 0.4 wt%. The emulsion stabilization and destabilization process was further studied for the hexadecane-in-aqueous mixture. No

emulsion formation took place at room temperature, and successful emulsion formation occurred at 65 degrees Celsius.

Separation Time: The ease of oil-aqueous phase separation was one property of the system that was studied, and both the particle concentration and the salinity of the aqueous phase were found to have a pronounced effect on separation rates. In order to quantify separation time, normalized transmittance measurements of the aqueous phase were made every ten minutes until the sample was found to have a transmittance of greater than or equal to about 90 percent. FIG. 5 shows that, at a given salinity, an increase in particle concentration led to an increase in the separation time. For example, under a 0.1 API Brine solution condition (API Brine is defined as 8 wt% NaCl and 2 wt% CaCl₂), with increasing particle concentration from 0.4 wt% to 1.2 wt%, the separation time increased from 70 to 130 minutes. The observed trend may have been due to changes in the particle assembly at the oil/aqueous interface of the emulsion droplet. For example, colloidal monolayers, which may have formed at lower particle concentrations, may have transitioned to stacked multilayer configurations at higher particle concentrations. The latter configuration may have made phase separation a significantly slower kinetic process because, in addition to particle desorption from the oil/aqueous interface, attractive inter-particle interactions within the multilayer would have needed to be overcome in order to promote droplet coalescence. This would have led to longer separation times.

A second factor that directly affected separation times was the electrolyte concentration in the aqueous phase. As shown in FIG. 5, an increase in the electrolyte concentration decreased separation times (an increase in the electrolyte concentration significantly accelerated the separation process). For example, FIG. 5 shows that, at a particle concentration of 0.4 wt%, a separation time of 70 minutes decreased to 10 minutes when the electrolyte concentration was increased from 0.1 API to 1 API. Substantially similar behavior was observed at all three particle concentrations investigated (see, e.g., FIG. 5).

The behavior observed in response to an increase in the electrolyte concentration may have been due to the behavior exhibited by polyelectrolytes that differs from that exhibited by polyelectrolytes consisting of monomers of like charge. This polyelectrolyte behavior may be attributed to the ability of a polyelectrolyte polymer chain to increase, rather than decrease, its aqueous solubility when exposed to a first aqueous environment of greater electrolyte concentration than a second aqueous environment. This response by polyelectrolytes to an increase in the concentration of one or more electrolytes is in direct contrast to the response observed in polyelectrolytes consisting of monomers of like charge, the aqueous solubility of

which decrease when electrolyte concentration increases. This rapid separation behavior is useful, for example, in applications where high electrolyte concentration environments are commonplace (e.g., in enhanced oil recovery), because the enhanced hydration of the polyelectrolyte block afforded by an electrolyte-rich environment (e.g., FIG. 5, 1 API) resulted in easier and faster separation than separations at lesser electrolyte concentrations (e.g., FIG. 5, 0.1 API).

Furthermore, the broad applicability of the novel functionalized nanoparticles in emulsifying/demulsifying different types of oils is indicated for example by the separation times observed for cyclohexane and silicone oil emulsions, which are tabulated in Table 1. The particle concentration was fixed at 0.4 wt%, and a 20/80 (v/v) oil/aqueous mixture was used. The composition of API Brine is 8 wt% NaCl and 2 wt% CaCl₂.

Table 1

Separation Times for Cyclohexane and Silicone Oil

Electrolyte Concentration	Cyclohexane (minutes)	Silicone Oil (minutes)
API	30	30
0.75 API	40	50
0.5 API	60	70
0.25 API	80	90
0.1 API	100	100

System Cyclability: The extent to which the surface activity of the polymer-functionalized nanoparticles increased and/or decreased reversibly was tested by subjecting the particles to five emulsification/de-emulsification cycles at different electrolyte concentrations and different particle concentrations, and by tracking the quality of the separation via transmittance measurements on the aqueous phase. In order to quantify the quality of the separation, transmittance values were recorded at the time required to attain 90% sample transmittance during the first cycle. That is, for the system cyclability measurements, the transmittance values were determined after the time allowed for separation was equal to that obtained from the sample transmittance measurements. FIG. 6A and FIG. 6B show that, under most conditions, the transmittance values did not deteriorate by more than 10%, indicating that the particles fostered strong cyclability in emulsion stabilization/destabilization processes by adsorbing to the interface and stabilizing the

emulsion at high temperature, and then desorbing from the interface to facilitate reversion back to a phase-separated state upon cooling the system.

This example illustrated the successful synthesis of polymer-functionalized nanoparticles that responsively exhibited increased surface activity at elevated temperatures, and decreased surface activity at room temperature. Emulsions comprising the polymer-functionalized nanoparticles were stable at high temperature and underwent facile phase separation at room temperature. The direction of the temperature response is opposite to that previously reported in the literature. Additionally, the system was shown to have cyclability over a broad range of conditions. Successful emulsification/de-emulsification behavior was demonstrated for multiple oil types.

EXAMPLE 2

This example describes the synthesis of random copolymer-functionalized nanoparticles, wherein the random copolymer comprises components substantially similar to the components of the block copolymer in Example 1, and the reverse temperature-responsive performance of emulsions comprising these random copolymer-functionalized nanoparticles in comparison to the performance of the emulsions in Example 1.

Effect of Polymer Architecture: The effect of polymer architecture on the overall behavior of the emulsion system was evaluated by comparing the effects of particles functionalized with the block copolymer discussed in Example 1 with those of particles functionalized with a random copolymer.

Random Copolymer Synthesis: 20mM SBMA, 5mM NIPMAM, 2.5 mM gamma-(trimethoxysilyl) propyl methacrylate, 0.1mM 4-Cyano-4(phenylcarbonothioylthio)pentanoic acid, and 0.035 mM 4,4'-Azobis(4-cyanovaleric acid) were dissolved in 7 ml trifluoroethanol. Nitrogen was bubbled through the solution for 30 minutes, and the reactor was heated to 70 degrees Celsius. The polymerization was terminated after 8 hours by exposure to atmospheric oxygen.

Preparation of Random Copolymer Conjugated Nanoparticles: 500 microliters of Ludox TM-40 was dissolved in a 50/50 (v/v) mixture of trifluoroethanol and aqueous phase. 2.5 grams of random copolymer solution was slowly added to the dispersion, and the reaction mixture was subsequently heated at 75 degrees Celsius for 10 hours. Next, the reaction mixture was diluted with 15 mL of 0.5 M NaCl solution, and the polymer-functionalized nanoparticles were separated from free polymer via three 90-minute centrifugation cycles at 16,128 RCF. The particles were finally dispersed in 0.5 M NaCl solution to a concentration of 50 mg/mL.

