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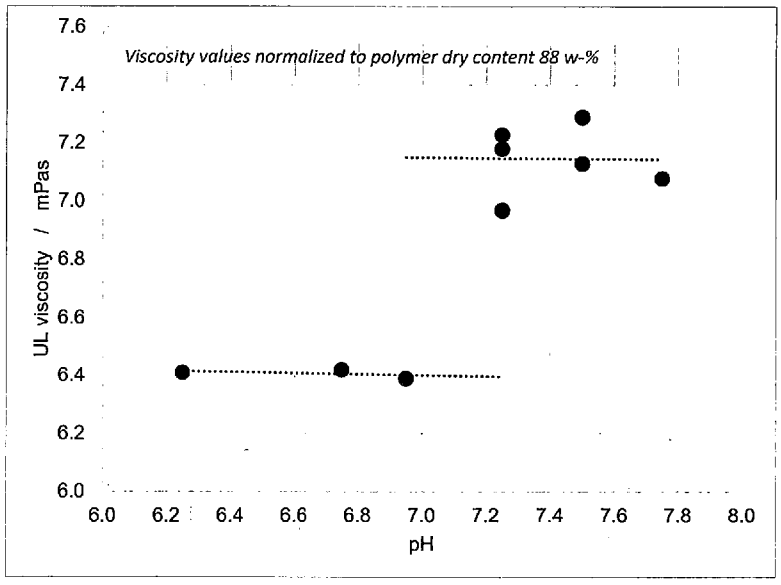

FIG 1

(57) Abstract: The present invention generally relates to compositions and methods for preparation of high reaction temperature dry polyacrylamide (DPAM) polymers. In particular, the disclosure provides methods for adiabatic redox initiated free-radical polymerization of reaction mixtures comprising at least acrylamide monomers, optional free-radical scavenger stabilizers, azo initiators, and redox initiators under pH and initial temperature conditions that allow heat of polymerization to increase reaction temperatures to above 100 °C (Tmax > 100 °C). Gel polymerization under these conditions produces anionic DPAM polymers for use in variety of industrial applications with improved standard viscosity and high water-solubility.

[Continued on next page]

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PREPARATION OF A HIGH REACTION TEMPERATURE DPAM HAVING IMPROVED STANDARD VISCOSITY AND WATER SOLUBILITY

FIELD OF THE INVENTION

[0001] The present application claims benefit of priority to US Provisional Application No.: 63/511,978, filed on July 5, 2023, and to Finnish Application Number 20236044 filed on September 21, 2023, the contents of both of which are incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention generally relates to compositions and methods for preparation of high reaction temperature dry polyacrylamide (DPAM) polymers. In particular, the disclosure provides methods for adiabatic redox initiated free-radical polymerization of reaction mixtures comprising at least acrylamide monomers, optional free-radical scavenger stabilizers, azo initiators, and redox initiators under pH and initial temperature conditions that allow heat of polymerization to increase reaction temperatures to above 100 °C (Tmax > 100 °C). Gel polymerization under these conditions produces anionic DPAM polymers for use in variety of industrial applications with improved standard viscosity and high water-solubility

BACKGROUND OF THE INVENTION

[0003] Polyacrylamide homopolymers and copolymers having high molecular weight, high water-solubility, and high standard viscosity in solution are used in many fields of industry, for example as thickeners, flocculants, strengtheners for paper, for enhanced oil recovery, for tailings treatment, wastewater treatment, drinking water treatment, and for mining applications.

[0004] Such polymers, especially high molecular weight polyacrylamides, are of critical importance for enhanced oil recovery (EOR). EOR techniques, such as polymer flooding wherein large volumes of a polymer solution are injected into a subterranean oil reservoir, can be used to increase the amount of unrefined petroleum (e.g., crude oil) that may be extracted from an oil reservoir (e.g., an oil field). By way of example, using EOR, about 40-60% of the reservoir's original oil can typically be extracted, compared with only 20-40% using traditional primary and secondary recovery techniques (e.g., by water injection or natural gas injection).

