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(54) Title: FUNCTIONAL POLYMER FOR ENHANCED OIL RECOVERY

(57) Abstract: The present invention relates compositions and methods for enhanced oil recovery. The method is directed to employing a water-soluble fThe present invention relates compositions and methods for enhanced oil recovery (EOR). The method is directed to employing a water-soluble functional polymeric surfactant (FPS), with a medium IFT value, preferably ranged from about 0.1 to about15 dyne/cm between water phase containing polymeric surfactant and hydrocarbon phase, for recovery of hydrocarbons from subterranean formations. The FPS solution demonstrates a strong interaction with oil and the great potential to increase both volumetric sweep efficiency and microscopic displacement efficiency in EOR.

FUNCTIONAL POLYMER FOR ENHANCED OIL RECOVERY

RELATED APPLICATION

The present application claims the priority to U.S. Provisional Application No. 60/853,468, filed October 23, 2006, which is hereby incorporated by reference in its entirety including drawings as fully set forth herein.

FIELD OF THE INVENTION

The present invention relates to the field of oil production. Particularly, the present invention relates to enhanced oil recovery by using functional surfactant polymers.

BACKGROUND OF THE INVENTION

Primary recovery of hydrocarbon (e.g., oil) from a hydrocarbon-bearing (e.g., oil-bearing) reservoirs relies upon the use of natural energy present in the reservoir as the main source of energy for the displacement of oil to production wells. Usually, however, this process merely recovers a minor portion of the original oil in place (OOIP). Thus, a variety of supplemental recovery techniques have been employed in order to increase the recovery of oil from subterranean reservoirs.

The viability of an oil recovery displacement process depends on two important factors: volumetric sweep efficiency and microscopic displacement efficiency. Enhanced oil recovery (EOR) processes are usually employed to involve the injection of a fluid or fluid of some type into a reservoir. The injected fluids and injection processes supplement the natural energy present in the reservoir to displace oil to a producing well. In addition, the injected fluids interact with the reservoir rock and oil system to create conditions favorable for oil recovery. The mobility control process and chemical process are two commonly used EOR processes.

The widely applied mobility control process is the polymer flood. In a typical application, the polymer solutions are designed to develop a favorable mobility ratio between the injected polymer solution and the oil/water bank being displacement ahead of the polymer. The purpose is to develop a uniform volumetric sweep of the reservoir, both vertically and areally, in order to prevent water from fingering by the oil and moving by the shortest path to the production well. A number of polymer projects have been implemented since 1960's. However, the mobility control process alone does not employ the microscopic displacement efficiency and suffers the low recovery efficiency, thus the incremental oil recovery is limited, usually under 10% OOIP of oil recovery. Manning et al. analyzed statistical data of the fieldwide projects, the median recovery of oil was 2.91% OOIP (1983, Report DOE/ET/10327-19). Schurz et al. summarized results from 99 projects initiated during 1980-1989 and the projected median incremental oil recovery ranges between 3.7% and 4.8% (1989, NMT 890029, New Mexico Tech Centennial Symposium). Gogarty et al discussed about much of incremental recovery by polymer flooding is the result of accelerated oil production before the economic limit is reached (1967, SPE 1566-A, pp. 149-160).

Chemical processes involve the injection of specific liquid chemicals that efficiently displace oil because of the phase behavior properties, which result in decreasing the interfacial tension (IFT) between the displacing liquid and oil. The surfactant/polymer process has been demonstrated to have the potential in application in enhanced oil recovery. In this process, the primary surfactant slug, a micellar solution, is followed by a mobility buffer, a solution that contains polymer which is often graded in concentration, becoming more dilute in polymer as more of the solution is injected. The recovery efficiency primarily uses a displacing fluid that has an ultra low IFT with the displaced oil. Green et al. specifically disclosed that the IFT of displacing fluid must be reduced to ultra low, about 10^{-3} dyne/cm, before a large reduction in the waterflood residue oil saturation is achieved (1998, ISBN 1-55563-077-4, SPE Textbook Series Vol. 6, pp. 35). There are drawbacks, however. The chemical solutions for generating ultra low IFT, which need to contain surfactant, cosurfactant, and sometimes oil, electrolytes, and

alkaline, are usually complicated and expensive, and may suffer chromatographic separation during the EOR operation.

Since the pioneering concept of polymeric soap published by Strauss et al. in 1951, there has been a vast amount of literature published on the polymerization of or in organized amphiphilic assemblies. To some extent, polymeric surfactants serve all the same functions as low molecular weight surfactants. Because of their high molecular weight and complex structures, however, they have some unique characteristics. For example, formation of monomolecular micelles in the dilute solution, various shapes of micelles at different concentrations, etc. Applications such as emulsion stabilizers in submicronic colloidal systems also have been published. Polymeric surfactants are a very attractive class of compounds since the presence of macromolecular chains at the surface of colloidal particles offer significant advantages. This combination of rheological features (e.g. thickening properties) and unique phase behavior properties has broad potential applications in super absorbency, latex paints, hydraulic fluids, flocculation, protein separation, controlled drug release, and biological and medical devices. However, there is only very few literature which explored the use of polymeric surfactant for enhance oil recovery.

The common theory of chemical processes believes that the microscopic displacement efficiency largely determines the residual oil saturation remaining in the reservoir rock at the end of the process, which is one of the key criteria in evaluating the success or failure of a chemical EOR process. Capillary and viscous forces govern phase trapping and mobilization of fluids in porous media and thus microscopic displacement efficiency. Green et al. studied the capillary number $N_{ca} = (v\mu_w)/\delta_{ow}$, wherein the N_{ca} = capillary number, v = interstitial velocity, μ_w = displacing phase viscosity, and δ_{ow} = the IFT between the displacing and displaced phases (1998, ISBN 1-55563-077-4, SPE Textbook Series Vol. 6, pp. 22). It has been widely accepted in the art that the residue oil saturation cannot be largely reduced unless the δ_{ow} becomes ultra low at 10^{-3} dyne/cm level. Therefore, attempts of design polymeric surfactant have so far be concentrated on selecting the polymeric surfactant or preparing the polymer surfactant-containing solution

with co-surfactant or other additives to generate low or ultra low IFT value between the oil and water phase.

For example, in early 80s, Chen et al. (1981, US Pat No. 4,284,517, 1982, US Pat No. 4,317,893) disclosed a method for the recovery of oil from a subterranean oil reservoir penetrated by spaced injection and production systems in which an aqueous fluid containing polymeric surfactant is introduced into reservoir via injection system to displace oil to said production system. Chen et al. specifically emphasized that the interfacial tension between oil and water should be less than 0.1 dyne/cm (e.g., a preferred the oil-water IFT having a value of 0.005 dyne/cm or less) in order to reach an optimum microscopic displacement efficiency.

Cao et al. (2002, European Polymer Journal, 38 (7), pp. 1457-1463) identified a novel family of polymeric surfactants which might have potential for enhance oil recovery. The novel series of polymeric surfactants is based on carboxy methyl cellulose and alkyl poly (etheroxy) acrylate. The IFT properties of this kind of polymeric surfactant change little with NaCl added. The formed micelles shrink, their size becomes smaller. Alcohols cause the IFT to decrease a little because a small amount of free chains present in solution. Under the influence of added alkali, the IFT of the polymeric surfactants, in aqueous solution, decreases to the level of less than 10^{-2} dyne/cm.

Influenced by the conventional wisdom of employing ultra low IFT displacing fluid in the chemical processes, even though the hydrophically modified water-soluble copolymers have recently attracted a great deal of interest, the attempt of using polymeric surfactant for the EOR application is mainly aimed at how to generate efficient and stable viscosity to improve the sweep efficiency as mobility controllers. McCormick et al conducted a coordinated, fundamental research program in lab with the ultimate goal of developing "smart" multi-functional polymers that can respond in situ to stimuli and result in significantly improved sweep efficiency in EOR processes (2004, 2005, DOE Report, Award Number DE-FC26-03NT15407). McCormick et al. merely investigated the improvement of sweep microscopic displacement efficiency and phase behavior of

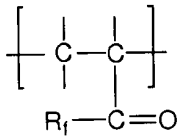
polymeric surfactants compared to polymers, but did not disclose the use of polymeric surfactants with oil-water with IFT values more than of 0.1 dyne/cm in EOR.

Contrary to the conventional wisdom, it is unexpectedly discovered that the polymeric surfactants with medium range oil-water IFT value, e.g., no less than about 0.1 dyne/cm (e.g., preferably ranged from about 0.1 to about 15 dyne/cm) have both volumetric sweep efficiency and microscopic displacement efficiency and can be used for hydrocarbon recovery from subterranean formation.

SUMMARY OF THE INVENTION

One aspect of the present invention relates to a method for recovering hydrocarbon from a hydrocarbon-bearing subterranean reservoir or formation by injecting into the reservoir or formation a displacing solution containing a functional polymeric surfactant which has an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm.

Another aspect of present invention relates to functional polymeric surfactants which have a partially hydrolyzed polyacrylamide backbone and a repeating monomer unit having the following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

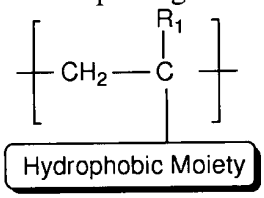


(Formula (1))

R_f = -NH_2, -ONa, -OR_L, -NHR_L, -R_LSO_3Na, -$(EO)_a(PO)_bR_L$, quaternary ammonium surfactant moiety, bis-ammonium Gemini surfactant moiety, -R_LSH, and the like, PO represents –CH2-CH(CH3)-O-, EO represents –CH2-CH2-O-, wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof), and a+b is an integer from 6 to 30.

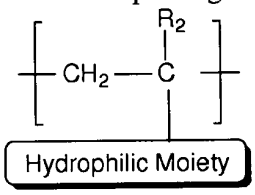
Another aspect of present invention relates to functional polymeric surfactants which comprise a first repeating monomer unit and a second repeating monomer unit having the following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating monomer unit with a hydrophobic moiety



(Formula (2))

a second repeating monomer unit with a hydrophilic moiety

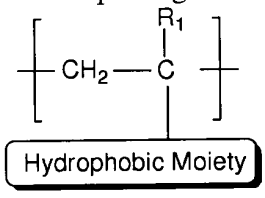


(Formula (3)

wherein R_1 and R_2 are hydrogen or C_1 –C_4 alkyl respectively.

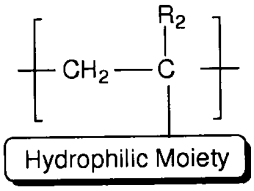
Another aspect of the present invention relates to functional polymeric surfactants comprising three repeating monomer units (a first repeating unit, a second repeating unit, and a third repeating unit) having the following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating monomer unit with a hydrophobic moiety



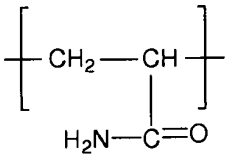
(Formula (2))

a second repeating monomer unit with a hydrophilic moiety



(Formula (3))

a third repeating monomer unit

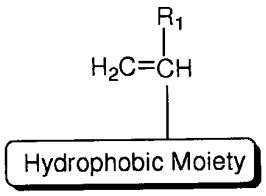


(Formula (4))

wherein R_1 and R_2 are hydrogen or C_1 –C_4 alkyl respectively.

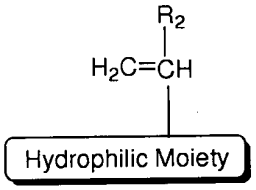
Another aspect of the present invention relates to functional polymeric surfactants comprising a polymeric reaction product of the following three repeating monomers, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating monomer:



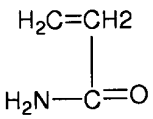
(Formula (5)

a second repeating monomer:



(Formula (6))

a third repeating monomer:



(Formula (7))

wherein R_1 and R_2 are hydrogen or C_1 –C_4 alkyl respectively.

DETAILED DESCRIPTION OF THE INVENTION

To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meaning as commonly understood by a person of ordinary skill in the area relevant to the present invention. Terms such as "a", "an", "the" are not

intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims.

As used herein, the term "reservoir condition" refers to the temperature, pressure, salinity, and other conditions that are commonly found in subterranean formation.

As used herein, the term "polymer" refers to a molecule of molecular weight of at least 1000 grams/mole, the structure of which essentially includes the multiple repetitions of units derived, actually or conceptually, from molecules of low relative molecular mass.

As used herein, the term "copolymer" or "heteropolymer" refers to a polymer derived from two or more monomeric species, as opposed to a homopolymer where only one monomer species is used.

As used herein, the term "polymeric" refers to including a polymer.

As used herein, the term "surfactant" refers to a surface-active material.

As used herein, the term "unit" refers to the moiety or building block in the polymer molecule. A unit in a polymer is covalently linked to another unit of the same structure or of a different structure.

As used herein, the term of "polymeric surfactant" refers to any polymer with the ability as a mobility control polymer but also has ability to form emulsion.

As used herein, the terms of "functional polymeric surfactant" or "FPS" refers to a polymeric surfactant, with oil-water IFT in the range from about 0.1 to about15 dyne/cm (e.g., about 0.1 to about 12.5 dyne/cm, about 0.1 to about 10 dyne/cm), that can provide

both viscosity for mobility control and the ability to form "Emulsion" between oil and water under reservoir conditions, and should be a candidate for EOR chemical process.

As used herein, the term of "mobility control" refers to the solution viscosity of a polymeric surfactant is greater than water, most of time; the viscosity is equal or greater than the viscosity of the oil need to be recovered under reservoir condition.