Differences in performance between the two polymer architectures were observed, with emulsions comprising the random copolymer-functionalized nanoparticles exhibiting significantly slower separation times than the emulsions in Example 1. The separation times for random and block copolymer architectures are shown in Table 2. The particle concentration was fixed at 0.4 wt%, and a 20/80 (v/v) oil/aqueous mixture was used. The composition of API Brine is 8 wt% NaCl and 2 wt% CaCl₂ in water.

Table 2

Separation Times for Random and Block Copolymers

Electrolyte Concentration	Random Copolymer (minutes)	Block Copolymer (minutes)
API	40	20
0.75 API	60	40
0.5 API	110	50
0.25 API	180	70
0.1 API	220	90

The observed differences in performance between the two polymer architectures may have been due to differences in the arrangement of the NIPMAM units along the random copolymer backbone and the arrangement of the NIPMAM units along the block copolymer backbone. In the block copolymer case (Example 1), the polymer was engineered such that the poly(NIPMAM) block segregated towards the core of the nanoparticle. This segregation actively hindered particle clustering by sterically limiting associative interactions between the poly(NIPMAM) blocks on different nanoparticles. The reduced tendency towards particle clustering, in turn, led to a better tolerance to cycling and shorter separation times. On the other hand, in the random copolymer case, NIPMAM units were distributed throughout the polymer backbone instead of being segregated towards the core. Accordingly, this lack of segregation facilitated associative interactions between NIPMAM units on different nanoparticles, which led to particle clustering above the LCST. This increased tendency towards particle clustering, in turn, led to lesser cyclability and longer separation times for emulsions comprising the random copolymer functionalized nanoparticles than for emulsions comprising the block copolymer functionalized nanoparticles.

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other

means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with “and/or” should be construed in the same fashion, i.e., “one or more” of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to “A and/or B”, when used in conjunction with open-ended language such as “comprising” can refer, in one

embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.”

As used herein in the specification and in the claims, the phrase “at least one,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, at least one, optionally including more than one, B (and optionally including other elements); etc.

When the word “about” is used herein in reference to a number, it should be understood that still another embodiment of the invention includes that number not modified by the presence of the word “about.”

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or acts

of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,”

5 “composed of,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

10 Having thus described several aspects of at least one embodiment of this invention, it is to be appreciated various alterations, modifications, and improvements will readily occur to those skilled in the art. Such alterations, modifications, and improvements are intended to be part of this disclosure, and are intended to be within the spirit and scope of the invention. Accordingly, the foregoing description and drawings are by way of example only.

CLAIMS

What is claimed is:

1. A material, comprising:
5 a particle; and
a plurality of polymers attached to the particle, wherein each of the plurality of polymers comprises a first portion having a lower critical solution temperature in a first phase and a second portion having an upper critical solution temperature in the first phase.
- 10 2. The material of claim 1, wherein the second portion comprises a polyzwitterion.
3. The material of claim 2, wherein the polyzwitterion comprises poly(sulfobetaine methacrylamide).
- 15 4. The material of any preceding claim, wherein the particle has an elastic modulus of greater than or equal to about 1 GPa.
5. The material of any preceding claim, wherein the particle has a density of greater than or equal to about 1.01 g/cm³.
20
6. The material of any preceding claim, wherein at least some of the plurality of polymers are attached to the particle by the first portion.
7. The material of any preceding claim, wherein the first phase comprises an aqueous
25 fluid.
8. The material of any one of claims 1-6, wherein the first phase comprises a non-aqueous fluid.
- 30 9. The material of any preceding claim, wherein the first phase is selected from the group consisting of water, brine, API Brine, cyclohexane, hexadecane, acetonitrile, n-hexane, mineral oil or a fraction of a mineral oil, fluorinated oils, and ionic liquids.

10. The material of any preceding claim, wherein the first portion has a lower critical solution temperature of greater than or equal to about 32 degrees Celsius and less than or equal to about 50 degrees Celsius in the first phase.
- 5 11. The material of claim 10, wherein the first portion has a lower critical solution temperature of greater than or equal to about 40 degrees Celsius and less than or equal to about 44 degrees Celsius in the first phase.
- 10 12. The material of any preceding claim, wherein the second portion has an upper critical solution temperature of greater than or equal to about 4 degrees Celsius and less than or equal to about 20 degrees Celsius in the first phase.
13. The material of claim 12, wherein the second portion has an upper critical solution temperature of greater than or equal to about 14 degrees Celsius and less than or equal to
15 about 18 degrees Celsius in the first phase.
14. The material of any preceding claim, wherein the plurality of polymers are block copolymers.
- 20 15. The material of claim 14, wherein the block copolymers comprise a first block comprising the first portion and a second block comprising the second portion.
16. The material of any one of claims 14-15, wherein at least some of the block copolymers are attached to the particle by the first block.
- 25 17. The material of any preceding claim, wherein the first portion comprises a poly(N-alkyl methacrylamide).
18. The material of claim 17, wherein the poly(N-alkyl methacrylamide) comprises
30 poly(N-isopropyl methacrylamide).
19. The material of any one of claims 1-16, wherein the first portion comprises a poly(N-alkyl acrylamide).

20. The material of any preceding claim, wherein the first portion further comprises a polysilane.
21. The material of claim 20, wherein the polysilane comprises poly(gamma-(trimethoxysilyl) propyl methacrylate).
22. The material of any one of claims 1-16 and 20-21, wherein the first portion comprises poly(ethylene glycol methacrylate).
23. The material of claim 19, wherein the poly(N-alkyl acrylamide) comprises poly(N-isopropyl acrylamide).
24. The material of any one of claims 1-16 and 20-21, wherein the first portion comprises poly(2-(dimethylamino)ethyl methacrylate).
25. The material of any preceding claim, wherein the first block is attached to the particle by siloxane conjugation.
26. The material of any preceding claim, wherein the plurality of polymers are random copolymers.
27. The material of any one of claims 1-25, wherein the plurality of polymers are gradient copolymers.
28. The material of any preceding claim, wherein the particle is a spherical particle.
29. The material of any preceding claim, wherein the particle comprises silica.
30. The material of any preceding claim, wherein the particle comprises iron oxide.
31. The material of any preceding claim, wherein the particle comprises graphene.
32. The material of any preceding claim, wherein the particle comprises magnetite.