[0005] One of the largest uses for polyacrylamide is to flocculate solids in a liquid for the purpose of dewatering and filtering. Many industrial processes use dewatering and filtering steps, in which the water content of a bulk solid or slurry is reduced by filtering or other methods. Dewatering processes are necessary, for example, in the treatment of sludge (for example, in sludge ponds or sludge from municipal wastewater treatment process), slurries and in paper-based pulp as well as in other paper treatment processes. Dewatering methods are also used in mining, for example, in dewatering of mine tailings, and metal ores. Specifically, the mining, processing, and purification of naturally occurring minerals often involve one or more processing or treatment operations in which fine mesh size particles of the mineral of interest are suspended or dispersed in a continuous medium, e.g., a continuous aqueous medium, and the mineral particles are then separated from the medium.

[0006] Flocculants that comprise polyacrylamide homopolymers and copolymers having high molecular weight are commonly used as a chemical treatment for dewatering oil sands tailings, sludge, and other wastewater. Polyacrylamide flocculants are widely employed in the purification of drinking water as well as in sewage treatment, storm-water treatment, treatment of industrial wastewater streams, and to facilitate settling in slurries comprising mined mineral and ore.

[0007] Polyacrylamides and copolymers thereof are also used extensively in pulp and paper applications. Polyacrylamide homopolymers and copolymers are used as retention aids (if molecular mass > 2 million g/mole), dry-strength resins, pitch-control agents, and micro-polymer drainage aids.

[0008] Preparation of homopolymers and copolymers of acrylamide having high molecular weight, high water-solubility, and high standard viscosity in solution is essential for the aforementioned industrial applications. Such polymers are typically prepared as dry polyacrylamides (DPAMs) using gel polymerization methods, such as adiabatic redox initiated free-radical gel polymerization.

[0009] Considerable effort has been directed toward gel polymerization methods for preparing high reaction temperature DPAMs (i.e., produced at high temperatures (Tmax) exceeding 100 °C) with high molecular weight, good solubility (low residual insoluble gel) and high viscosity (SV 6-7.5 mPas). Use of high monomer concentration is beneficial for achieving optimal molecular weight and high viscosity. However, such efforts have been unsuccessful due to unwanted side reactions at Tmax greater than 100 °C and possible ultra-high molecular weight polymer strand formation during polymerization at high monomer concentration. Such phenomena cause undesirable amounts of insolubles in the final produced DPAM, leading to insoluble and therefore unusable DPAMs.

[0010] Therefore, it is an object of the present invention to provide a process for preparing polyacrylamides by means of gel polymerization, in which the polymerization can be performed at maximum temperatures above 100 °C, to provide industrially available DPAMs having high molecular weight and good solubility.

SUMMARY OF THE INVENTION

[0011] The present invention generally relates to compositions and methods for preparation of high reaction temperature dry polyacrylamide (DPAM) polymers. In particular, the disclosure provides methods for adiabatic redox initiated free-radical polymerization of reaction mixtures comprising at least acrylamide monomers, optional free-radical scavenger stabilizers, azo initiators, and redox initiators under initial pH and redox initiation temperature conditions that allow heat of polymerization to increase reaction temperatures to above 100 °C (Tmax > 100 °C). Gel polymerization under these conditions produces anionic DPAM polymers for use in variety of industrial applications with improved standard viscosity, high water-solubility, and little to no residual insolubles.

[0012] In one aspect, the present invention provides a method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization, the method comprising:

[0013] (a) providing or producing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers capable of copolymerizing with acrylamide;

[0014] (b) optionally adding one or more stabilizers;

[0015] (c) optionally adding one or more additives, including but not limited to, one or more chelators, and optionally, one or more chaotropic agents, one or more chain transfer agents, or any combination thereof;

[0016] (d) adding one or more azo initiators;

[0017] (e) adjusting the pH to a range of 7-9, 7-8, 7.1-7.8, or 7.25-7.75;

[0018] (f) cooling to a redox initiation temperature of less than 25 °C;

[0019] (g) adding one or more redox initiators, thereby producing a redox initiated reaction mixture;

[0020] (h) allowing a gel polymerization to occur under essentially adiabatic conditions, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) of greater than 100° C; and

[0021] (i) maintaining said Tmax for a curing time, thereby providing a high reaction temperature polyacrylamide gel.