As used herein, the term "emulsion" refers to heterogeneous systems of an oil and water phase, include micellar, microemulsion, miscible phase, thermodynamic instable emulsion, double emulsion, and multiple emulsions.

As used herein, the term "interaction" refers to the interaction between the polymeric surfactant solution and oil with the tendency to form emulsion.

As used herein, the term "enhanced oil recovery" or "EOR" refers to the process which usually involves the injection of a fluid or fluid of some type into a subterranean reservoir or formation. The injected fluids and injection processes supplement the natural energy present in the reservoir to displace oil to a producing well. In addition, the injected fluids interact with the reservoir rock and oil system to create conditions favorable for oil recovery displacement. After the waterflood to irreducible oil saturation, the typical EOR process can yield 5-25% of Original Oil In Place (OOIP) as the incremental oil recovery. Moreover, the EOR process can also been implemented wherein the waterflood has not yet reached the irreducible oil saturation.

As used herein, the term "Subterranean Formation" or "Subterranean Reservoir" refers to a place where the crude hydrocarbons found in reservoirs forms in the Earth's crust. It exists anywhere from 1,000 to 30,000 ft below the surface and has a variety of shapes, sizes and ages. The subterranean formation may have been exposed to water injection, polymer flood or chemical processes.

As used herein, the term "displacing fluid" or "displacing solution" refers to an aqueous fluid used for enhanced oil recovery in subterranean formation.

Conventional wisdom believes the emulsion is contributed by low IFT and thus leads to the searching of ultra low IFT (10^{-4} to 10^{-2} dyne/cm between the displacing fluid and oil) to form emulsion with oil for efficient micellar/polymer flood. However, the present invention demonstrates the unexpected testing results, suggesting that the polymeric surfactants with medium oil-water IFT (0.1 dyne/cm or higher) can also efficiently emulsify oil and be used for EOR chemical processes based on the coreflood tests and field tests

Without being bound to any theory, since the functional polymeric surfactants according to the present invention can not only yield viscosity as a mobility controller, but also efficiently emulsify oil, the requirement of low or ultra low IFT as commonly recognized in the art may not be applicable to the functional polymeric surfactants. The use of FPS with only small IFT reduction, as single primary agent for EOR chemical process, may provide a game change technology for future enhance oil recovery since one can design hundreds of new FPS for cost effective EOR process based on the disclosure in the present invention.

Due to its unexpected feature, the FPS for the EOR chemical processes described in present invention disclosure not only serves as a polymer for mobility control but also a pseudo surfactant which can form emulsions under reservoir conditions. The FPS can achieve both volumetric sweep efficiency and microscopic displacement efficiency. The key features of FPS in the water flood for EOR will have following properties: (1) The FPS water solution will increase the apparent viscosity to lower the water mobility; (2) FPS may be able homogenize permeability by selective adsorption and mechanical entrapment of FPS on the rock; (3) FPS may also have certain degree of viscoelaticity effects, and (4) FPS is a surface active agent which lowers oil-water IFT.

Accordingly, one aspect of the present invention is directed to a new and improved oil recovery process wherein a displacing fluid comprising a functional polymeric surfactant with medium oil-water IFT value is injected to hydrocarbon-bearing subterranean formation.

In one embodiment, the IFT value is about 0.1 to about 15 dyne/cm, preferably, about 0.1 to about 10 dyne/cm, more preferably about 0.5 to about 10 dyne/cm. The IFT value can be measured by a method known in the art. In the present invention, the IFT value is measured as follows. An oil phase (e.g., n-heptane) and an aqueous phase (e.g., the FPS solution in 3% NaCl) were mixed at 86 F using a spinning drop interfacial tensiometer: The interfacial tension between the two phases was measured as a function of time, usually for 2 hours. The measurement was recorded if the values vary within 1-2% variation for a period of 20 minutes .

In another embodiment, the concentration of the functional polymeric surfactant in the displacing solution or fluid ranges from about 20ppm to about 10,000ppm, from about 100ppm to about 6000ppm, from 200ppm to about 3000ppm, from about 300ppm to about 1500ppm.

In another embodiment, the subterranean formation or reservoir contain remaining hydrocarbon (e.g. oil) after the displacement of original oil to producing wells through natural energy. In addition, the subterranean formation may have been water-flooded and reached the irreducible water saturation. Further, the subterranean formation may have been subject to a chemical process and deemed as unrecoverable.

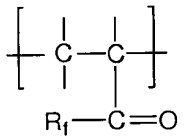
In another embodiment, the displacing solution is delivered to the subterranean formation through an injection system (e.g., an injection well) and the hydrocarbon (e.g., oil) is recovered through a production system (e.g., a production well). In certain embodiment, the injection well is the same as the production well. For example, in the "huff and puff" method, a FPS solution is injected via a well to the subterranean hydrocarbon-bearing

formation. The injection well is then shut-in for a soaking period, after which it is placed for production.

In another embodiment, the enhance oil recovery method using the FPS renders typically about 5-30% OOIP, preferably about 10-30% OOIP, preferably about 15-30% OOIP, more preferably 15-25% OOIP.

Another aspect of this invention is directed to a functional polymeric surfactant composition which comprises a variety of different synthetically produced carbon-based and siloxane-based polymeric surfactants, wherein the polymeric surfactant includes at least one hydrophilic monomer unit and at least one hydrophobic monomer unit, with the oil-water IFT value greater than 0.1 dyne/cm. The preferred polymeric surfactants include the functionalized polyacrylamide and the derivatives thereof.

Another aspect of present invention relates to functional polymeric surfactants which have a partially hydrolyzed polyacrylamide backbone and a repeating monomer unit having the following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:



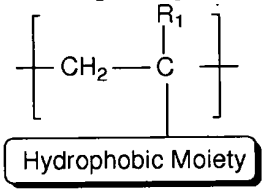
(Formula (1))

R_f = -NH_2, -ONa, -OR_L, -NHR_L, -R_LSO_3Na, -$(EO)_a(PO)_bR_L$, quaternary ammonium surfactant moiety, bis-ammonium Gemini surfactant moiety, -R_LSH, and the like, PO represents –CH2-CH(CH3)-O-, EO represents –CH2-CH2-O-, wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof), and a+b is integer from 6 to 30.

Another aspect of present invention relates to functional polymeric surfactants which comprise a first repeating monomer unit and a second repeating monomer unit having the

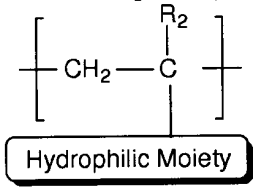
following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating monomer unit with a hydrophobic moiety



(Formula (2))

a second repeating monomer unit with a hydrophilic moiety

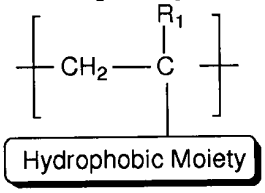


(Formula (3)

wherein R_1 and R_2 are hydrogen or C_1 –C_4 alkyl respectively.

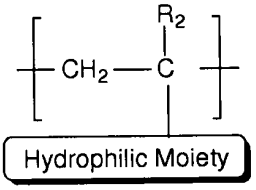
Another aspect of the present invention relates to functional polymeric surfactants comprising three repeating monomer units (a first repeating unit, a second repeating unit, and a third repeating unit) having the following formula, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating monomer unit with a hydrophobic moiety



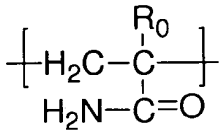
(Formula (2))

a second repeating monomer unit with a hydrophilic moiety



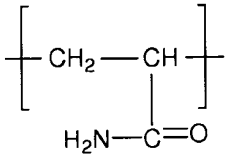
(Formula (3))

a third repeating monomer unit



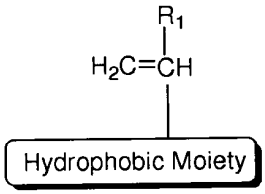
(Formula (4))

wherein R_0, R_1, and R_2 are hydrogen (H) or C_1 –C_4 alkyl respectively. When R_0, is H, the third repeating monomer unit is



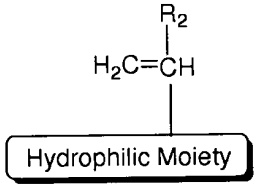
Another aspect of the present invention relates to functional polymeric surfactants comprising a polymeric reaction product of the following three repeating monomers, the FPS having an oil-water IFT value of no less than about 0.1 dyne/cm, preferably about 0.1 to about 15 dyne/cm:

a first repeating hydrophobic monomer:



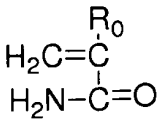
(Formula (5)

a second repeating hydrophilic monomer:



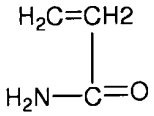
(Formula (6))

a third repeating monomer:



(Formula (7))

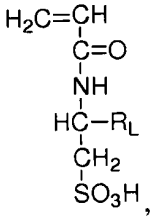
wherein R_0, R_1, and R_2 are hydrogen (H) or C_1 –C_4 alkyl respectively. When R_0 is H, the third repeating monomer is



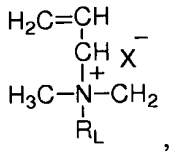
In another embodiment, the hydrophobic moiety is anionic, cationic, nonionic, zwitterionic, betaine, or amphoteric ion pair. In particular, the nonionic moiety is [-COO-alkyl], [-CO-N(X_1)(X_2)], -alkyl, -phenyl, or the derivatives thereof, wherein X_1 = C_3 –C_{30} alkyl; C_1 –C_3 alkyl substituted by 1-3 phenyl, phenyl or C_1 –C_6 cycloalkyl and X_2 = H or C_3 –C_{10} alkyl. The cationic moiety is alkyl group-containing, phenyl group-containing quaternary ammonium salts, or derivatives thereof (salt is selected from the group consisting -CO-CH_2-quaternary ammonium-alkyl group, -CO-NH-quaternary ammonium-alkyl group, bis-ammonium Gemini surfactants, and derivatives thereof).

In another embodiment, the hydrophilic moiety is anionic, cationic, nonionic, zwitterionic, betaine, or amphoteric ion pair. In particular, the nonionic moiety is [-COO-(EO)n-alkyl group], [-COO-(EO)c-fluoroalkyl group], or the derivatives thereof, wherein n is an integer from 6-30, c is an integer from 6-30 and EO represents –CH2-CH2-O-. The anionic moiety is an organic acid salt (e.g., acryl acid, methacrylic acid, maleic acid, itaconic acid, acrylamido methylpropane sulfonic acid, vinylphosphonic acid, styrene sulfonic acid, or derivatives thereof).

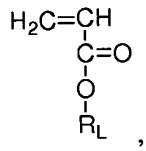
In another embodiment, the hydrophobic monomer is selected from the following:



(Formula (8))

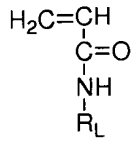


(Formula (9))



(Formula (10))

or

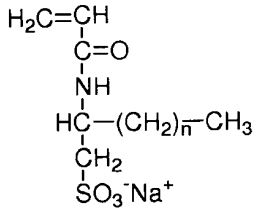


(Formula (11))

wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); and X^- is a Cl^- or Br^-.

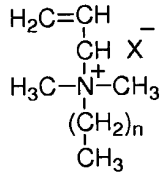
In another embodiment, the hydrophobic monomer is selected from the following:

$CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)_n-CH_3)$,



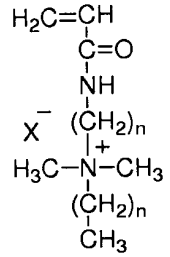
(Formula (12))

$CH_2=CH-CH_2-N^+(CH_3)_2-(CH_2)n-CH_3.\ X^-$,



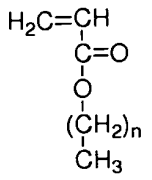
(Formula (13))

$CH_2=CH-CO-NH-(CH_2)_n-N^+(CH_3)_2-(CH_2)_n-CH_3.\ X^-$,



(Formula (14))

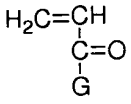
$CH_2=CH-CO-O-(CH_2)_n-CH_3$,



(Formula (15))

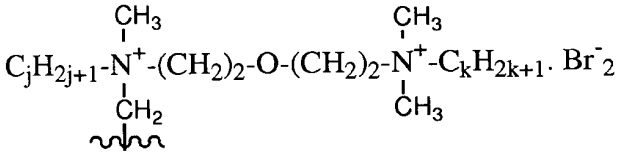
or

CH_2=CH-CO-G;



(Formula (16))

wherein n is an integer from 8 to 20 and $X^- = Cl^-$, Br^-, and G represent a bis-ammonium Gemini surfactant moiety. In particular, G has the following formula:

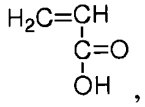


(Formula (17)

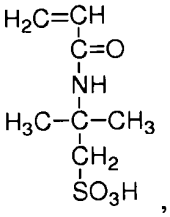
wherein (j + k = 24, j = 12, 13, 14, 16, 18).

In another embodiment, the hydrophilic monomer is selected from the following:

,

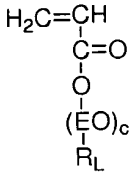


, (Formula (18)



, (Formula (19))

or

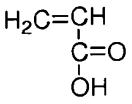


(Formula (20))

wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); EO represents $-CH_2-CH_2-O-$, and c is an integer from 8 to 18.