33. The material of any preceding claim, wherein the particle comprises gold.
34. The material of any preceding claim, wherein the particle comprises polystyrene.
- 5 35. The material of any preceding claim, wherein the particle has a largest cross-sectional dimension of greater than or equal to about 1 nm and less than or equal to about 40 nm.
36. The material of claim 35, wherein the particle has a largest cross-sectional dimension of greater than or equal to about 10 nm and less than or equal to about 25 nm.
- 10 37. The material of any preceding claim, wherein the first portion comprises a polymer and the second portion comprises a polymer.
38. The material of any preceding claim, wherein the mole ratio of repeat units of the first portion to repeat units of the second portion is greater than or equal to about 1:5 and less than or equal to about 1:2.
- 15 39. The material of any preceding claim, wherein each of the plurality of polymers has a solvated length in the first phase of greater than or equal to about 1 nm and less than or equal to about 40 nm.
- 20 40. The material of any preceding claim, wherein the material has a solvated diameter in the first phase of greater than or equal to about 25 nm and less than or equal to about 40 nm.
- 25 41. The material of any preceding claim, wherein each of the plurality of polymers has a solvated length in the first phase of greater than or equal to about 0.5 times and less than or equal to about 1.5 times the largest cross-sectional dimension of the particle.
42. An emulsion, comprising:
30 a first phase;
a second phase; and
a stabilizing agent comprising a polymer attached to a particle, wherein the critical micelle temperature of the emulsion is greater than or equal to about 32 degrees Celsius.

43. The emulsion of claim 42, wherein the stabilizing agent is soluble at greater than or equal to about 0.005 wt% and less than or equal to about 10 wt% in at least one of the first phase and the second phase at a temperature below the critical micelle temperature.

5 44. The emulsion of any one of claims 42-43, wherein the first phase is an aqueous fluid, and the second phase is a non-aqueous fluid.

45. The emulsion of any one of claims 42-43, wherein the first phase is a non-aqueous fluid, and the second phase is an aqueous fluid.

10

46. The emulsion of any one of claims 42-43, wherein the first phase is a non-aqueous fluid, and the second phase is a non-aqueous fluid.

15 47. The emulsion of any one of claims 42-45, wherein each of the first phase and the second phase is selected from the group consisting of water, brine, API Brine, cyclohexane, hexadecane, acetonitrile, n-hexane, mineral oil or a fraction of a mineral oil, fluorinated oils, and ionic liquids.

20 48. The emulsion of any one of claims 42-47, wherein the polymer comprises a first portion and a second portion, wherein the first portion has a lower critical solution temperature in the first phase.

49. The emulsion of claim 48, wherein the second portion has an upper critical solution temperature in the first phase.

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50. The emulsion of claim 44, wherein the non-aqueous phase comprises cyclohexane.

51. The emulsion of claim 44 or 50, wherein the non-aqueous phase comprises hexadecane.

30

52. The emulsion of any one of claims 44 and 50-51, wherein the non-aqueous phase comprises silicone oil.

53. The emulsion of any one of claims 44 and 50-52, wherein the non-aqueous phase comprises a fluorinated oil.

54. The emulsion of claim 44, wherein the non-aqueous phase comprises an ionic liquid.

55. The emulsion of any one of claims 44 and 50-53, wherein the non-aqueous phase comprises mineral oil or a fraction of a mineral oil.

56. The emulsion of any one of claims 42-55, wherein the emulsion has a particle concentration of greater than or equal to about 0.3 wt% and less than or equal to about 1.2 wt%.

57. The emulsion of any one of claims 42-56, wherein the emulsion has a particle concentration of greater than or equal to about 0.3 wt% and less than or equal to about 0.5 wt%.

58. The emulsion of any one of claims 42-45 and 47-57, wherein the emulsion has an electrolyte concentration of greater than or equal to about 0.1 API Brine and less than or equal to about 1 API Brine.

59. The emulsion of any one of claims 42-45 and 47-58, wherein the emulsion has an electrolyte concentration of greater than or equal to about 0.9 API Brine and less than or equal to about 1.1 API Brine.

60. The emulsion of claim 48, wherein the second portion comprises a polyzwitterion.

61. The emulsion of claim 60, wherein the polyzwitterion comprises poly(sulfobetaine methacrylamide).

62. The emulsion of any one of claims 42-61, wherein the particle has an elastic modulus of at least about 1 GPa.

63. The emulsion of any one of claims 42-62, wherein the particle has a density of at least about 1.01 g/cm³.

64. The emulsion of any one of claims 42-63, wherein the polymer is attached to the particle by the first portion.

5 65. The emulsion of any one of claims 48-49 and 60-61, wherein the first portion has a lower critical solution temperature in aqueous solution.

66. The emulsion of any one of claims 48-49, 60-61, and 65, wherein the first portion has a lower critical solution temperature of greater than or equal to about 32 degrees Celsius and
10 less than or equal to about 50 degrees Celsius in the first phase.

67. The emulsion of any one of claims 48-49, 60-61, and 65-66, wherein the first portion has a lower critical solution temperature of greater than or equal to about 40 degrees Celsius and less than or equal to about 44 degrees Celsius in the first phase.

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68. The emulsion of claim 49, wherein the second portion has an upper critical solution temperature in aqueous solution.

69. The emulsion of claim 49 or 68, wherein the second portion has an upper critical
20 solution temperature of greater than or equal to about 4 degrees Celsius and less than or equal to about 20 degrees Celsius in the first phase.

70. The emulsion of any one of claims 49 and 68-69, wherein the second portion has an upper critical solution temperature of greater than or equal to about 14 degrees Celsius and
25 less than or equal to about 18 degrees Celsius in the first phase.

71. The emulsion of any one of claims 42-70, wherein the polymer is a block copolymer.

72. The emulsion of claim 71, wherein the block copolymer comprises a first block
30 comprising the first portion and a second block comprising the second portion.

73. The emulsion of claim 71 or 72, wherein the block copolymer is attached to the particle by the first block.

74. The emulsion of any one of claims 48-49 and 60-61 and 65-67, wherein the first portion comprises a poly(N-alkyl methacrylamide).

5 75. The emulsion of claim 74, wherein the poly(N-alkyl methacrylamide) comprises poly(N-isopropyl methacrylamide).

76. The emulsion of any one of claims 48-49 and 60-61 and 65-67, wherein the first portion comprises a poly(N-alkyl acrylamide).

10 77. The emulsion of claim 74 or claim 75, wherein the first portion further comprises a polysilane.