[0022] In some exemplary embodiments the method further comprises, after step (i) drying and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM as a homopolymer, copolymer, or terpolymer.

[0023] In some exemplary embodiments of the method said gel polymerization occurs:

[0024] (a) under an atmosphere comprising nitrogen, argon, helium, or a combination thereof;

[0025] (b) occurs under a high pressure which is greater than atmospheric pressure and is maintained optionally by heating by said exothermic heat of polymerization or by pressurizing with an inert gas, including but not limited to, nitrogen, argon, helium, or any combination thereof, and further wherein said high pressure is sufficient to prevent boiling of the aqueous reaction mixture when subjected to temperatures greater than 100 °C.

[0026] In some exemplary embodiments of the method:

[0027] (a) said redox initiation temperature ranges from -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C;

[0028] (b) said final reaction temperature ranges from 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, 100 to 110 °C, or 100 to 105 °C;

[0029] (c) after addition of said one or more redox initiators, said final reaction temperature is reached over a time ranging from 5-120 min, 10-90, 20-90, or 20-60 min; and

[0030] (d) said curing time ranges from 10-240 min, 30-180, or 60-120 min.

[0031] In some exemplary embodiments of the method, said one or more additional monomers comprises:

[0032] (a) one or more ethylenically unsaturated, preferably water-soluble, nonionic monomers, including but not limited to, (meth)acrylamide; N-alkylacrylamides, including but not limited to, N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, and N-butylacrylamide; N,N-dialkylacrylamides, including, but not limited to, N,N-dimethylacrylamide and N,N-diethylacrylamide; N-alkyl methacrylamides; alkyl acrylates; hydroxyalkyl acrylates and methacrylates, including but not limited to, hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxymethyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, and 4-hydroxybutyl methacrylate; dihydroxyalkyl acrylates and methacrylates, including but not limited to, 2,3-dihydroxypropyl acrylate, 3,4-dihydroxybutyl acrylate, 2,3-dihydroxypropyl methacrylate (DHPMA), and 3,4-dihydroxybutyl methacrylate; alkyl acrylates, including but not limited to, methyl methacrylate; acrylonitrile; N-vinylmethylacetamide, N-vinylmethylformamide; N-vinyl acetate, glyoxalated acrylamides, and vinyl pyrrolidone; and

[0033] (b) one or more ethylenically unsaturated anionic monomers, including but not limited to, acrylic acid, methacrylic acid; sulfonic acids, phosphonic acids, maleic acid, itaconic acid, vinyl sulfonic acid, acrylamido tertiary butyl sulfonic acid (ATBS) , acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl phosphonic acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof; and

[0034] (c) any combination of the foregoing.

[0035] In some exemplary embodiments of the method, said aqueous solution of ethylenically unsaturated monomers comprises:

[0036] (a) acrylamide,

[0037] (b) acrylamide and acrylic acid, or

[0038] (c) acrylamide, acrylic acid, and ATBS.