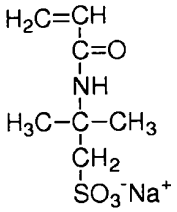
In another embodiment, the hydrophilic monomer is selected from the following:

$CH_2=CH-CO-OH$,



(Formula (21))

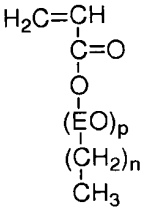
$CH_2=CH-CO-NH-C(CH_3)_2-CH_2SO_3^- Na^+$,



(Formula (22))

Or

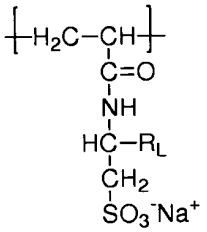
$CH_2=CH-CO-O-(EO)_p-(CH_2)_n-CH_3$,



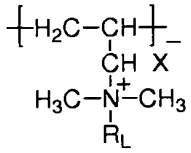
(Formula (23))

wherein n is an integer from 8 to 20; EO represents $-CH_2CH_2O-$, and p is an integer from 6-20.

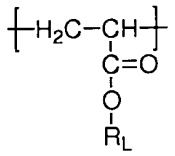
In another embodiment, the repeating hydrophobic monomer unit in a FPS is selected from the following:



(Formula (24))

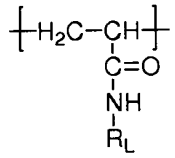


(Formula (25))



(Formula (26))

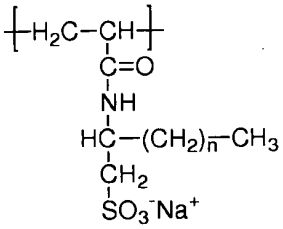
or



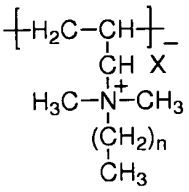
(Formula (27))

wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); and X^- is a Cl^- or Br^-.

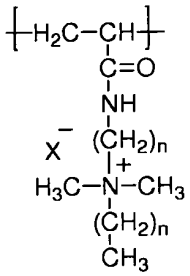
In another embodiment, the repeating hydrophobic monomer unit in a FPS is selected from the following



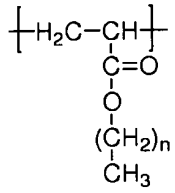
(Formula (28))



(Formula (29))

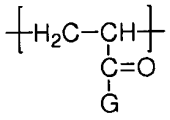


(Formula (30))



(Formula (31))

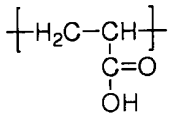
or



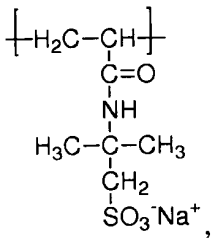
(Formula (32))

wherein n is an integer from 8 to 20 and $X^- = Cl^-$, Br^-, and G represents a bis-ammonium Gemini surfactant moiety. In particular, G has a structure as shown in Formula (17).

In another embodiment, the repeating hydrophilic monomer unit in a FPS is selected from the following:

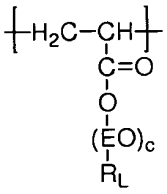


(Formula (33)



(Formula (34))

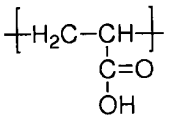
or



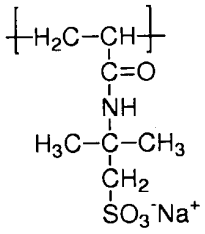
(Formula (35))

wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); EO represents $-CH_2-CH_2-O-$, and c is an integer from 8 to 18.

In another embodiment, the repeating hydrophilic monomer unit is selected from the following:

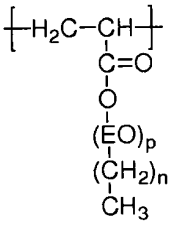


(Formula (36))



(Formula (37))

or



(Formula (38))

wherein n is an integer from 8 to 20; EO represents $-CH_2CH_2O-$, and p is an integer from 6-20.

In another embodiment, the FPS comprises a variety of different biologically produced polymeric surfactants, wherein the biologically produced or synthesized functional polymeric surfactants have the oil-water IFT value greater than 0.1 dyne/cm. Preferred

biological polymeric surfactants include xanthan gum, polysaride, and the derivatives thereof.

Besides the direct reaction between polymer and reactants, examples that use primary amine to react with polymers include succinic anhydride moieties (which may have limitation in both yield and low molecular weight, Hill et al. (1993, Macromolecules, 26, pp. 4521-4532). Other researchers have published numerous papers to introduce various copolymerization approaches. The polymeric surfactants, with medium oil-water IFT, can be prepared by the techniques known in the art, including heterogeneous, inverse emulsion, micro-emulsion, precipitation, and micellar free radical copolymerization processes. The exemplary preparations of polymeric surfactants include free radical initiated copolymerization of hydrophilic group-containing monomers (e.g. acrylamide, acrylacid, poly-alkyleneoxy, or alkylsulfonate acrylate, or mixtures thereof) with hydrophobic group-containing monomers (e.g. alkyl acrylamide, phenyl acrylamide, Gemini quaternary ammonium acrylate, or mixtures thereof). Adjusting the concentration and activity of the initiator, the concentration of monomers, the temperature, and the chain-transfer agents can control the molecular weight of the polyacrylate copolymer, which contains two or more monomeric species.

The skilled artisan, after reviewing the instant disclosure, will recognize that various degree of branching, molecular weight and stereo configuration of the polymeric surfactant unit may also be considered along with chemical constituents (e.g. HLB, functional groups, and ionic nature) to determine the application for EOR chemical processes.

Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be constructed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Example I. The representative examples of FPSs are conducted by the general laboratory methods consist of the following analysis:

1) Phase behavior is analyzed through methods known in the art (See the following references)

a. Reed, R.L. and Healy, R.N.: "Some Physicochemical Aspects of Microemulsion Flooding." Improved Oil Recovery by Surfactant and Polymer Flooding (D.O. Shah and R.S. Schechter, Eds), Academic Press, New York, New York (1977) 383-437.

b. Healy, R.N. and Reed, R.L.: "Physicochemical Aspects of Mictoremulsion Flooding," Transactions, AIME, Volume 257 (1974) 491-501.

c. Dreher, K.D. and Jones, S.C.: "An Approach to the Design of Fluids for Microemulsion Flooding," Solution Chemistry of Surfactants, Volume 2 (K.L. Mittal, Editor), Plenum Publishing Corporation (1979).

d. Healy, R.N., Reed, R.L., and Stenmark, D.G..: "Multiphase Microemulsion Systems," Transactions, AIME, Volume 261 (1976) 147-160.

e. Nelson, R.C. and Pope, G.A.: "Phase Relationships in Chemical Flooding," Transactions, AIME, Volume 265 (1978) 325-338.

of emulsion book) of emulsion system. The exemplary systems have hydrocarbon, water and FPS pseudoternary phase. Typically the lower ratio of the oil phase, the longer the period of miscible displacement which can lead to higher oil recovery, as the oil is emulsified.

2) Core flood experiment was conducted through methods known in the art (See the following references)

f. Holm, L.W. and Knight, R.K.: "Soluble Oil Flooding," Petroleum Engineer (November 1976).

g. Gogarty, W.B.: "Rheological Properties of Pseudoplastic Fluids in Porous Media," Journal of Petroleum Technology (June 1967) 149-160.

Because of the interacting effect of the emulsion with the reservoir rock, phase and physical property studies alone are not sufficient to properly design the emulsion system. The coreflood is a critical to predict the EOR performance in field. Many literatures have been published to show a direct correlation of core flood results with field observation. Green et al. used the coreflood as one of the key design procedures and criteria, by measuring such factors as adsorption, effect of micellar slug size, and effectiveness of mobility control (1998, ISBN 1-55563-077-4, SPE Textbook Series Vol. 6, pp. 285). Gogarty et al. used coreflood to study how to optimize surfactant concentration for field application, and to simulate the displacement, adsorption, mobility control, and scaling behavior in the field (1976, SPE 5559 PA, pp. 93-102).

Example 2

Six synthetic exemplary FPS samples were prepared via free radical initiated copolymerization (Table 1).

Step 1, according to the monomer ratio in the Table 1, the acrylamide, hydrophilic monomers, lipophilic monomers, and sodium carbonate were dissolved with deionized water to form a solution in a 3-neck round bottle flask, followed by sodium formate and ammonium hydroxide. The total mass of all reactants was about 25-30% of total mass of the solution in the flask.

Step 2, the flask was placed in water bath, and was deoxygenated with nitrogen flow for 20 minutes. Under nitrogen protection, the initiator system, including azo initiator (e.g. ABIN), reducer (e.g. sodium bisulfate), and oxidator (e.g., sodium persulfate), was added into the flask. The total mass of the initiator system was 0.01% - 0.1% of the total mass of the total mass of all reactants.

Step 3, the flask was allowed to deoxygenate with nitrogen flow for another 10 minutes, and then the flask was sealed. Observed the change of reacting solution and recorded the change of reaction solution temperature to determine the completion of reaction.

Step 4, after the reaction was completed, the water bath temperature was raised to 185 F, and keep the flask in water batch for 4 hours.

Step 5, the resulting gel was then smashed, granulated and dried to obtain samples for further use.

TABLE 1

Monomer	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c
acrylamide	60-80%	60-80%	60-80%	0-40%	0-40%	0-40%
H1	0-35%	0-35%	0-35%	50-90%	50-90%	50-90%
H2		1-5%	1-5%			1-5%
H3	1-5%	1-5%		1-5%	1-5%	1-5%
L1			1-5%	1-5%		
L2		1-5%			1-5%	
L3	1-5%			1-5%		
L4	0-5%	0-5%	0-5%			1-5%
L5	1-5%		1-5%	1-5%	1-5%	1-5%

FPS-1a, 1b, 1c each has molecular weight ranged from 5 mil to 10 mil;

FPS-2a, 2b, 2c each has molecular weight ranged from 0.2 mil to 3 mil;

H1, H2, and H3 are hydrophilic monomers, and

H1 = [CH_2=CH-CO-OH],

H2 = [CH_2=CH-CO-NH-C(CH_3)$_2$-$CH_2SO_3^-$.Na^+],

H3 = [CH_2=CH-CO-O-$(EO)_p$-$(CH_2)_n$-CH_3];

L1, L2, L3, L4, L5 are hydrophilic monomers, and

L1 = [CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)$_n$-CH_3)],

L2 = [CH_2=CH-CH_2-$N^+(CH_3)_2$-(CH_2)n-CH_3. X^-],

L3 = [CH_2=CH-CO-NH-$(CH_2)_n$-$N^+(CH_3)_2$-$(CH_2)_n$-CH_3. X^-],

L4 = [CH_2=CH-CO-O-$(CH_2)_n$-CH_3],

L5 = [CH_2=CH-CO-G];

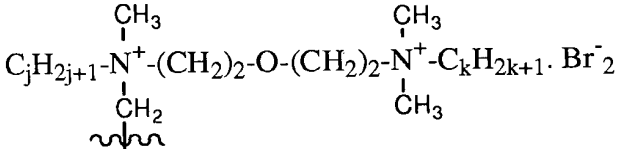
n is an integer from 8 to 20;

EO represents –CH_2CH_2O-,

p is an integer from 6-20;

X^- = Cl^-, Br^-

G represent a bis-ammonium Gemini surfactant moiety, covalent bonding with carbonyl group in the monomer, as



(j + k = 24, j = 12, 13, 14, 16, 18)

The IFT measurements reported in the following examples were determined using the following procedure. IFT values for these systems (Oil phase as n-heptane, aqueous phase as 1000 ppm FPS solution in 3% NaCl) were determined at 86 F using a spinning drop interfacial tensiometer. These IFT values were determined in the following way: the interfacial tension of a system was measured as a function of time, usually for 2 hours. If the values for the last 20 minutes agreed to within 1-2%, the 2-hour measurement was reported; if not, the measurements were continued until the 1-2% agreement for a 20-minute period was obtained. All the testing results were listed in Table 2.

The 6 FPS samples (in Table 1) were evaluated for oil-water IFT measurements.
The IFT values of a commercial partially hydrolyzed polyacrylamide previously used in polymer flooding system (MO4000 by Mitsubishi) with an IFT value of 34.33 dyne/cm.

The control reading of n-heptane and 3% NaCl was 44.80 dyne/cm.

TABLE 2

	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c	MO4000	control
IFT	5.34	7.29	3.47	0.91	0.86	1.36	34.33	44.80

Example 3

Coreflood tests were carried out at 185 F in epoxy-coated Berea sandstone 12 inch cores (average 487 md air permeability). The dry core was preflushed with 2 pore volumes of brine before it was flooded to an irreducible water saturation with a representative crude oil having a viscosity of about 7.2 cP. The oil saturation was typically from 0.65. The core was then waterflooded with the same brine to irreducible oil saturation (watercut 98%) of about 0.42 from 0.65.

The chemical flood began with the injection of a 0.3 pore volume slug of 1500 ppm FPS samples (FPS-1a, 1b, 1c, 2a, 2b, 2c in 6 separated coreflood tests) prepared with 0.5% NaCl brine, followed by 0.5% NaCl brine to irreducible oil saturation (watercut 98%). The resulting residue oil saturation is listed in the table 3.

A separated chemical flood began with the injection of a 0.3 pore volume slug of 1500 ppm PAM-25 (polyacrylamide, hydrolysis degree = 23%, molecular weight 25 mil) prepared with 0.5% NaCl brine, followed by 0.5% NaCl brine to irreducible oil saturation (watercut 98%) (See Table 3).