78. The emulsion of claim 77, wherein the polysilane comprises poly(gamma-(trimethoxysilyl) propyl methacrylate).

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79. The emulsion of any one of claims 48-49 and 65-67, wherein the first portion comprises poly(ethylene glycol methacrylate).

20 80. The emulsion of claim 76, wherein the poly(N-alkyl acrylamide) comprises poly(N-isopropyl acrylamide).

81. The emulsion of any one of claims 48-49 and 60-61 and 65-67 and 77-78, wherein the first portion comprises poly(2-(dimethylamino)ethyl methacrylate).

25 82. The emulsion of claim 73, wherein the first block is attached to the particle by siloxane conjugation.

83. The emulsion of any one of claims 42-82, wherein the polymer is a random copolymer.

30

84. The emulsion of any one of claims 42-82, wherein the polymer is a gradient copolymer.

85. The emulsion of any one of claims 42-84, wherein the particle is a spherical particle.

86. The emulsion of any one of claims 42-85, wherein the particle comprises silica.
87. The emulsion of any one of claims 42-86, wherein the particle comprises iron oxide.
- 5 88. The emulsion of any one of claims 42-87, wherein the particle comprises graphene.
89. The emulsion of any one of claims 42-88, wherein the particle comprises magnetite.
- 10 90. The emulsion of any one of claims 42-89, wherein the particle comprises gold.
91. The emulsion of any one of claims 42-90, wherein the particle comprises polystyrene.
92. The emulsion of any one of claims 42-91, wherein the particle has a largest cross-
15 sectional dimension of greater than or equal to about 1 nm and less than or equal to about 40 nm.
93. The emulsion of any one of claims 42-92, wherein the particle has a largest cross-
20 sectional dimension of greater than or equal to about 10 nm and less than or equal to about 25 nm.
94. The emulsion of any one of claims 42-93, wherein the first portion comprises a polymer and the second portion comprises a polymer.
- 25 95. The emulsion of any one of claims 42-94, wherein the mole ratio of repeat units of the first portion to repeat units of the second portion is greater than or equal to about 1:5 and less than or equal to about 1:2.
96. The emulsion of any one of claims 42-95, wherein the polymer has a solvated length
30 in the first phase of greater than or equal to about 1 nm and less than or equal to about 40 nm.
97. The emulsion of any one of claims 42-96, wherein the material has a solvated diameter in the first phase of greater than or equal to about 25 nm and less than or equal to about 40 nm.

98. The emulsion of any one of claims 42-97, wherein the polymer has a solvated length in the first phase of greater than or equal to about 0.5 times and less than or equal to about 1.5 times the largest cross-sectional dimension of the particle.

5

99. A method, comprising:
destabilizing an emulsion by changing the temperature of the emulsion from a first temperature to a second temperature, wherein
the first temperature is greater than the second temperature.

10

100. The method of claim 99, wherein the emulsion comprises the emulsion of any one of claims 42-98.

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101. The method of claim 100, wherein the stabilizing agent is soluble at greater than or equal to about 0.0001 g/mL in at least one of the first phase and the second phase at the second temperature.

20

102. The method of any one of claims 99-101, wherein the first temperature is greater than or equal to about 32 degrees Celsius and less than or equal to about 80 degrees Celsius.

103. The method of any one of claims 99-102, wherein the first temperature is greater than or equal to about 60 degrees Celsius and less than or equal to about 70 degrees Celsius.

25

104. The method of any one of claims 99-103, wherein the second temperature is greater than or equal to about 10 degrees Celsius and less than or equal to about 25 degrees Celsius.

105. The method of any one of claims 99-104, wherein the second temperature is greater than or equal to about 20 degrees Celsius and less than or equal to about 25 degrees Celsius.

30

106. The method of any one of claims 99-105, wherein the emulsion phase separates into a destabilized state in less than or equal to about 230 minutes.

107. The method of any one of claims 99-106, wherein the emulsion phase separates into a destabilized state in less than or equal to about 100 minutes.

108. The method of any one of claims 99-107, further comprising cycling the emulsion between a stabilized state and a destabilized state greater than or equal to about 4 times.

5 109. The method of any one of claims 99-108, wherein the normalized transmittance of an aqueous phase of the emulsion in a destabilized state, after cycling the emulsion greater than or equal to about 4 times, of greater than or equal to about 80%.

110. A method, comprising:

10 exposing an emulsion to a first temperature to destabilize the emulsion, wherein the critical micelle temperature of the emulsion is greater than the first temperature.

111. The method of claim 110, wherein the critical micelle temperature of the emulsion is greater than or equal to about 32 degrees Celsius and less than or equal to about 50 degrees
15 Celsius.

112. The method of any one of claims 110-111, wherein the emulsion comprises the emulsion of any preceding claim.

20 113. The method of claim 112, wherein the stabilizing agent is soluble at greater than or equal to about 0.0001 g/mL in at least one of the first phase and the second phase below the critical micelle temperature.

114. The method of any one of claims 110-113, wherein the first temperature is greater
25 than or equal to about 10 degrees Celsius and less than or equal to about 25 degrees Celsius.

115. The method of any one of claims 110-114, wherein the first temperature is greater than or equal to about 20 degrees Celsius and less than or equal to about 25 degrees Celsius.

30 116. The method of any one of claims 110-115, wherein the emulsion phase separates into a destabilized state in less than or equal to about 230 minutes.

117. The method of any one of claims 110-116, wherein the emulsion phase separates into a destabilized state in less than or equal to about 100 minutes.

118. The method of any one of claims 110-117, comprising exposing the emulsion to a second temperature before exposing the emulsion to the first temperature.

5 119. The method of claim 118, wherein the second temperature is greater than the critical micelle temperature of the emulsion.

120. The method of any one of claims 110-119, wherein the second temperature is greater than or equal to about 32 degrees Celsius and less than or equal to about 80 degrees Celsius.

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121. The method of any one of claims 110-120, wherein the second temperature is greater than or equal to about 60 degrees Celsius and less than or equal to about 70 degrees Celsius.

122. The method of any one of claims 110-121, further comprising cycling the emulsion
15 between a stabilized state and a destabilized state at least about 4 times.

123. The method of claim 122, wherein the normalized transmittance of an aqueous phase of the emulsion in a destabilized state, after cycling the emulsion greater than or equal to about 4 times, is greater than or equal to about 80%.

20

124. A method of enhanced oil recovery, comprising:
delivering a first composition comprising a material of any preceding claim into an oil and/or gas well; and
withdrawing a second composition comprising an aqueous phase, an oil phase, and
25 the material from the oil and/or gas well.