[0039] In some exemplary embodiments of the method:

[0040] (a) said one or more optional stabilizers comprise one or more radical scavengers, including but not limited to, thiourea, N,N'-dimethylthiourea, N,N'-diethylthiourea, N,N'-diphenylthiourea, thiocyanates, tetramethylthiuram disulfide, 2-mercaptobenzothiazole (MBT) and salts thereof, 2-mercaptobenzimidazole and salts thereof, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate 2,2'-dithiobis(benzothiazole), 4,4'-thiobis(6-t-butyl-m-cresol), dicyandiamide, cyanamide, paramethoxyphenol, 2,6-di-t-butyl-4-methylphenol, butylhydroxyanisole, 8-hydroxyquinoline, 2,5-di(t-amyl)hydroquinone, 5-hydroxy-1,4-naphthoquinone, dimedone, propyl-3,4,5-trihydroxybenzoate, ammonium N-nitrosophenylhydroxylamine, 4-hydroxy-2,2,6,6-tetramethyoxylpiperidine, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, 1,2,2,6,6-pentamethyl-4-piperidinol, or any combination of the foregoing;

[0041] (b) said one or more additives comprise:(i) said one or more chelators, including but not limited to, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid (EDTA) and salts thereof, 2,2’,2’’,2’’’-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid (DOTA), phosphoric acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof; (ii)

said one or more chaotropic agents, including but not limited to, urea, thiourea, alcohols, glycerol, guanidine, and guanidinium halide salts; (iii) said one or more chain transfer agents, including but not limited to, hypophosphorous acid and salts thereof, sodium hypophosphite, sodium formate, pentamethyldisilane (PMDS), isopropyl alcohol, n-butyl mercaptan, chloroform, carbon tetrachloride, carbon tetrabromide, bromotrichloromethane, 4-methylbenzenethiol, and 4,4'-thiobisbenzenethiol; or (iv) any combination of the foregoing;

[0042] (c) said one or more azo initiators are selected from the group consisting of azobisisobutyronitrile (AIBN), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2-azobis(2-methylpropionamidine) dihydrochloride; 2,2'-azobis(N-(2-carboxyethyl)-2-methylpropionamidine hydrate; 2,2'-azobis{ 2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propene} dihydrochloride; and 2,2'-azobis(l-imino-l-pyrrolidino-2-ethylpropane) dihydrochloride; and

[0043] (d) said one or more redox initiators are selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS); tert-butyl hydroperoxide and sodium sulfite (tBHP/SS); Fe(II)/Fe(III)-hydrogen peroxide systems, Fe(II)/Fe(III)-alkyl hydroperoxides systems, alkyl hydroperoxides-sulfite systems, peroxides-thiosulfate systems, alkyl hydroperoxides-sulfinates systems; alkyl hydroperoxides-hydroxymethanesulfinate systems, and t-butyl hydroperoxide-sodium hydroxymethanesulfinate systems.

[0044] In some exemplary embodiments of the method:

[0045] (a) said one or more optional stabilizers comprise sodium 2-mercaptobenzothiazole (Na-2-MBT);

[0046] (b) said one or more azo initiators comprise AIBN; and

[0047] (c) said one or more redox initiators comprise ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) or tert-butyl hydroperoxide and sodium sulfite (tBHP/SS).

[0048] In some exemplary embodiments of the method, said one or more additives comprise:

[0049] (a) diethylenetriaminepentaacetic acid;

[0050] (b) diethylenetriaminepentaacetic acid and urea;

[0051] (c) diethylenetriaminepentaacetic acid and sodium hypophosphite; or

[0052] (d) diethylenetriaminepentaacetic acid, sodium hypophosphite, and urea.

[0053] In some exemplary embodiments of the method, said redox initiated reaction mixture comprises:

[0054] (a) a total monomer concentration ranging from 30-60%, 32-55%, 32-50%, or 36-42% by wt based on all components therein, wherein said total monomer concentration is sufficient to heat said redox initiated reaction mixture from said redox initiation temperature to said Tmax of greater than 100° C, wherein said redox initiated reaction mixture is heated by said exothermic heat of polymerization;

[0055] (b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

[0056] (c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

[0057] (d) optionally a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein; and

[0058] (e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) ranging from 50-6000, 100-5000, 200-5000, 500-5000, 1000-5000, or 1000-3000 [$(\mu mol/kg)^2$].