TABLE 3

	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c	PAM-25
Saturation	0.30	0.35	0.32	0.27	0.29	0.30	0.38

The resulting irreducible oil saturation data Table 3 indicate that the FPS, generally speaking at lower molecular weight, has better oil recovery performance than the ultra high molecular weight polyacrylamide. The FPS-2b was used in the 100% watercut mature field trial (113 F, 0.3-0.4% salinity, onshore sandstone, irreducible oil saturation after waterflood), and recovered more than incremental 9.5% of original oil in place.

Example 4

Two coreflood tests were carried out at 113 F in epoxy-coated Berea sandstone 12 inch medium permeability cores. The dry core was preflushed with 2 pore volumes of brine before it was flooded to an irreducible water saturation with a typical Daqing crude oil. The core was then waterflooded with 0.3% salinity brine to irreducible oil saturation (watercut 98%). Wherein, the accumulated recovery of core 1, after the water flood, was 46% of original oil saturation, and the accumulated recovery of core 2, after the water flood, was 47% of original oil saturation.

In the core 1, a FPS-2c solution (about 0.5 million molecular weight, 7.3 cP, 0.6 pore volume) was injected to obtain incremental 17% of original oil saturation.

In the core 2, a PAM-15 solution (regular polyacrylamide, about 15 million molecular weight, 20.6 cP, 0.6 pore volume) was injected to obtain incremental 10% of original oil saturation.

The FPS-2c, with about one-third of the viscosity of PAM-15, had 70% more oil recovery performance.

Example 5

Two coreflood tests were carried out at 113 F in epoxy-coated Berea sandstone 6 inch low permeability (50 - 80 md) cores. The dry core was preflushed with 2 pore volumes of brine before it was flooded to an irreducible water saturation with a typical Daqing crude oil. The core was then waterflooded with 0.3% salinity brine to irreducible oil saturation (watercut 98%).

A 100 ppm FPS-2b in 0.3% NaCl brine was injected (0.3 pore volume) to obtain incremental 10% of original oil saturation. It demonstrated the uncommon oil recovery ability of FPS-2b even at the low concentration.

It will be understood that particular embodiments described herein are shown by way of illustration and not as limitation of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

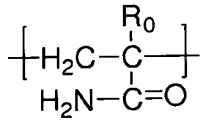
While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention.

CLAIMS

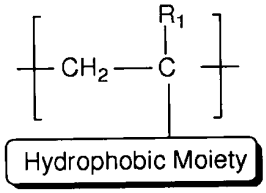
What is claimed is:

1. A functional polymeric surfactant composition, comprising:

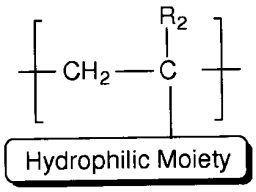
a) a first repeating monomer unit having a first formula of



b) a second repeating monomer unit having a second formula of



c) a third repeating monomer unit having a third formula of



wherein R_0, R_1, and R_2 are hydrogen or C_1 –C_4 alkyl respectively;

wherein the hydrophobic moiety is hydrophobic and selected from the group consisting of anionic, cationic, nonionic, zwitterionic, betaine, and amphoteric ion pair;

wherein the hydrophilic moiety is hydrophilic and selected from the group consisting of anionic, cationic, nonionic, zwitterionic, betaine, and amphoteric ion pair;

wherein an IFT value of the functional polymeric surfactant composition is from about 0.1 to about 15 dyne/cm.

2. The functional polymeric surfactant composition of claim 1 wherein the hydrophobic nonionic moiety is selected from the group consisting of nonionic moieties include [–COO-alkyl], [-CO-N(X_1)(X_2)], -alkyl, -phenyl, and the derivatives thereof, wherein X_1 = C_3 –C_{15} alkyl; C_1 –C_3 alkyl substituted by 1-3 phenyl, phenyl or C_1 –C_6 cycloalkyl and X_2 = H; or C_3 –C_{10} alkyl.

3. The functional polymeric surfactant composition of claim 1 wherein the hydrophobic cationic moiety is selected from the group consisting of alkyl group-containing, phenylgroup-containing quaternary salts, and derivatives thereof.

4. The functional polymeric surfactant composition of claim 3 wherein the salt is selected from the group consisting -CO-CH_2-quaternary ammonium-alkyl group, -CO-NH-quaternary ammonium-alkyl group, bis-ammonium Gemini surfactants, and derivatives thereof.

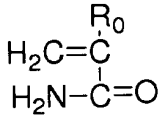
5. The functional polymeric surfactant composition of claim 1 wherein the hydrophilic nonionic moiety is selcted from the group consisting of [-COO-(EO)n-alkyl group], [-COO-(EO)n-fluoroalkyl group], and the derivatives thereof, wherein n=6-30 and EO is $-CH_2CH_2O-$.

6. The functional polymeric surfactant composition of claim 1 wherein the hydrophilic anionic is an organic acid salt.

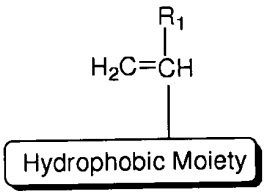
7. The functional polymeric surfactant composition of claim 6 wherein the organic acid is selected from the group consisting of acryl acid, methacrylic acid, maleic acid, itaconic acid, acrylamido methylpropane sulfonic acid, vinylphosphonic acid, styrene sulfonic acid, and derivatives thereof.

8. A functional polymeric surfactant composition, comprising a polymeric reaction product of:

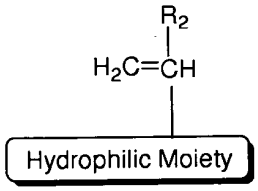
a) a first monomer having a first formula of



b) a hydrophobic monomer having a second formula of



c) a hydrophilic monomer having a third formula of



Wherein R_0, R_1, and R_2 are hydrogen or C_1 –C_4 alkyl respectively;

wherein the hydrophobic moiety is hydrophobic and selected from the group consisting of anionic, cationic, nonionic, zwitterionic, betaine, and amphoteric ion pair;

wherein the hydrophilic moiety is hydrophilic and selected from the group consisting of anionic, cationic, nonionic, zwitterionic, betaine, and amphoteric ion pair;

wherein an IFT value of the functional polymeric surfactant composition is from about 0.1 to about 15 dyne/cm.

9. The functional polymeric surfactant composition of claim 8 wherein the hydrophobic nonionic moiety is selected from the group consisting of nonionic moieties include [–COO-alkyl], [-CO-N(X_1)(X_2)], -alkyl, -phenyl, and the derivatives thereof, wherein X_1 = C_3 –C_{15} alkyl; C_1 –C_3 alkyl substituted by 1-3 phenyl, phenyl or C_1 –C_6 cycloalkyl and X_2 = H; or C_3 –C_{10} alkyl.

10. The functional polymeric surfactant composition of claim 8 wherein the hydrophobic cationic moiety is selected from the group consisting of alkyl group-containing, phenylgroup-containing quaternary salts, and derivatives thereof.

11. The functional polymeric surfactant composition of claim 10 wherein the salt is selected from the group consisting -CO-CH_2-quaternary ammonium-alkyl group, -CO-NH-quaternary ammonium-alkyl group, bis-ammonium Gemini surfactants, and derivatives thereof.

12. The functional polymeric surfactant composition of claim 8 wherein the hydrophilic nonionic moiety is selected from the group consisting of [-COO-(EO)n-alkyl group], [-COO-(EO)n-fluoroalkyl group], and the derivatives thereof, wherein n=6-30 and EO is –CH_2CH_2O-.

13. The functional polymeric surfactant composition of claim 8 wherein the hydrophilic anionic is an organic acid salt.

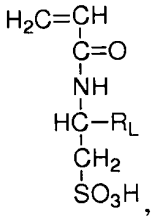
14. The functional polymeric surfactant composition of claim 13 wherein the organic acid is selected from the group consisting of acryl acid, methacrylic acid, maleic

acid, itaconic acid, acrylamido methylpropane sulfonic acid, vinylphosphonic acid, styrene sulfonic acid, and derivatives thereof.

15. The functional polymeric surfactant composition of claim 8 wherein the hydrophobic monomer is selected from the group consisting of CH_2=CH-CO-OH, CH_2=CH-CO-NH-C(CH_3)$_2$-CH_2SO_3Na, and CH_2=CH-CO-O-(EO)$_p$-(CH_2)$_n$-CH_3, wherein n is an integer from 4-20, p is an interger from 6-20, and E is –CH_2CH_2O-.

16. The functional polymeric surfactant composition of claim 8 wherein the hydrophilic monomer is selected from the group consisting of CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)$_n$-CH_3), CH_2=CH-CH_2-N(CH_3)$_2$-(CH_2)$_n$-CH_3, X,CH_2=CH-CO-NH-(CH_2)$_n$-N(CH_3)$_2$-(CH_2)$_m$-CH_3, X, CH_2=CH-CO-O-(CH_2)$_n$-CH_3], and CH_2=CH-CO-G, wherein n and m are each integer from 4 to 20; X is F^-, Cl^-, Br^-, Ac^-, NO_3^-, or $1/2SO_4^{2-}$, and G is a cationic Gemini moiety.

17. The functional polymeric surfactant composition of claim 8 wherein the hydrophobic monomer is selected from the group consisting of



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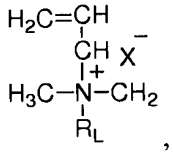

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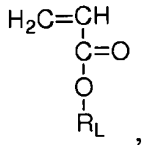

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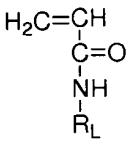
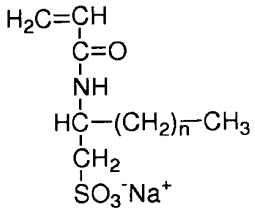


wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); and X- is a Cl- or Br-.

18. The functional polymeric surfactant composition of claim 8 wherein the hydrophobic monomer is selected from the group consisting of



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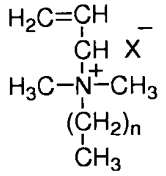

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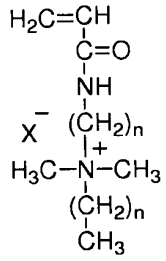

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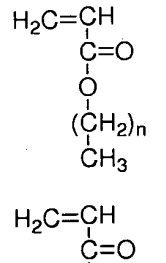
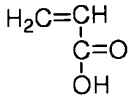


, and

wherein n is an integer from 8 to 20 and $X^- = Cl^-$, Br^-, and G represent a bis-ammonium Gemini surfactant moiety.

19. The functional polymeric surfactant composition of claim 8 wherein the hydrophilic monomer is selected from the group consisting of



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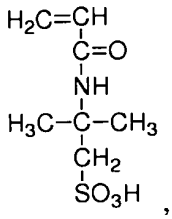

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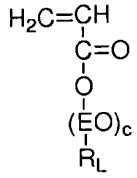
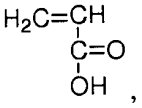


wherein R_L is a hydrophobic moiety (e.g., an alkyl, phenyl or the derivatives thereof); EO represents $-CH_2-CH_2-O-$, and c is an integer from 8 to 18.

20. The functional polymeric surfactant composition of claim 8 wherein the hydrophilic monomer is selected from the group consisting of



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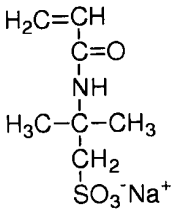
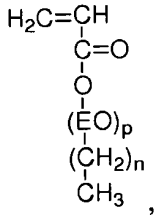


, and



,

wherein n is an integer from 8 to 20; EO represents $-CH_2CH_2O-$, and p are integer from 6-20.

21. A method for recovering hydrocarbon from a hydrocarbon-bearing subterranean formation, comprising the step of injecting a displacing solution containing a functional polymeric surfactant having an IFT value from about 0.1 to about 15 dyne/cm into the hydrocarbon-bearing subterranean formation through an injection well and collecting the hydrocarbon from a production well.

22. The method of claim 21 wherein the concentration of the functional polymeric surfactant composition in the displacing solution is from about 20 ppm to about 10,000 ppm.

23. The method of claim 22 wherein the concentration is from about 100 ppm to about 6,000 ppm.

24. The method of claim 23 wherein the concentration is from about 200 ppm to about 3,000 ppm.

25. The method of claim 21 wherein the IFT of the functional polymeric surfactant composition is about 0.1 to about 12.5 dyne/cm.

26. The method of claim 25 wherein the IFT of the functional polymeric surfactant composition is about 0.1 to about 10 dyne/cm.

27. The method of claim 21 wherein the hydrocarbon-bearing subterranean formation has been subjected to a water flooding.

28. The method of claim 27 wherein the hydrocarbon-bearing subterranean formation has been deemed as unrecoverable by the water flooding.

29. The method of claim 21 wherein the injection well is the same as the production well.

30. The method of claim 21 wherein the hydrocarbon is oil.

31. The method of claim 21 wherein injecting the displace solution renders about 5% to about 30% original oil in place.

32. The method of claim 21 wherein the functional polymeric surfactant comprises the functional polymeric surfactant composition of claims 1-20.

33. The method of claim 21 wherein the functional polymeric surfactant is biological or biologically synthesized.

34. The method of claim 21 wherein the functional polymeric surfactant is selected from xanthan gum, polysaride, and the derivatives thereof.

35. The functional polymeric surfactant composition of claims 1-7 wherein the repeating monomer unit is covalently linked with each other or another repeating monomer unit.