125. The method of claim 124, comprising injecting into said oil and/or gas well a first composition comprising said material dissolved in an aqueous medium in which the material is soluble or substantially soluble below its LCST, at an injection temperature between 0
30 degrees Celsius and 40 degrees Celsius, wherein the material has a lower critical solution temperature higher than the injection temperature by from 5 degrees Celsius to 30 degrees Celsius.

126. The method of claim 125, wherein the injection temperature is between 10 degrees Celsius and 30 degrees Celsius.

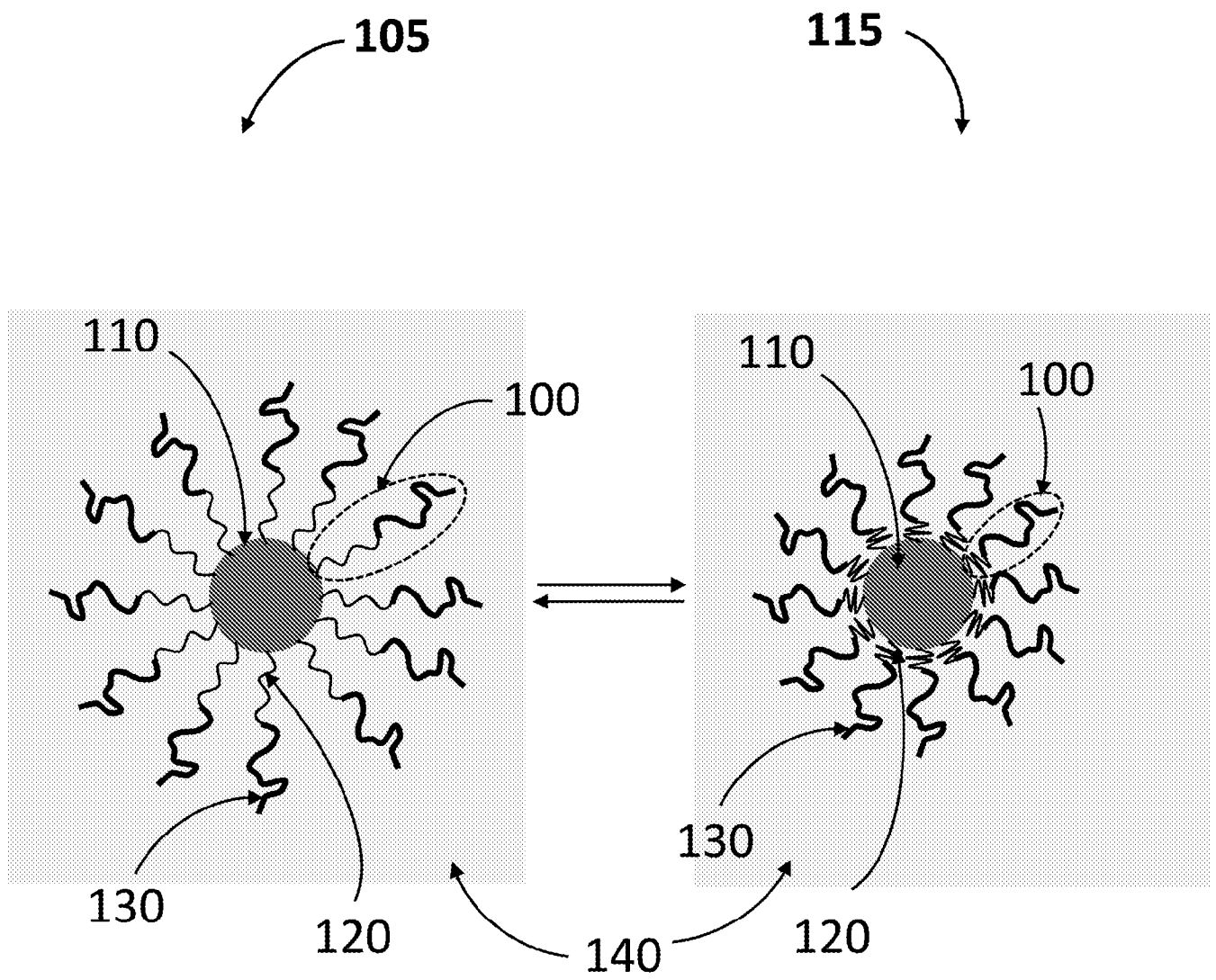


FIG. 1

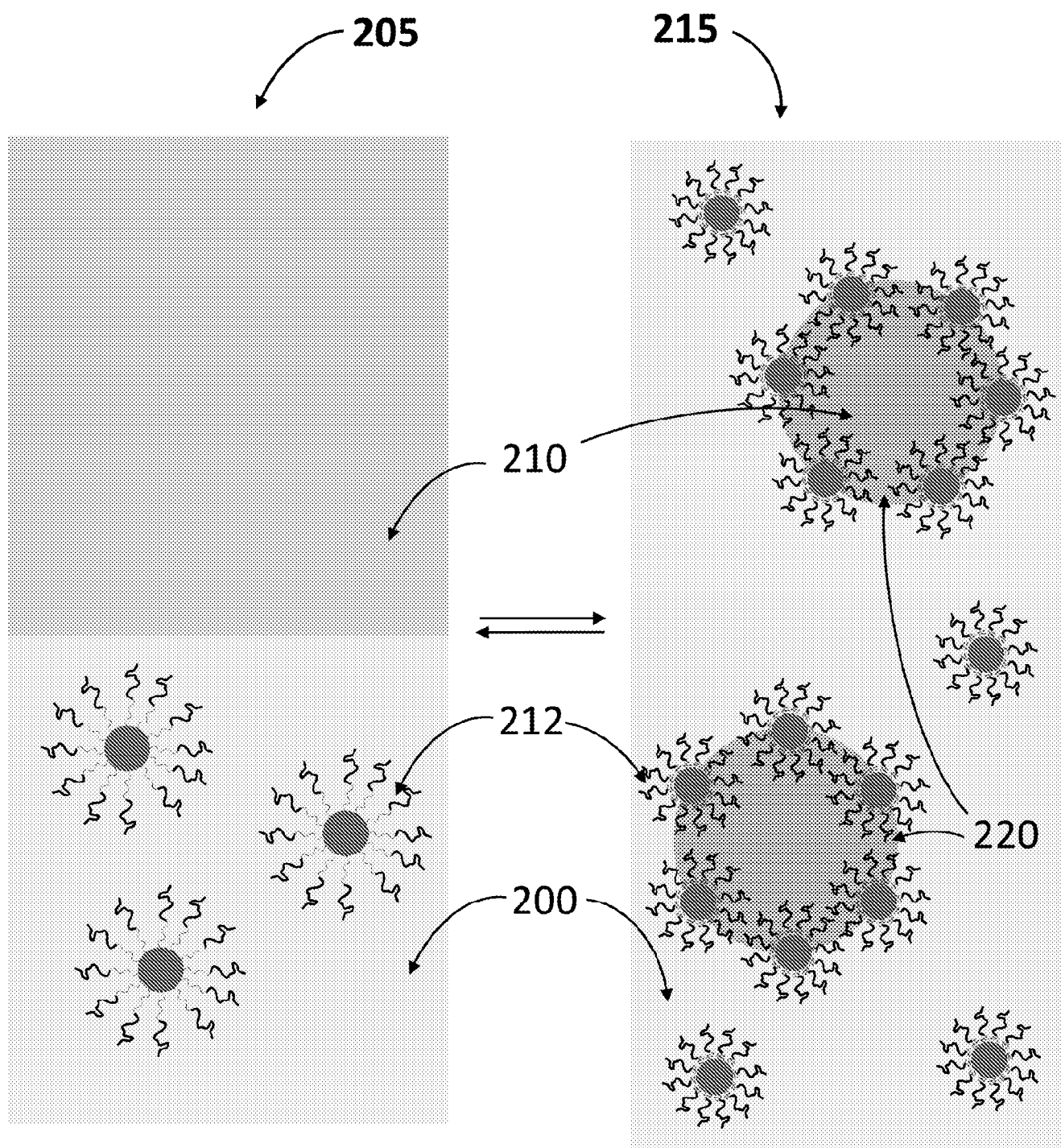


FIG. 2

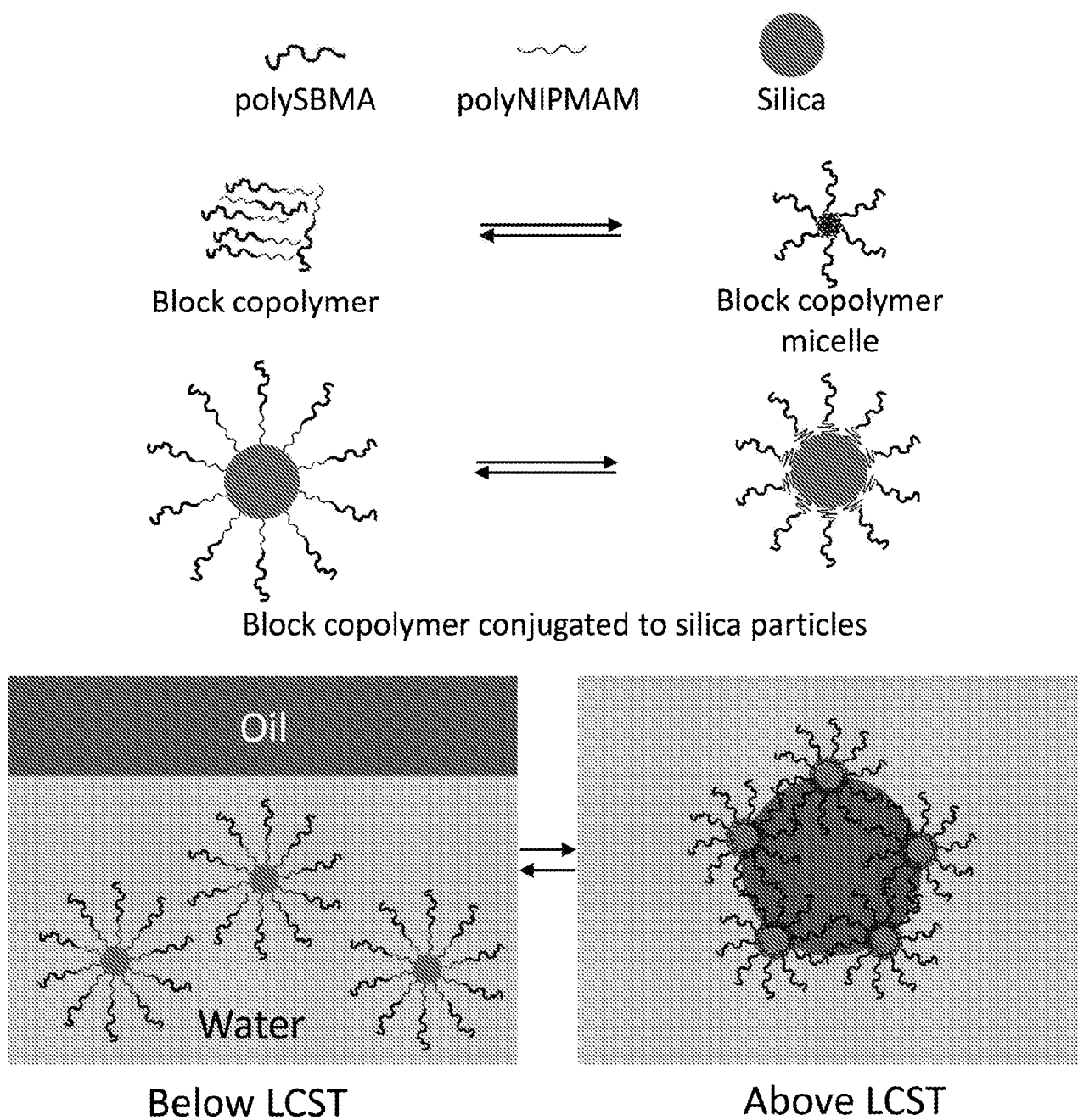


FIG. 3

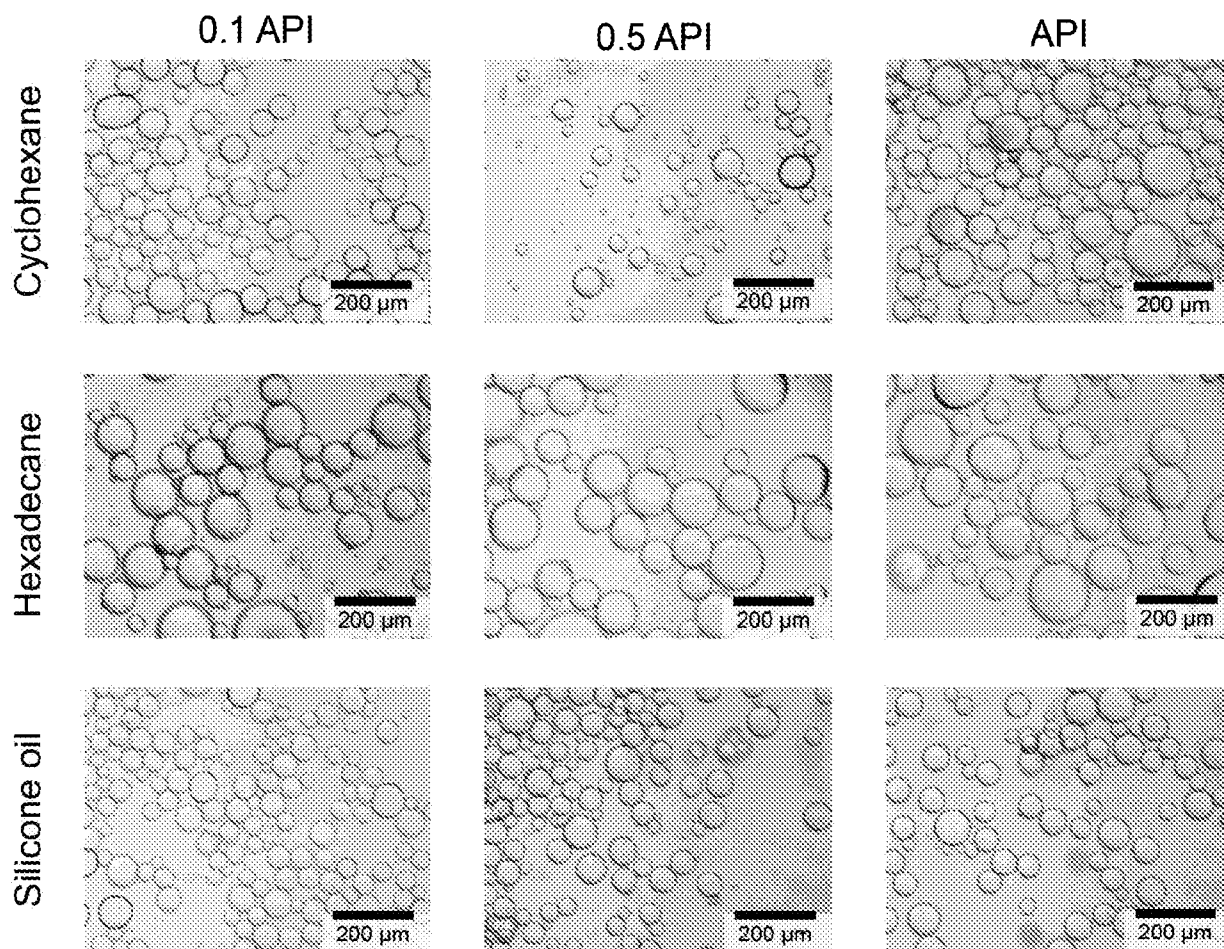


FIG. 4

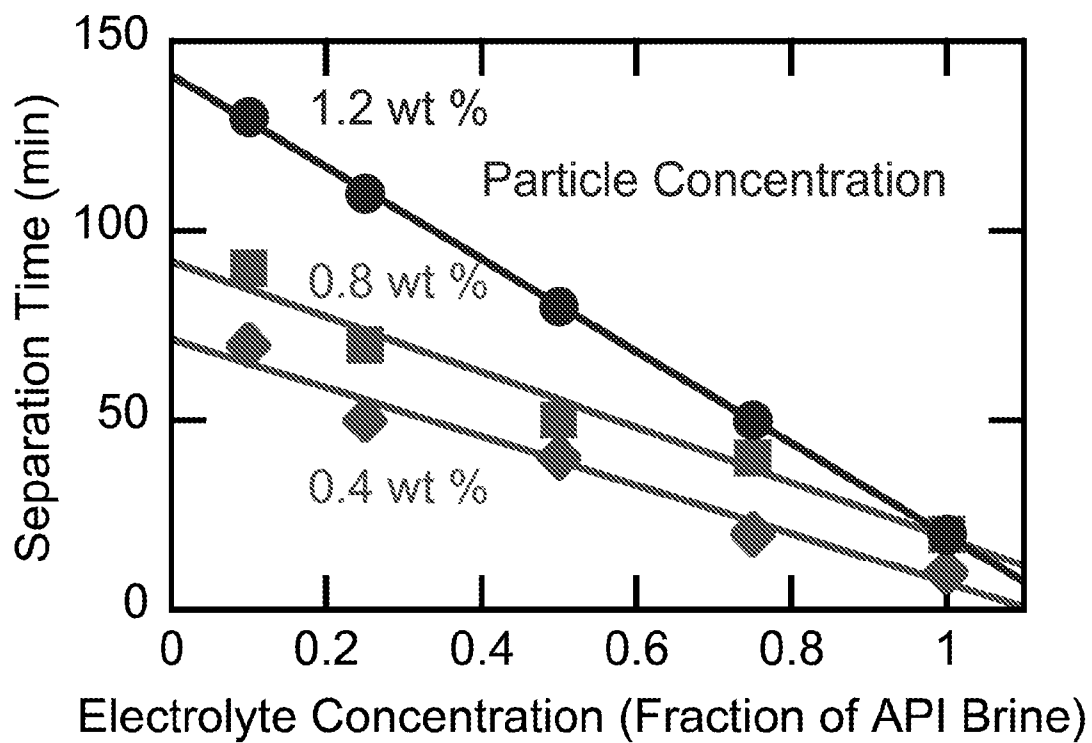