[0059] In some exemplary embodiments of the method:

[0060] (a) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of tBHP/SS ranges from 750-5000 [$(\mu mol/kg)^2$], the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt; or

[0061] (b) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of APS/FAS ranges from 50-400 [$(\mu mol/kg)^2$], and the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt.

[0062] In some exemplary embodiments of the method, said high reaction temperature DPAM:

[0063] (a) has a standard viscosity (SV) ranging from 6.0-7.5 mPas, 6.5-7.4 mPas, or 7.0-7.2 mPas, determined using a Brookfield viscometer DV1MLV with a UL adapter and a ULA-DIN-Y spindle at 25 °C ± 0.2 °C and 60 rpm;

[0064] (b) has a high water solubility as determined by residual insoluble gel content ranging from 0-0.5% by wt, 0-0.2% by wt, 0-0.1% by wt, or 0-<0.1% by wt, determined by dissolving 1 g of said high reaction temperature DPAM in 1 L of water at 25 °C and then filtering through a 300 µm aperture;

[0065] (c) has a higher standard viscosity (SV) and higher water solubility compared to a DPAM polymer prepared using the same monomers and same high temperature (Tmax > 100 °C) method with the exceptions of lower pH; or

[0066] (d) any combination of the foregoing.

[0067] In another aspect, the present invention provides a method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization, the method comprising:

[0068] (a) providing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers selected from the group consisting of acrylic acid and salts thereof, acrylamido tertiary butyl sulfonic acid (ATBS) and salts thereof, or a combination of acrylic acid and sodium ATBS;

[0069] (b) adding 2-mercaptobenzothiazole (MBT) or salts thereof;

[0070] (c) adding diethylenetriaminepentaacetic acid;

[0071] (d) adding azobisisobutyronitrile (AIBN);

[0072] (e) adjusting the pH to a range of 7-8, 7.1-7.8, or 7.25-7.75;

[0073] (f) cooling to a redox initiation temperature ranging from less than 25 °C, -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C ;

[0074] (g) adding one or more redox initiators selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) system; tert-butyl hydroperoxide and sodium sulfite (tBHP/SS) system, thereby producing a redox initiated reaction mixture;

[0075] (h) allowing a gel polymerization to occur under essentially adiabatic conditions and under a high pressure inert gas atmosphere, wherein said high pressure is sufficient to prevent boiling, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) ranging from greater than 100 °C, 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, or 100 to 110 °C, wherein said gel polymerization occurs;

[0076] (i) maintaining said Tmax for a curing time ranging from 10-240 min, 30-180 min, or 60-120 min, thereby providing a high reaction temperature polyacrylamide gel;

[0077] (j) optionally drying and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM;

[0078] wherein said high reaction temperature DPAM is a homopolymer, copolymer, or terpolymer.

[0079] In some exemplary embodiments of the method, said redox initiated reaction mixture comprises:

[0080] (a) a total monomer concentration ranging from 32-50%, or 36-42% by wt based on all components therein;

[0081] (b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

[0082] (c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

[0083] (d) optionally a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein;

[0084] (e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of tBHP/SS ranging from 750-5000, 1000-5000, or 1000-3000 [$(\mu mol/kg)^2$] or an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of APS/FAS ranging from 50-1000, 50-600, or 50-400 [$(\mu mol/kg)^2$]; or

[0085] (f) any combination of the foregoing.

[0086] In another aspect, the present invention provides a composition comprising a high reaction temperature dry polyacrylamide (DPAM), obtainable by a method according to any of the foregoing.

BRIEF DESCRIPTION OF THE DRAWINGS

[0087] The invention will be described in more detail with reference to appended drawings, described in detail below.

[0088] **FIG 1** provides an exemplary graph of SV (UL Viscosity) vs. pH of reaction for high reaction temperature DPAMs prepared according to **Examples 1-6 and Comparative Examples 1-3**.

[0089] **FIG 2** provides an exemplary graph of SV (UL Viscosity) vs. maximun reaction temperature (Tmax) for high reaction temperature DPAMs prepared at varying pH, redox level, and monomer concentration including **Examples 1-10 and Comparative Examples 1-6**.