[19] 中华人民共和国国家知识产权局

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权利要求书 6 页 说明书 19 页

[54] 发明名称

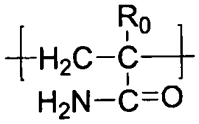
可提高石油采收率的功能性聚合物

[57] 摘要

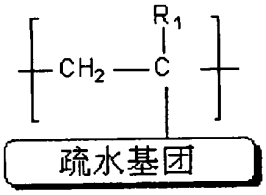
本发明涉及可提高石油采收率的组合物及其方法。该方法涉及使用水溶性的本发明涉及可提高石油采收率(EOR)的组合物及其方法。该方法在含有聚合物表面活性剂的水相和油气相间使用一种水溶性的，具有中等 IFT 值的功能性聚合物表面活性剂(FPS)，用于采收地层中的碳氢化合物。其 IFT 值优选为约 0.1 至约 15 达因/厘米。该 FPS 溶液被证实能与石油发生强烈作用，具有增加 EOR 中的体积波及效率和微观驱油效率的潜力。

1. 一种功能性聚合物表面活性剂组合物，其包括：

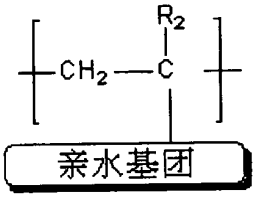
a) 第一化学式所示的第一重复单体单元



b) 第二化学式所示的第二重复单体单元



c) 第三化学式所示的第三重复单体单元



其中 R_0，R_1 和 R_2 分别为氢或者 C_1–C_4 烷基；

其中疏水基团具有疏水性并选自于阴离子、阳离子、非离子、两性离子、内铵盐和两性离子对；

其中亲水基团具有亲水性并选自于阴离子、阳离子、非离子、两性离子、内铵盐和两性离子对；

其中功能性聚合物表面活性剂组合物 IFT 值为约 0.1 至约 15 达因/厘米。

2. 根据权利要求 1 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性非离子基团选自于非离子基团，包括[–COO-烷基]，[-CO-N(X_1)(X_2)]，烷基，苯基，及其衍生物，其中 X_1 = C_3–C_{15} 烷基；1-3 苯基、苯基或 C_1–C_6 环烷基取代的 C_1–C_3 烷基而 X_2 = H；或 C_3–C_{10} 烷基。

3. 根据权利要求 1 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性阳离子基团选自于带有烷基、苯基的季盐及其衍生物。

4. 根据权利要求 3 所述的功能性聚合物表面活性剂组合物，其中所述的盐选自于-CO-CH_2-季铵-烷基，-CO-NH-季铵-烷基，双铵基的 Gemini 表面活性剂，及其衍生物。

5. 根据权利要求 1 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性非离子基团选自于[-COO-(EO)n-烷基]，[-COO-(EO)n-氟烷基]，及和其衍生物，其中 n 为 6-30 的整数，

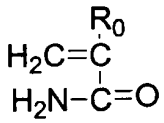
EO 为–CH_2-CH_2-O-。

6. 根据权利要求 1 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性阴离子为有机酸盐。

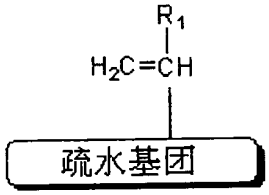
7. 根据权利要求 6 所述的功能性聚合物表面活性剂组合物，其中所述的有机酸选自于丙烯酸、甲基丙烯酸、马来酸、衣康酸、丙烯酰胺甲基丙基磺酸、乙烯基磷酸、苯乙烯磺酸，及其衍生物。

8. 一种功能性聚合物表面活性剂组合物，其包括以下聚合反应产物：

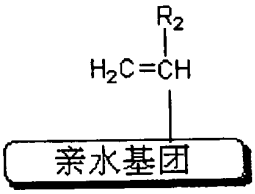
a) 第一化学式所示的第一重复单体



b) 第二化学式所示的疏水单体



c) 第三化学式所示的亲水单体



其中 R_0，R_1 和 R_2 分别为氢或者 C_1–C_4 烷基；

其中疏水基团具有疏水性并选自于阴离子、阳离子、非离子、两性离子、内铵盐和两性离子对；

其中亲水基团具有亲水性并选自于阴离子、阳离子、非离子、两性离子、内铵盐和两性离子对；

其中功能性聚合物表面活性剂组合物 IFT 值为约 0.1 至约 15 达因/厘米。

9. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性非离子基团选自非离子基团，包括[–COO-烷基]，[-CO-N(X_1)(X_2)]，烷基，苯基，及其衍生物，其中 X_1 = C_3–C_{15} 烷基；1-3 苯基、苯基或 C_1–C_6 环烷基取代的 C_1–C_3 烷基，而 X_2 = H；或 C_3–C_{10} 烷基。

10. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性阳离子基团选自于带有烷基、苯基的季盐，及其衍生物。

11. 根据权利要求 10 所述的功能性聚合物表面活性剂组合物，其中所述的盐选自于-CO-CH_2-季铵-烷基，-CO-NH-季铵-烷基，双铵盐 Gemini 表面活性剂，及其衍生物。

12. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性非离子基团选自于[-COO-(EO)n-烷基]，[-COO-(EO)n-氟烷基]，及其衍生物，其中 n 为 6-30 的整数，EO 代表–CH_2-CH_2-O-。

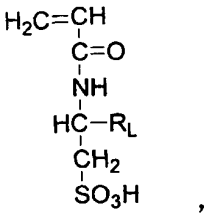
13. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性阴离子为有机酸盐。

14. 根据权利要求 13 所述的功能性聚合物表面活性剂组合物，其中所述的有机酸选自于丙烯酸，甲基丙烯酸，马来酸，衣康酸，丙烯酰胺甲基丙基磺酸，乙烯基磷酸，苯乙烯磺酸，及其衍生物。

15. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性单体选自于 CH_2=CH-CO-OH，CH_2=CH-CO-NH-$C(CH_3)_2$-CH_2SO_3Na 和 CH_2=CH-CO-O-$(EO)_p$-$(CH_2)_n$-CH_3，其中 n 为 4-20 的整数，p 为 6-20 的整数，E 为–CH_2CH_2O-。

16. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性单体选自于 CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)$_n$-CH_3), CH_2=CH-CH_2-$N(CH_3)_2$-$(CH_2)_n$-CH_3, X, CH_2=CH-CO-NH-$(CH_2)_n$-$N(CH_3)_2$-$(CH_2)_m$-CH_3, X, CH_2=CH-CO-O-$(CH_2)_n$-CH_3 和 CH_2=CH-CO-G，其中 n 和 m 分别为 4-20 的整数；X 为 F^-、Cl^-、Br^-、Ac^-、NO_3^-或 $1/2SO_4^{2-}$，G 为 Gemini 阳离子基团。

17. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性单体选自于



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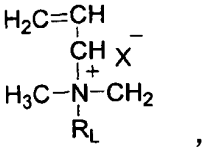

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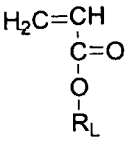

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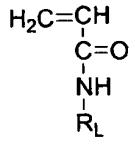
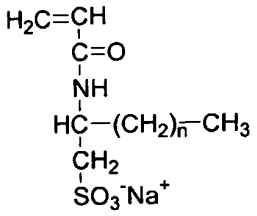


其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物）；X^- 为 Cl^- 或 Br^-。

18. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的疏水性单体选自于



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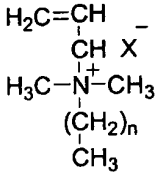

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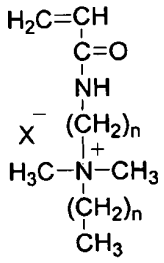

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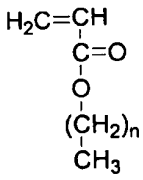

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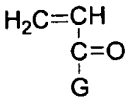
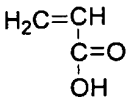


其中 n 为 8-20 的整数，$X^- = Cl^-, Br^-$，G 代表双铵盐 Gemini 表面活性剂基团。

19. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性单体选自于



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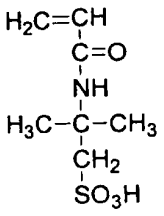

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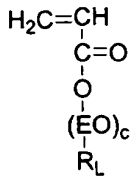
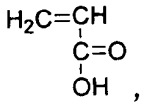
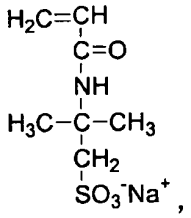


其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物）；EO 为–CH_2-CH_2-O-；c 为 8-18 的整数。

20. 根据权利要求 8 所述的功能性聚合物表面活性剂组合物，其中所述的亲水性单体选自于





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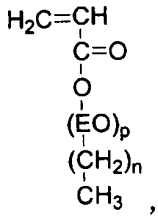


其中 n 为 8-20 的整数；EO 为–CH_2CH_2O-；p 为 6-20 的整数。

21. 一种从含有碳氢化合物地层中采收碳氢化合物的方法，该方法包括通过注入井将含有 IFT 值在约 0.1 至约 0.5 达因/厘米的功能性聚合物表面活性剂的驱替溶液注入含有碳氢化合物地层中，收集生产井中的碳氢化合物。

22. 根据权利要求 21 所述的方法，其中所述的功能性聚合物表面活性剂组合物在驱替溶液中的浓度在约 20 ppm 至约 10,000 ppm。

23. 根据权利要求 22 所述的方法，其中所述浓度在约 100 ppm 至约 6,000 ppm。

24. 根据权利要求 23 所述的方法，其中所述浓度在约 200 ppm 至约 3,000 ppm。

~~25. 根据权利要求 21 所述的方法，其中所述的功能性聚合物表面活性剂组合物的 IFT 在约 0.1~~ 至约 12.5 达因/厘米。

26. 根据权利要求 25 所述的方法，其中所述的功能性聚合物表面活性剂组合物的 IFT 在约 0.1 至约 10 达因/厘米。

27. 根据权利要求 21 所述的方法，其中所述的含碳氢化合物的地层受到过水驱。

28. 根据权利要求 27 所述的方法，其中所述的含碳氢化合物的地层受水驱后已被视为不可采收。

29. 根据权利要求 21 所述的方法，其中所述的注入井就是采油井。

30. 根据权利要求 21 所述的方法，其中所述的碳氢化合物是石油。

31. 根据权利要求 21 所述的方法，其中所述的注入驱替溶液可提供产出约 5%至约 30%的原始原油地质储量。

32. 根据权利要求 21 所述的方法，其中所述的功能性聚合物表面活性剂包括权利要求 1-20 中的功能性聚合物表面活性剂组合物。

33. 根据权利要求 21 所述的方法，其中所述的功能性聚合物表面活性剂具有生物性或是生物合成的。

34. 根据权利要求 21 所述的方法，其中所述的功能性聚合物表面活性剂选自黄原胶，多糖，及其衍生物。

35. 根据权利要求1-7所述的功能性聚合物表面活性剂组合物，其中所述的重复单体单元是通过共价键相互连接或与另一重复单体单元连接。

可提高石油采收率的功能性聚合物

相关申请

本专利申请要求源自2006年10月23日递交的美国临时专利申请60/853,468的优先权。该临时申请的全部内容包括附图包含在本发明专利申请中。

技术领域

本发明涉及石油生产领域。具体地说，本发明涉及使用功能性表面活性聚合物提高石油采收率。

背景技术

从含碳氢化合物（如含石油）的储层中采收碳氢化合物（如石油）主要是依靠储层中的自然能量，将其作为主能源驱油至生产井。但这种方法通常只能采收原始原油地质储量（OOIP）的一小部分。因此，为了提高采收地下石油，大量辅助采收技术被投入使用。

石油采收驱替的实现取决于两个重要因素：体积波及效率和微观驱油效率。提高石油采收率（EOR）的方法通常是将某种流体或某类流体注入到储层中。注入的流体和注入方法补充储层中的自然能量，一同将原油驱替到生产井。此外，注入的流体与储层岩石和石油体系相互作用，创造了有利于石油采收的条件。流度控制方法和化学方法是提高石油采收的两种常用方法。

广泛应用的流度控制方法为聚合物驱。其中典型的是设计使用一种聚合物溶液，使其在注入的聚合物溶液和聚合物前方正被驱替的石油/水带之间形成一个有利的流度率。目的是在储层纵向和面向上形成统一体积波及，以防止水突进，同时防止水通过最短的路径到达生产井。20世纪60年代以来，许多聚合物项目被投入应用。然而流度控制方法本身并未采用微观驱油效率，而且该方法的采收率低，从而限制了石油采收率的增加，其通常低于原始原油地质储量的10%。Manning等人对所有本领域聚合物项目的统计学数据进行了分析，石油采收率中值为2.91%OOIP（1983，Report DOE/ET/10327-19）。Schurz等人总结了1980－1989年间的99个项目，结果显示增加的石油采收率中值在3.7%到4.8%之间（1989，NMT 890029, New Mexico Tech Centennial Symposium）。Gogarty等人论述了许多有关聚合物驱提升石油采收率是经济到达极限之前加速生产石油的结果（1976, SPE 1566-A, pp. 149-160）。

化学方法采用注入某种特定液态化学物质，该化学物质的相态性质使得驱替液体和石油之间的界面张力（IFT）减小，从而有效驱油。表面活性剂/聚合物方法被证明是具有提高原油采收率应用潜力的。该方法先注入一种胶束溶液作为表面活性剂主段塞，然后注入流度缓冲液，通常是一种含有梯度浓度的聚合物溶液。随着注入溶液的增多，该表面活性剂主段塞在聚合物中被逐渐稀释。采收率主要是利用驱替流体和被驱替油之间超低的IFT。Green等