FIG. 5

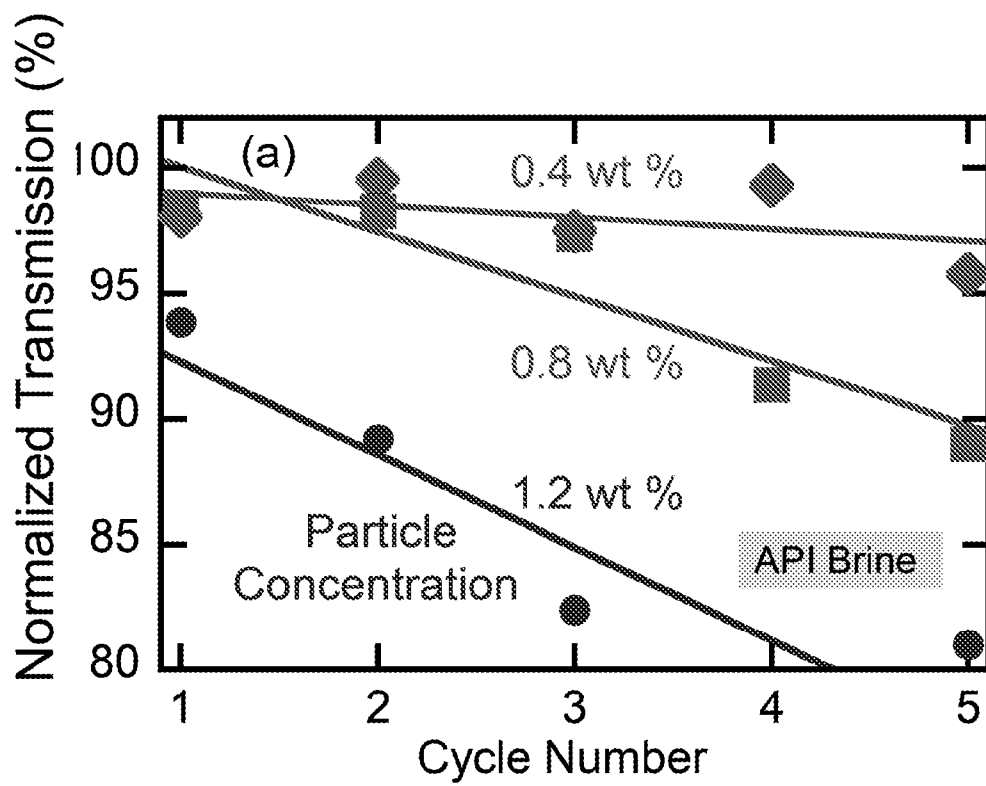


FIG. 6A

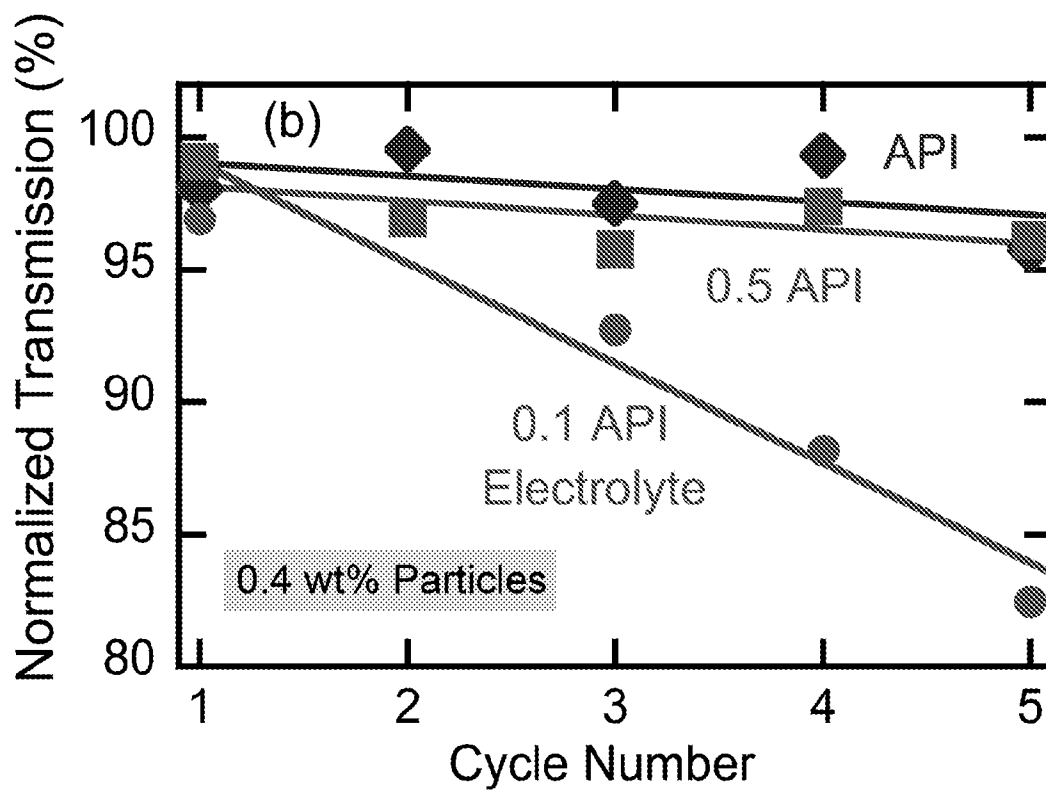


FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/034089

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/58 C09K8/88 C09K8/92
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)
C09K

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, COMPENDEX, INSPEC, 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	WO 2016/040921 A1 (MASSACHUSETTS INST TECHNOLOGY [US]) 17 March 2016 (2016-03-17) claims; examples	1-41, 124-126
X	----- MIKHIL RANKA ET AL: "Responsive Stabilization of Nanoparticles for Extreme Salinity and High-Temperature Reservoir Applications", ACS APPLIED MATERIALS & INTERFACES, vol. 7, no. 35, 27 August 2015 (2015-08-27), pages 19651-19658, XP055490744, US ISSN: 1944-8244, DOI: 10.1021/acsami.5b04200 page 19652 - page 19657; figures ----- -/--	1-41

☒ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

6 July 2018

Date of mailing of the international search report

14/09/2018

Name and mailing address of the ISA/

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Authorized officer

Doslik, Natasa

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/034089

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ROGER J. COULSTON ET AL: "Supramolecular gold nanoparticle-polymer composites formed in water with cucurbit[8]uril", CHEMICAL COMMUNICATIONS, vol. 47, no. 1, 1 January 2011 (2011-01-01), pages 164-166, XP055490595, ISSN: 1359-7345, DOI: 10.1039/C0CC03250F page 164 - page 165 -----	1,33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/034089

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-41, 124-126

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-41, 124-126

The first group discloses a material comprising a particle coated/functionalized with polymers and its application in EOR.

2. claims: 42-98

The second group discloses an emulsion comprising a first phase, a second phase and a stabilizing agent comprising a polymer attached to a particle.

3. claims: 99-109

The third group discloses a method comprising destabilizing an emulsion by changing the temperature.

4. claims: 110-123

The fourth group discloses a method comprising exposing an emulsion to a temperature.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/034089

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016040921 A1	17-03-2016	US 2017283537 A1 WO 2016040921 A1	05-10-2017 17-03-2016