DETAILED DESCRIPTION OF THE INVENTION

[0090] Before describing the invention, the following definitions are provided. Unless stated otherwise all terms are to be construed as they would be by a person skilled in the art.

DEFINITIONS

[0091] As used herein the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise.

[0092] As used herein, the term "enhanced oil recovery" or "EOR" (sometimes also known as improved oil recovery ("IOR") or tertiary mineral oil production) generally refers to techniques for increasing the amount of unrefined petroleum (for example, crude oil) that may be extracted from an oil reservoir , such as an oil field . Examples of EOR techniques include, for example, miscible gas injection (e.g., carbon dioxide flooding), chemical injection (sometimes referred to as chemical enhanced oil recovery ("CEOR"), and which includes, for example, polymer flooding, alkaline flooding, surfactant flooding, micellar polymer flooding, conformance control operations, as well as combinations thereof such as alkaline - polymer flooding or alkaline – surfactant - polymer flooding), microbial injection, and thermal recovery (e.g., cyclic steam, steam flooding, or fire flooding). In some embodiments, the EOR operation may include a polymer ("P") flooding operation, an alkaline – polymer ("AP") flooding operation, a surfactant - polymer ("SP") flooding operation, an alkaline - surfactant - polymer ("ASP") flooding operation, a conformance control operation, or any combination thereof.

[0093] As used herein, the terms "polymer flood" or "polymer flooding" generally refer to a chemical enhanced EOR technique that typically involves injecting an aqueous fluid that is viscosified with one or more water – soluble polymers through injection boreholes into an oil reservoir to mobilize oil left behind alter primary and / or secondary recovery. As a general result of the injection of one or more polymers, the oil may be forced in the direction of the production borehole, and the oil may be produced through the production borehole. Details of exemplary polymer flooding and of polymers suitable for this purpose are disclosed, for example, in "Petroleum, Enhanced Oil Recovery, Kirk - Othmer, Encyclopedia of Chemical Technology, online edition, John Wiley & Sons, 2010", which is herein incorporated by reference in its entirety.

[0094] As used herein, the terms "polyacrylamide" or "PAM" generally refer to polymers and co-polymers comprising acrylamide moieties, and the terms encompass any polymers or copolymers, including terpolymers, comprising acrylamide moieties, e.g., one or more acrylamide (co)polymers of acrylamide and additional monomers capable of copolymerizing with acrylamide. Furthermore, PAMs may comprise any of the polymers or copolymers discussed herein.

[0095] As used herein, the term "high reaction temperature DPAM" refers to DPAMs that have been produced by a method wherein the maximum reaction temperature (Tmax) reached during polymerization is greater than 100 °C. High reaction temperature DPAMs produced by exemplary

embodiments of the present methods may be used in friction reduction, papermaking retention, as strengtheners for paper, as thickeners and/or flocculants, water treatment, tailings treatment, wastewater treatment, drinking water treatment, mineral ore mining applications, and oil and gas mining applications, such as any EOR technique, including but not limited to, polymer flooding.

[0096] As used herein, the term “monomer” generally refers to nonionic monomers, anionic monomers, cationic monomers, zwitterionic monomers, betaine monomers, and amphoteric ion pair monomers.

[0097] As used herein, the terms “polymer” or “polymeric additives” and similar terms are used in their ordinary sense as understood by one skilled in the art, and thus may be used herein to refer to or describe a large molecule (or group of such molecules) that may comprise recurring units. Polymers may be formed in various ways, including by polymerizing monomers and/or by chemically modifying one or more recurring units of a precursor polymer. Unless otherwise specified, a polymer may comprise a “homopolymer” that may comprise substantially identical recurring units that may be formed by, for example, polymerizing a particular monomer. Unless otherwise specified, a polymer may also comprise a "copolymer” that may comprise two or more different recurring units that may be formed by, for example, copolymerizing, two or more different monomers, and/or by chemically modifying one or more recurring units of a precursor polymer. Unless otherwise specified, a polymer or copolymer may also comprise a “terpolymer” or a “tetrapolymer” which generally refer to polymers that comprise three, four, or more different recurring monomer units. The term “polymer” as used herein is intended to include both the acid form of the polymer as well as its various salts. Polymers may be amphoteric in nature, that is, containing both anionic and cationic substituents, although not necessarily in the same proportions.