人特别指出在水驱残余油饱和度锐减之前，驱替流体的界面张力必须降至超低，大概在 10^{-3} 达因/厘米（1998，ISBN 1-55563-077-4, SPE Textbook Series Vol. 6, pp. 35）。但这也存在着不足。为了获得超低的 IFT，化学溶液需要加入表面活性剂、辅助表面活性剂，有时还需加入油、电解质和碱。这使化学溶液变得复杂且昂贵，同时也可能需要在 EOR 操作中增加色谱分离。

自 1951 年 Strauss 等人首次公开聚合物肥皂概念以来，有大量关于两亲分子有序组合体中和两亲分子有序组合体的聚合的文献出版。在一定程度上，聚合物表面活性剂和低分子量表面活性剂具有相同功能。然而聚合物表面活性剂的高分子量和复杂的结构又使其具有一些独特的特征。比如，稀溶液中单分子胶束的形成和不同浓度下不同的胶束形状等。其在亚微米胶体系统中作为乳化稳定剂的应用也已公开。胶粒表面带有大分子链能带来非常大的优势，这使聚合物表面活性剂越来越受到人们的注意。其流变特征（如变厚的特性）与独特相态性质的结合在超吸收性、乳剂漆、液压、絮凝、蛋白质分离、药物控释和生物、医学设备上有广泛应用潜力。但仅有少数几篇文献探究了利用聚合物表面活性剂来提高石油采收率。

化学方法理论通常认为，微观驱油效率在很大程度上决定了储层岩石中残余油驱替后的饱和度，这是评定一个化学 EOR 方法成功与否的主要标准之一。毛细管压力和粘稠力决定着相位捕获和流体在多孔介质中的移动，进而决定微观驱油效率。Green 等人研究了毛细管数 $N_{ca} = (v\mu_w)/\delta_{ow}$，其中，$N_{ca}$ 为毛细管数，v 为孔隙速度，μ_w 为驱替相粘度，δ_{ow} 为驱替相和被驱替相间的 IFT（1998, ISBN 1-55563-077-4, SPE Textbook Series Vol.6, pp. 22）。除非 δ_{ow} 到达 10^{-3} 达因/厘米的超低水平，残余油饱和度则不可能大幅度降低，这点已被人们广泛接受。因此，目前对聚合物表面活性剂的研制主要集中在选择聚合物表面活性剂或制备含有聚合物表面活性剂，及辅助表面活性剂或其它添加剂的溶液，从而在油相和水相间产生较低或超低的 IFT 值。

例如，在 20 世纪 80 年代早期，Chen 等人（1981, US Pat No. 4,284,517, 1982, US Pat No. 4,317,893）公开了一种利用间隔注入和生产系统渗透至地下石油储层采收石油的方法。该方法将含有聚合物表面活性剂的水溶液通过注入系统引入储层，将油驱替到生产系统中。Chen 等人特别强调油-水间界面张力应当小于 0.1 达因/厘米（比如：较为理想的油-水 IFT 为 0.005 达因/厘米或更小）以获得最好的微观驱油效率。

Cao 等人（2002, European Polymer Journal, 38 (7), pp. 1457-1463）发现了具有提高石油采收潜力的新的聚合物表面活性剂家族。该新的聚合物表面活性剂是基于羧基甲基纤维素和~~烷基聚氧乙烯醚丙烯酸酯。加入 NaCl 后，此聚合物表面活性剂的 IFT 特性变化很小。成型的~~胶束收缩，体积变小。由于酒精溶液中存在少量自由链，它能使其 IFT 微降。在加入碱后，聚合物表面活性剂在水溶液中的 IFT 降低到 10^{-2} 达因/厘米以下。

虽然亲水性修饰的水溶性共聚物近期受到极大的关注，但在化学方法利用超低 IFT 驱替液传统理论的影响下，使用聚合物表面活性剂来提高石油采收率的尝试主要还是针对如何

产生有效、稳定的粘度以改进其作为流度控制器的波及效率。McCormick 等人在实验室进行了一个全面、深入的研究，其最终目标是开发一种“聪明”的多功能聚合物。该聚合物能够做出实时反应，刺激并大大提高 EOR 方法中的波及效率（2004, 2005, DOE Report, Award Number DE-FC26-03NT15407）。McCormick 等人仅研究了聚合物表面活性剂与聚合物相比在波及微观驱油效率和相态性质上所取得进步，但并未揭示油-水界面张力值大于 0.1 达因/厘米的聚合物表面活性剂在 EOR 中的使用。

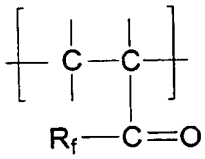
与传统理论相反，本发明出乎意料地发现具有中等油-水 IFT 的聚合物表面活性剂，如不小于约 0.1 达因/厘米（如优选在约 0.1-约 15 达因/厘米），同时具有体积波及效率和微观驱油效率，并能被用于采收地层中的碳氢化合物。

发明简介

本发明涉及通过向储层或地层中注入含有功能性聚合物表面活性剂的驱替溶液，从含碳氢化合物的地下储层或地层中采收碳氢化合物的方法。该功能性聚合物表面活性剂的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米。

本发明还涉及带有部分水解聚芳胺骨架和以下化学式所示的重复单体单元的功能性聚合物表面活性剂，FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米，

该重复单体单元公式如下：

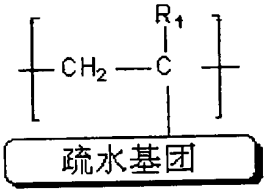


（化学式（1））

R_f = -NH_2, -ONa, -OR_L, -NHR_L, -R_LSO_3Na, -$(EO)_a(PO)_bR_L$, 季铵表面活性基团，双铵盐 Gemini 表面活性基团，-R_LSH 及类似基团，PO 代表–CH_2-$CH(CH_3)$-O-，EO 代表–CH_2-CH_2-O-，其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物），a + b 为 6-30 的整数。

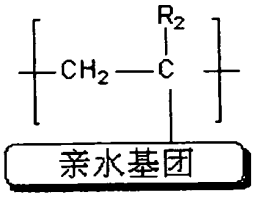
本发明还涉及包括如下式所示的第一重复单体单元和第二重复单体单元的功能性聚合物表面活性剂，该 FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米，其公式如下：

带疏水基团的第一重复单体单元



（化学式（2））

带亲水基团的第二重复单体单元

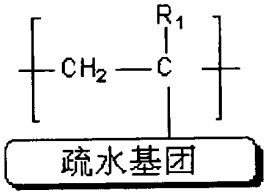


（化学式（3））

其中，R_1 和 R_2 分别为氢或 C_1-C_4 烷基。

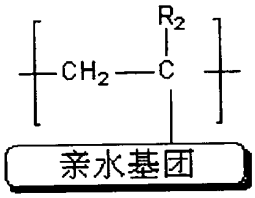
本发明还涉及包括三种重复单体单元（第一重复单体单元，第二重复单体单元和第三重复单体单元）的功能性聚合物表面活性剂，该 FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米，其公式如下：

带疏水基团的第一重复单体单元



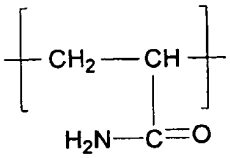
（化学式（2））

带亲水基团的第二重复单体单元



（化学式（3））

第三重复单体单元

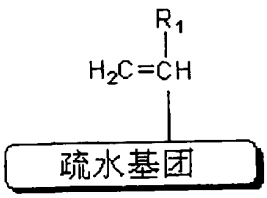


（化学式（4））

其中，R_1 和 R_2 分别为氢或 C_1-C_4 烷基。

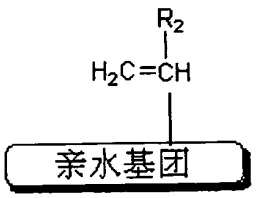
本发明还涉及包括以下三种重复单体单元的聚合反应产物的功能性聚合物表面活性剂，FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米，其公式如下

第一重复单体



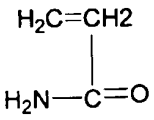
（化学式（5））

第二重复单体



（化学式（6））

第三重复单体



（化学式（7））

其中，R_1 和 R_2 分别为氢或 C_1-C_4 烷基。

发明内容

为了便于对本发明的理解，下文对一些术语的含义做了界定。本申请定义的术语含义与本发明相关领域普通技术人员理解意义相同。词语如“一个”或“这个”并不仅指单个实体，而是包含用于解释说明的某一特例所属的一般类别。本文术语用来描述本发明的某特定实施例，除权利要求书的界定外，其使用不构成对本发明的限制。

本发明所述的“储层环境”是指温度、压力、盐度以及其它常见地层条件。

本发明所述的“聚合物”是指单个分子量至少是 1000 克/摩尔的分子，其结构包括从相对分子量较低的分子在实际或理论上衍生得到的单元的多次重复。

本发明所述的“共聚物”或“杂聚合物”是指由两种或更多种单体物聚合形成的聚合物，与只用一种单体的均聚物相反。

本发明所述的“聚合物的”是指包括有聚合物。

本发明所述的“表面活性剂”是指表面活性物质。

本发明所述的“单元”是指聚合物分子的一部分或结构元件。聚合物的一个单元与相同结构或不同结构的另一个单元共价连接。

本发明所述的“聚合物表面活性剂”是指任何能够作为流度控制的聚合物，该聚合物同时也能形成乳剂。

本发明所述的“功能性聚合物表面活性剂”或“FPS”，是指油-水 IFT 在约 0.1-约 15 达因/厘米（如约 0.1-约 12.5 达因/厘米；约 0.1-约 10 达因/厘米）的聚合物表面活性剂；其能在流度控制中改变粘度，同时也能在储层环境下在油水之间形成“乳剂”，且应当成为 EOR 化学方法的备选物质。

本发明所述的“流度控制”在多数情况下是指聚合物表面活性剂溶液的粘度大于水的粘度。该粘度与储层中需采收的石油粘度相同，或更大。

本发明所述的“乳剂”是指油相和水相的非均相体系，包括胶束、微乳剂、混相、热力不稳定乳剂、双乳剂和多乳剂。

本发明所述的“相互作用”是指聚合物表面活性剂溶液和油之间，趋向于形成乳剂的相互作用。

本发明所述的“提高石油采收率”即“EOR”，是指通常包括将一种或某类流体注入到地下储层或地层中的方法。注入的流体和注入方法补充储层中的自然能源把油驱替到生产井。此外，注入的流体与储层岩石和石油系统相互作用，产生有利于石油采收、驱替的环境。水洗达到束缚油饱和度后，典型的 EOR 方法可多采收 5－25%的原始原油地质储量（OOIP）。此外，EOR 方法在水洗未达到束缚油饱和度前也可以使用。

本发明所述的“地层”或“地下储层”是指地壳中以矿藏形式存在的原始碳氢化合物的地方。它存在于地表以下 1,000-3,000 英尺的任何地方，且其形状、大小和年代各异。地层可能已经受到注水、聚合物注入或化学方法的侵蚀。

本发明所述的“驱替流体”或“驱替溶液”是指用于提高地层中石油采收率的水溶液。

传统理论认为乳剂的形成有赖于低的 IFT，这驱使人们寻找超低 IFT（驱替流体和油之间为 10^{-4}-10^{-2} 达因/厘米）来形成油乳剂，以产生更有效的胶束/聚合物驱。但本发明证实了一个出人意料的实验结论，即具有中等油-水 IFT（约 0.1 达因/厘米或更高）的聚合物表面活性剂也可以有效乳化油，并被岩心驱替实验和实地实验证明可用于 EOR 化学方法。

不被任何理论限制，由于本发明中的功能性聚合物表面活性剂不仅可以作为流度控制产生粘性，还可以有效乳化油，现有技术公认的低或超低 IFT 要求可能并不适用于功能性聚合物表面活性剂。使用只是微降 IFT 的 FPS，作为 EOR 化学方法的唯一主要试剂将有可能革命性地改变今后提高石油采收率的技术。人们基于本发明可以设计出数百种新型 FPS，用于有成本效益的 EOR 方法。

基于其意想不到的特征，本发明所述 EOR 化学方法中用的 FPS 不仅可用于流度控制，而且也可作为拟表面活性剂，在储层环境下形成乳剂。FPS 既可以获得体积波及效率也可以获得微观驱油效率。用于 EOR 水驱中的 FPS 的主要特征如下：（1）FPS 水溶液会增加表观粘度，从而降低水的流动性；（2）FPS 能够通过选择性吸附和机械截留岩石上的 FPS 实现均匀渗透；（3）FPS 也可以有一定的粘弹性；和（4）FPS 是降低油-水 IFT 的表面活性剂。

相应地，本发明还涉及一种新型的和改良的石油采收方法。该方法将含有中等油-水 IFT 值的功能性聚合物表面活性剂驱替液注入含有碳氢化合物的地层中。

在某一实施例中，IFT 值在约 0.1 至约 15 达因/厘米，优选为约 0.1 至约 10 达因/厘米，更优选为约 0.5 至约 10 达因/厘米。IFT 值可通过本领域的公知技术测得。在本发明中，IFT 值通过以下方法测得：在 86 F 条件下，使用旋转液滴界面张力仪混合油相（如正庚烷）与水相（如 FPS 的 3%氯化钠的溶液）：两个相之间的界面张力作为时间函数进行测量，通常为 2 个小时。若 20 分钟内数值持续在 1-2%之间变化，则记录该测试。

在另一实施例中，功能性聚合物表面活性剂在驱替溶液或液体中的浓度约为 20 ppm 至约 10,000 ppm，约 100 ppm 至约 6000 ppm，约 200 ppm 至约 3000 ppm，约 300 ppm 至约 1500ppm。