[0098] As used herein the term "nonionic monomer” generally refers to a monomer that possesses a neutral charge. Exemplary nonionic monomers may comprise but are not limited to comprising monomers selected from the group consisting of acrylamide (“AMD”), methacrylamido, vinyl, allyl, ethyl, and the like, all of which may be substituted with a side chain selected from, for example, an alkyl, arylalkyl, dialkyl, ethoxyl, and/or hydrophobic group. In an exemplary embodiment, a nonionic monomer may comprise AMD. In some embodiments, nonionic monomers may comprise but are not limited to comprising vinyl amide (e.g., acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide), 4-acryloylmorpholine, maleic anhydride, N-vinylpyrrolidone, vinyl acetate, N-vinyl formamide and their derivatives, such as hydroxyethyl(methyl(acrylate CH2=CR-COO-CH2CH2OH (I) and CH2=CR-CO-N(Z1)(Z2) (2) N-substituted (methyl) acrylamide (II), R=H or Me; Z1=5-15C alkyl; 1-3C alkyl substituted by 1-3 phenyl , phenyl or 6-12C cycloalkyl (both optionally substituted) and Z2=H; or Z1 and Z2 are each 3-10C alkyl; (II) is N-tert. hexyl, tert. octyl, methylundecyl, cyclohexyl, benzyl, diphenylmethyl or triphenyl acrylamide. Nonionic monomers include N-isopropylacrylamide, N-vinyl formamide, methacrylamide; N-alkylacrylamides, including but not limited to, N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, and N-butylacrylamide; N,N-dialkylacrylamides, including, but not limited to, N,N-dimethylacrylamide and N,N-diethylacrylamide; N-alkyl methacrylamides; alkyl acrylates; hydroxyalkyl acrylates and methacrylates, including but not limited to, hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxymethyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, and 4-hydroxybutyl methacrylate; dihydroxyalkyl

acrylates and methacrylates, including but not limited to, 2,3-dihydroxypropyl acrylate, 3,4-dihydroxybutyl acrylate, 2,3-dihydroxypropyl methacrylate (DHPMA), and 3,4-dihydroxybutyl methacrylate; alkyl acrylates, including but not limited to, methyl methacrylate; acrylonitrile; N-vinylmethylacetamide, N-vinylmethylformamide; N-vinyl acetate, glyoxalated acrylamides, and vinyl pyrrolidone. Nonionic monomers can be combined for example to form copolymers with acrylamide.

[0099] As used herein, the term "anionic monomers" may refer to either anionic monomers that are substantially anionic in whole or (in equilibrium) in part, at a pH in the range of about 1.0 to about 10.0. The "anionic monomers" may be neutral at low pH (e.g., from a pH of about 0-1, 0-2, or 0-3) depending on the pKa values of acidic protons contained therein. Some anionic monomers are obtained in anionic form as alkali metal salts, alkaline earth metal salts, and ammonium salts, e.g., acrylic acid and sodium acrylamido tertiary butyl sulfonic acid (ATBS).