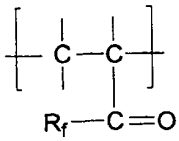
在另一个实施例中，通过自然能源将石油驱替至采油井后，地层或储层含有残余碳氢化合物（如石油）。另外，地层可能已经经过水洗达到束缚水饱和度。而且，地层可能已经过化学处理，被视为不可采收。

在另一实施例中，通过注入系统（如注入井）将驱替溶液传到地层中，并通过采油系统（如采油井）采收碳氢化合物（如石油）。在某些实施例中，注入井就是采油井。例如，在"蒸汽吞吐"方式中，将 FPS 溶液通过井注入含有碳氢化合物的地层。随后将该注入井关闭浸泡一段时间，之后再使用该井采油。

在另一实施例中，利用 FPS 提高石油采收的方法一般可获得约 5-30%的 OOIP，优选为约 10-30%的 OOIP，更优选为约 15-30%的 OOIP，更优选为约 15-25%的 OOIP。

另一方面，本发明涉及一种功能性聚合物表面活性剂组合物。该组合物包括多种不同的合成的碳基和硅基聚合物表面活性剂，其中聚合物表面活性剂包括至少一种亲水性单体单元和至少一种疏水性单体单元，其油-水 IFT 值大于 0.1 达因/厘米。优选聚合物表面活性剂包括功能化的聚芳胺及其衍生物。

另一方面，本发明涉及一种功能性聚合物表面活性剂。其具有部分水解的聚芳胺骨架和如以下式所示的重复单体单元。该功能性聚合物表面活性剂的 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米：

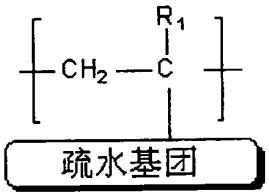


（化学式（1））

R_f = -NH_2, -ONa, -OR_L, -NHR_L, -R_LSO_3Na, -$(EO)_a(PO)_bR_L$，季铵表面活性基团，双铵盐 Gemini 表面活性剂基团，－R_LSH 及类似基团，PO 代表–CH_2-$CH(CH_3)$-O-，EO 代表 –CH_2-CH_2-O-，其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物），a+b 为 6-30 的整数。

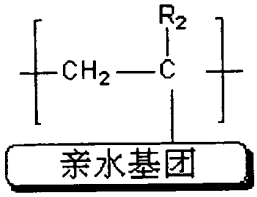
另一方面，本发明涉及一种功能性聚合物表面活性剂。其包括如下式所示的第一重复单体单元和第二重复单体单元。该 FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米：

带有疏水基团的第一重复单体单元



（化学式（2））

带有亲水基团的第二重复单体单元

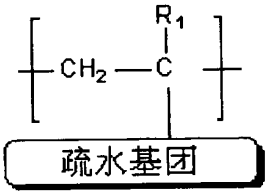


（化学式（3））

其中 R_1 和 R_2 分别为氢或者 C_1 –C_4 烷基。

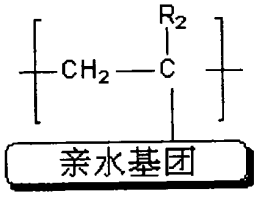
另一方面，本发明涉及一种功能性聚合物表面活性剂，其包括如下所示的三种重复单体单元（第一重复单体单元，第二重复单体单元和第三重复单体单元）。该 FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米。

带有疏水基团的第一重复单体单元



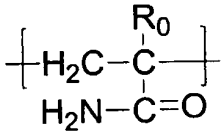
（化学式（2））

带有亲水基团的第二重复单体单元



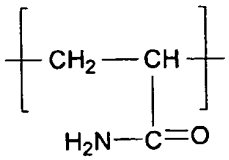
（化学式（3））

第三重复单体单元



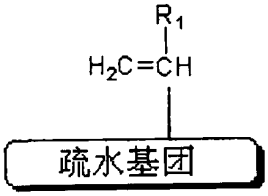
（化学式（4））

其中 R_0，R_1 和 R_2 分别为氢（H）或者 C_1–C_4 烷基。当 R_0 为 H 时，第三重复单体单元为



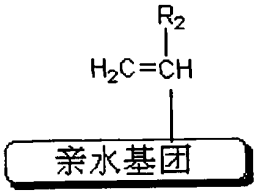
另一方面，本发明涉及一种功能性聚合物表面活性剂。其包括了以下三种重复单体聚合反应的产物。FPS 的油-水 IFT 值不小于约 0.1 达因/厘米，优选为约 0.1-约 15 达因/厘米。

带有疏水基团的第一重复单体



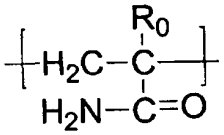
（化学式（5））

带有亲水基团的第二重复单体



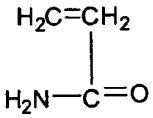
（化学式（6））

第三重复单体单元



（化学式（7））

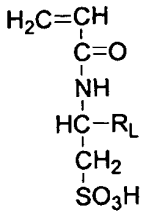
其中 R_0，R_1 和 R_2 分别为氢（H）或者 C_1–C_4 烷基。当 R_0 为 H 时，第三重复单体为



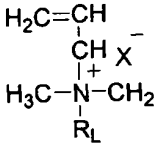
在另一实施例中，疏水基团为阴离子、阳离子、非离子、两性离子、内铵盐或者两性离子对。具体地说，非离子基团为[–COO-烷基]、[-CO-N(X_1)(X_2)]、烷基、苯基、或其衍生物，其中 X_1 = C_3–C_{30} 烷基；1-3 苯基、苯基或 C_1–C_6 环烷基取代的 C_1–C_3 烷基而 X_2 = H 或 C_3–C_{10} 烷基。阳离子基团为带有烷基、苯基的季铵盐或其衍生物（盐选自于-CO-CH_2-季铵-烷基，-CO-NH-季铵-烷基，双铵盐 Gemini 表面活性剂及其衍生物）。

在另一实施例中，亲水基团为阴离子、阳离子、非离子、两性离子、内铵盐或者两性离子对。具体地说，非离子基团为[-COO-(EO)n-烷基]、[-COO-(EO)c-氟烷基]、或其衍生物，其中 n 为 6-30 的整数，c 为 6-30 的整数，EO 代表–CH_2-CH_2-O-。阴离子基团为一种有机酸盐（例如：丙烯酸、甲基丙烯酸、马来酸、衣康酸、丙烯酰胺甲基丙基磺酸、乙烯基磷酸、苯乙烯磺酸，或其衍生物）。

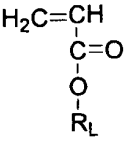
在另一实施例中，疏水单体选自如下所示化学式：



，（化学式（8））

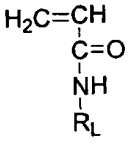


，（化学式（9））



，（化学式（10））

或者

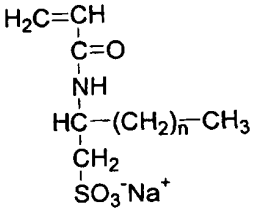


（化学式（11））

其中 R_L 为疏水基团（例如：烷基、苯基、或其衍生物）；X^- 为 Cl^- 或 Br^-。

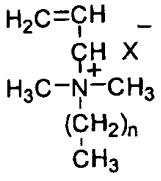
在另一实施例中，疏水单体选自如下所示化学式：

$CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)_n-CH_3)$，



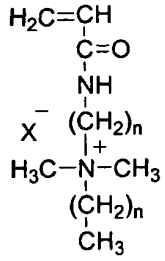
（化学式（12））

$CH_2=CH-CH_2-N^+(CH_3)_2-(CH_2)n-CH_3 \bullet X^-$，



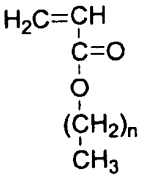
（化学式（13））

$CH_2=CH-CO-NH-(CH_2)_n-N^+(CH_3)_2-(CH_2)_n-CH_3 \bullet X^-$，



（化学式（14））

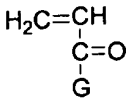
$CH_2=CH-CO-O-(CH_2)_n-CH_3$，



（化学式（15））

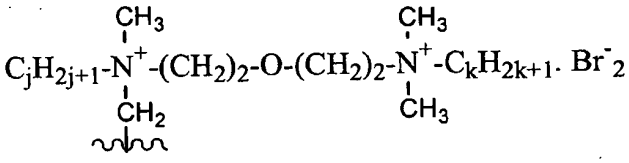
或者

$CH_2=CH-CO-G$；



（化学式（16））

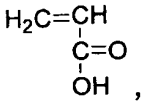
其中 n 为 8-20 的整数，$X^- = Cl^-, Br^-$，G 代表双铵盐 Gemini 表面活性剂基团。具体的说，G 如下式所示：



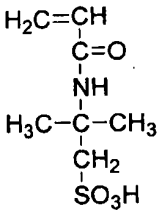
（化学式（17））

其中，（j + k = 24, j = 12, 13, 14, 16, 18）。

在另一实施例中，亲水单体选自如下所示化学式：

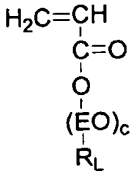


（化学式（18））



（化学式（19））

或者

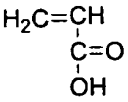


（化学式（20））

其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物）；EO 为$-CH_2-CH_2-O-$；c 为 8-18 的整数。

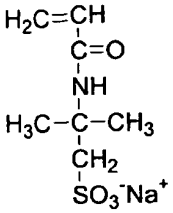
在另一实施例中，亲水单体选自如下所示化学式：

$CH_2=CH-CO-OH$，



（化学式（21））

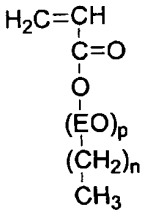
$CH_2=CH-CO-NH-C(CH_3)_2-CH_2SO_3^-.Na^+$，



（化学式（22））

或者

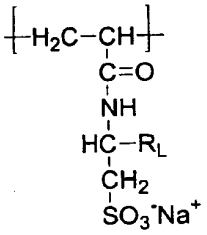
$CH_2=CH-CO-O-(EO)_p-(CH_2)_n-CH_3$，



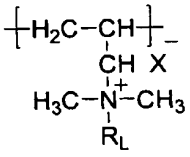
（化学式（23））

其中 n 为 8-20 的整数；EO 为$-CH_2CH_2O-$；p 为 6-20 的整数。

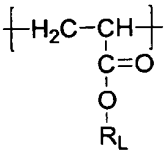
在另一实施例中，FPS 中重复的疏水单体单元选自如下所示化学式：



（化学式（24））

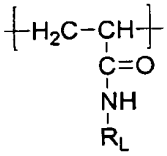


（化学式（25））



（化学式（26））

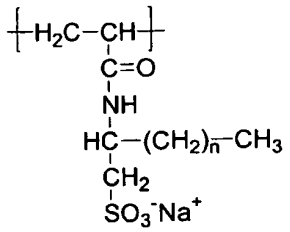
或者



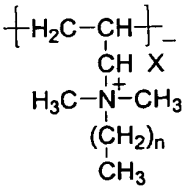
（化学式（27））

其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物），$X^- = Cl^-$ 或 Br^-。

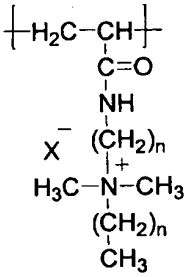
在另一实施例中，FPS 中重复的疏水单体单元选自如下所示化学式：



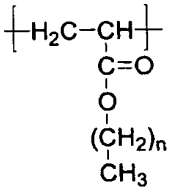
（化学式（28））



（化学式（29））

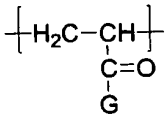


（化学式（30））



（化学式（31））

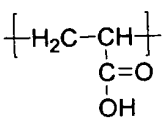
或者



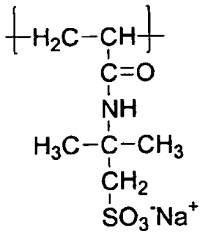
（化学式（32））

其中 n 为 8-20 的整数；$X^- = Cl^-$，Br^-；G 代表双铵盐 Gemini 表面活性剂基团。具体地说，G 具有化学式（17）所示的结构。

在另一实施例中，FPS 中重复的亲水单体单元选自如下所示化学式：

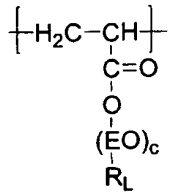


，（化学式（33））



（化学式（34））

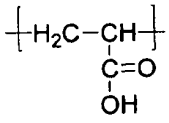
或者



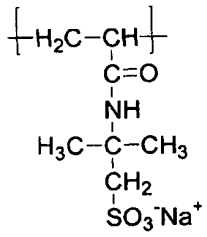
（化学式（35））

其中 R_L 为疏水基团（例如：烷基、苯基或其衍生物）；EO 为–CH_2-CH_2-O-；c 为 8-18 的整数。

在另一实施例中，重复的亲水单体单元选自如下所示化学式：

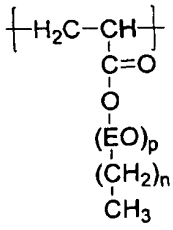


（化学式（36））



（化学式（37））

或者



（化学式（38））

其中 n 为 8-20 的整数；EO 为–CH_2CH_2O-；p 为 6-20 的整数。

在另一实施例中，功能性聚合物表面活性剂包括各种不同的生物制备的聚合物表面活性剂，其中通过生物制备或者合成的功能性聚合物表面活性剂的油-水 IFT 值大于 0.1 达因/厘米。优选的生物聚合物表面活性剂包括黄原胶、多糖，及其衍生物。

除了聚合物与反应物直接反应外，使用伯胺与聚合物反应的例子还包括琥珀酸酐基团（其产率及低分子量均可能受到限制，Hill 等（1993, Macromolecules, 26, pp. 4521-4532）。

其他研究者已经公开许多文献，介绍各种共聚反应的方法。具有中等油-水 IFT 值的聚合物表面活性剂可以通过本技术领域已知的方法制备，其中包括非均相的，反向乳剂，微乳状液，沉淀和自由基胶束共聚法。聚合物表面活性剂典型的制备方法包括自由基引发的含亲水基团单体（例如：丙烯酰胺、丙烯酸、聚烯氧基或烷基磺化丙烯酸盐、或其混合物）与含疏水基团单体（例如：烷基丙烯酰胺、苯基丙烯酰胺、Gemini 丙烯酸基季铵盐、或其混合物）共聚。通过调整引发剂的浓度、活性，单体的浓度，温度，链传导介质，我们可以控制聚丙烯酸酯共聚物的分子量。单体可以是两种或更多。

在阅读本发明后，本领域的技术人员会发现在考虑化学组分的同时还可以根据支化度、分子量、聚合物表面活性剂单元的空间构象来决定其在 EOR 化学过程中的应用（例如：HLB，官能团和离子性能）。

以下实施例将进一步说明本发明的优点及其实施方式。但在实施例中使用的特定材料及其数量，及其他环境和细节不应视为对本发明的限制。除非特别指出，所有百分比均为质量百分比。

实施例

实施例 1.FPS 实施例通过一般实验方法进行，包括下列分析：

1）通过本领域的公知技术分析相行为（见下列参考资料）

a. Reed, R.L. and Healy, R.N.: "Some Physicochemical Aspects of Microemulsion Flooding." Improved Oil Recovery by Surfactant and Polymer Flooding (D.O. Shah and R.S. Schechter, Eds), Academic Press, New York, New York (1977) 383-437.

b. Healy, R.N. and Reed, R.L.: "Physicochemical Aspects of Mictoremulsion Flooding," Transactions, AIME, Volume 257 (1974) 491-501.

c. Dreher, K.D. and Jones, S.C.: "An Approach to the Design of Fluids for Microemulsion Flooding," Solution Chemistry of Surfactants, Volume 2 (K.L. Mittal Editor), Plenum Publishing Corporation (1979).

d. Healy, R.N., Reed, R.L., and Stenmark, D.G.: "Multiphase Microemulsion Systems," Transactions, AIME, Volume 261 (1976) 147-160.

e. Nelson, R.C. and Pope, G.A.: "Phase Relationships in Chemical Flooding," Transactions, AIME, Volume 265 (1978) 325-338.

乳化类书籍）乳化系统。典型的体系包括碳氢化合物、水以及 FPS 拟三元相。通常油相比率越低，混相驱油时间就越长，这样可以产生更高的石油采收率，因为油已被乳化。

2）通过本领域的公知技术进行岩心驱替实验（见下列参考资料）

f. Holm, L.W. and Knight, R.K.: "Soluble Oil Flooding," Petroleum Engineer (November 1976).

g Gogarty, W.B.: "Rheological Properties of Pseudoplastic Fluids in Porous Media," Journal of Petroleum Technology (June 1967) 149-160.

由于储层岩石与乳剂的相互影响，仅凭相和物理性质研究不足以正确设计出乳化体系。岩心驱替是在现场预测 EOR 特性的关键。许多发表的文献已表明岩心驱替结果与现场观测之间具有直接相关性。Green 等人将岩心驱替作为关键的设计步骤与标准之一，测量诸如吸附量、胶束段塞大小的影响以及流度控制的有效性等因素（1998, ISBN 1-55563-077-4, SPE Textbook Series Vol. 6, pp. 285）。Gogarty 等人使用岩心驱替研究如何在现场应用中优化表面活性剂浓度，并模拟驱替、吸附、流度控制及现场标度行为（1976, SPE 5559 PA, pp. 93-102）。

实施例 2

通过自由基引发共聚，合成六个 FPS 的示范样品（见表一）。

第一步，根据表一中的单体比例，在一个三颈圆底烧瓶中加入丙烯酰胺、亲水单体、亲油单体及碳酸钠，溶于去离子水中形成溶液，随后加入甲酸钠和氨水。所有反应物的总质量占烧瓶中溶液总质量的 25-30%。

第二步，将烧瓶放入水浴中，通氮气脱氧 20 分钟。在氮气保护下，将包括偶氮引发剂（如 ABIN）、还原剂（如硫酸氢钠）及氧化剂（如过硫酸钠）在内的引发体系加入烧瓶中。引发体系的总质量占所有反应物质量的 0.01%-0.1%。

第三步，使烧瓶在氮气中再脱氧 10 分钟，然后将其密闭。观察反应液的变化并记录反应液的温度，以确定反应完成。

第四步，反应完成后，水浴的温度上升至 185 F，使烧瓶在水浴中保持 4 个小时。

第五步，将合成的凝胶弄碎、切粒并烘干，获得样品以备后用。

表一

单体	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c
丙烯酰胺	60-80%	60-80%	60-80%	0-40%	0-40%	0-40%
H1	0-35%	0-35%	0-35%	50-90%	50-90%	50-90%
H2		1-5%	1-5%			1-5%
H3	1-5%	1-5%		1-5%	1-5%	1-5%
L1			1-5%	1-5%		

L2		1-5%			1-5%	
L3	1-5%			1-5%		
L4	0-5%	0-5%	0-5%			1-5%
L5	1-5%		1-5%	1-5%	1-5%	1-5%

FPS-1a、1b、1c 的分子量分别在 5 百万（mil）至 10 mil 之间；

FPS-2a、2b、2c 的分子量分别在 0.2 mil 至 3 mil 之间；

H1、H2、H3 均为亲水单体，并且

H1 = [CH_2=CH-CO-OH],

H2 = [CH_2=CH-CO-NH-C(CH_3)$_2$-$CH_2SO_3^-$•Na^+],

H3 = [CH_2=CH-CO-O-(EO)$_p$-(CH_2)$_n$-CH_3];

L1、L2、L3、L4、L5 均为亲水单体，并且

L1 = [CH_2=CH-CO-NH-CH(CH_2-SO_3Na)((CH_2)$_n$-CH_3)],

L2 = [CH_2=CH-CH_2-N^+(CH_3)$_2$-(CH_2)$_n$-CH_3•X^-],

L3 = [CH_2=CH-CO-NH-(CH_2)$_n$-N^+(CH_3)$_2$-(CH_2)$_n$-CH_3•X^-],

L4 = [CH_2=CH-CO-O-(CH_2)$_n$-CH_3],

L5 = [CH_2=CH-CO-G];

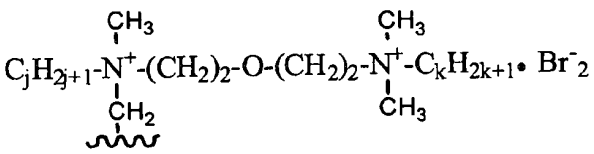
n 是 8-12 的整数；

EO 代表–CH_2CH_2O–，

p 是 6-20 的整数；

X^-=Cl^-，Br^-

G 代表双铵盐 Gemini 表面活性剂基团，共价键合到单体中的羰基，如



(j + k = 24, j = 12, 13, 14, 16, 18)

以下实施例中所示的 IFT 测试程序如下。利用旋转液滴界面张力仪，在 86 F 条件下测定这些体系（油相如正庚烷，水相如 1000 ppm FPS 的 3%氯化钠溶液）的 IFT 值。这些 IFT 值通过以下方法测定：将一个体系的界面张力作为时间函数进行测量，通常为 2 个小时。若

最后 20 分钟的数值持续在 1-2%之间变化，则记录该 2 小时的测试；如果不是，则继续进行测试，直至数值持续 20 分钟在 1-2%之间变化。表二中已列出所有的测试结果。

对 6 个 FPS 样品（在表一中）进行了油-水 IFT 测试。之前聚合物驱体系（三菱生产的 MO4000）中的商业用的部分水解聚丙烯酰胺的 IFT 值为 34.33 达因/厘米。用于对照的正庚烷及 3%氯化钠的读数为 44.80 达因/厘米。

表二

	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c	MO4000	控制
IFT	5.34	7.29	3.47	0.91	0.86	1.36	34.33	44.80

实施例 3

在 185 F 条件下，对环氧涂层贝雷砂岩的 12 英寸岩心（平均空气渗透率为 487 md）进行岩心驱替测试。用 2 个孔隙体积的浓盐水冲洗干岩心，直至达到束缚水饱和度，得到粘度约为 7.2 cP 的典型原油。该油饱和度一般为 0.65。再次用相同的浓盐水冲洗岩心，直至达到在约 0.42 至 0.65 之间的残余油饱和度（含水率 98%）。

注入 0.3 个孔隙体积的 1500 ppm FPS 样品（分别在 6 个岩心驱替测试中使用 FPS-1a、1b、1c、2a、2b、2c）段塞开始化学驱，该 FPS 样品由 0.5%氯化钠盐水制备。再注入 0.5%氯化钠盐水直至达到残余油饱和度（含水率 98%）。表三中列出了产生的残余油饱和度。

注入 0.3 个孔隙体积的 1500 ppm PAM-25（聚丙烯酰胺，水解率=23%，分子量为 25 mil）段塞开始另一次化学驱，该样本由 0.5%氯化钠盐水制备。再注入 0.5%氯化钠盐水直至达到残余油饱和度（含水率 98%）（见表三）。

表三

	FPS-1a	FPS-1b	FPS-1c	FPS-2a	FPS-2b	FPS-2c	PAM-25
饱和度	0.30	0.35	0.32	0.27	0.29	0.30	0.38

表三中的束缚油饱和度数据表明，总体上分子量较小的 FPS 与超高分子量聚丙烯酰胺相比具有更好的石油采收效果。将 FPS-2b 用于 100%含水量的成熟油田试验（113 F，0.3-0.4%盐度，陆上砂岩，水驱后达到束缚油饱和度），增加采收超过原始原油地质储量的 9.5%。

实施例 4

在 113 F 条件下，对环氧涂层贝雷砂岩的 12 英寸中等渗透率的岩心进行两个岩心驱替测试。先用 2 个孔隙体积的浓盐水冲洗干岩心，再用典型的大庆原油冲洗直至达到束缚水饱和度。再用 0.3%矿化度的浓盐水水驱岩心，直至达到束缚油饱和度（含水率 98%）。其中，

岩心 1 在水驱后的累积采收率为原油饱和度的 46%，岩心 2 在水驱后的累积采收率为原油饱和度的 47%。

向岩心 1 中注入 FPS-2c 溶液（约 50 万分子量，7.3 cP，0.6 孔隙体积），得到增量 17%的原油饱和度。

向岩心 2 中注入 PAM-15 溶液（常规聚丙烯酰胺，约 1500 万分子量，20.6 cP，0.6 孔隙体积），得到增量 10%的原油饱和度。

FPS-2c 的粘度约为 PAM-15 的三分之一，具有超过 70%的原油采收效果。

实施例 5

在 113 F 条件下，对环氧涂层贝雷砂岩的 6 英寸低渗透率（50-80 md）的岩心进行两个岩心驱替测试。先用 2 个孔隙体积的浓盐水冲洗干岩心，再用典型的大庆原油冲洗直至达到束缚水饱和度。再用 0.3%矿化度的浓盐水驱替岩心，直至达到束缚油饱和度（含水率 98%）。

注入含有 100 ppm FPS-2b 的 0.3%氯化钠盐水（0.3 孔隙体积）得到增量 10%的原油饱和度。这证明了即便在低浓度情况下，FPS-2b 仍具有的非同寻常的原油采收能力。

本发明所述的具体实施例旨在说明本发明内容，不应理解为对本发明的限制。本发明的主要技术特征可以应用于其它实施例中且仍属于本发明范围内。本领域的普通技术人员能够知道，或通过一般实验获得与本发明所述方法等同的方法。所有这些都属于本发明及权利要求范围内。

本发明以优选实施例的方式说明了本发明的组合物及方法，基于本发明组合物和/或方法，以及所描述方法中的步骤或步骤顺序所作的修饰或改变对于本领域普通技术员而言是显而易见的，是属于本发明范围内的。

Our Ref.: PT20100001-HK-PCT

發明名稱：可提高石油采收率的功能性聚合物

說明書摘要

本發明涉及可提高石油采收率的組合物及其方法。該方法在含有聚合物表面活性劑的水相和油氣相間使用一種水溶性的，具有中等 IFT 值的功能性聚合物表面活性劑（FPS），用於采收地層中的碳氫化合物。其 IFT 值優選爲約 0.1 至約 15 達因/厘米。該 FPS 溶液被證實能與石油發生強烈作用，具有增加 EOR 中的體積波及效率和微觀驅油效率的潛力。

Title of Invention: FUNCTIONAL POLYMER FOR ENHANCED OIL RECOVERY

ABSTRACT

The present invention relates compositions and methods for enhanced oil recovery. The method is directed to employing a water-soluble fThe present invention relates compositions and methods for enhanced oil recovery (EOR). The method is directed to employing a water-soluble functional polymeric surfactant (FPS), with a medium IFT value, preferably ranged from about 0.1 to about15 dyne/cm between water phase containing polymeric surfactant and hydrocarbon phase, for recovery of hydrocarbons from subterranean formations. The FPS solution demonstrates a strong interaction with oil and the great potential to increase both volumetric sweep efficiency and microscopic displacement efficiency in EOR.