[0100] Examples of anionic monomers which may be used herein include but are not limited to those comprising acrylic, methacrylic, maleic monomers and the like, acrylic acid, calcium diacrylate, and/or any monomer substituted with a carboxylic acid group or salt thereof. In some embodiments, anionic monomers may be substituted with a carboxylic acid group and include, for example, acrylic acid, and methacrylic acid. In some embodiments, an anionic monomer which may be used herein may be a (meth)acrylamide monomer wherein the amide group has been hydrolyzed to a carboxyl group. Said monomer may be a derivative or salt of a monomer according to other embodiments. Additional examples of anionic monomers comprise but are not limited to those comprising sulfonic acids or a sulfonic acid group, or both. In some embodiments, the anionic monomers which may be used herein may comprise a sulfonic function that may comprise, for example, 2-acrylamido-2-methylpropane sulfonic acid (acrylamido tertiary butyl sulfonic acid or "ATBS"). In some embodiments, anionic monomers may comprise organic acids. In some embodiments, anionic monomers may comprise acrylic acid, methacrylic acid, maleic acid, itaconic acid, acrylamido methylpropane sulfonic acid, vinylphosphonic acid, styrene sulfonic acid and their salts such as sodium, ammonium and potassium. In other embodiments, anionic monomers may comprise acrylic acid, methacrylic acid; sulfonic acids, phosphonic acids, maleic acid, itaconic acid, vinyl sulfonic acid, acrylamido tertiary butyl sulfonic acid (ATBS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl phosphonic acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof. Anionic monomers can be combined for example to form a terpolymer of acrylamide , acrylic acid and acrylamido tertiary butyl sulfonic acid (ATBS). In an exemplary embodiment, one or more acrylamide (co)polymers may comprise at least one monoethylenically unsaturated monomer comprising acid groups, for example monomers that comprise at least one group selected from -COOH, SO3H, or -PO3H2. Examples of such monomers may include , but are not limited to, acrylic acid, methacrylic acid, vinyl sulfonic acid, allyl sulfonic acid or 2-acrylamido -2-methylpropane sulfonic acid, particularly preferably acrylic acid and/or 2-acrylamido-2–methylpropane sulfonic acid, and most preferred acrylic acid or the salts thereof. In an exemplary embodiment, one or more acrylamide (co)polymers, or each of the one or more acrylamide (co)polymers, may comprise acrylic acid and/or 2-acrylamido-2-methylpropanesulfonic acid or salts thereof.

[0101] The term "water-soluble polymer" generally refers to any polymer that may dissolve and/or disperse in water. Said polymers may modify the physical properties of aqueous systems undergoing

gelation, thickening, viscosification, or emulsification/stabilization. Said polymers may perform a variety of functions, including but not limited to use as dispersing and suspending agents, stabilizers, thickeners, viscosifiers, gellants, flocculants and coagulants, film-formers, humectants, binders, and lubricants.

[0102] As used herein, the term "aqueous solution" or "solution" generally refers to a mixture of water and a water-soluble solute or solutes which are completely dissolved with little to no residual undissolved polymer gel. The solution may be homogenous. When mixed with excess of water, the polymer product is preferably fully dissolved and the obtained polymer solution is preferably free from discrete polymer particles or granules or residual gel.

[0103] The term "gel polymerization" refers to a polymerization reaction that is performed without stirring and results in a solid polymer gel. The preparation of high molecular weight polyacrylamides can particularly advantageously be undertaken by means of adiabatic gel polymerization. In this case, a solution of acrylamide and optionally water-soluble copolymers is first made up in water. The concentration of the monomers maybe 20 to 70% or 30 to 60% by weight. The solution is polymerized without stirring and the reactor is typically neither heated nor cooled. This gives rise to a solid polymer gel, which is dried and ground to give granules or powder.

[0104] The term "redox initiated free-radical polymerization" refers to a free-radical polymerization that is initiated by free radicals formed by single electron transfer redox reactions between an oxidizing agent and a reducing agent. "Free-radical polymerization" is a polymerizing approach by which successive addition of free radicals takes place to form a polymer unit. It is a type of chain-growth polymerization by which a polymer forms by the successive addition of free-radical building blocks (repeat units). Free radicals can be formed by a number of different mechanisms, usually involving separate initiator molecules. Following its generation, the initiating free radical adds (nonradical) monomer units, thereby growing the polymer chain. Chain lengthening ends via a termination step, in which two radicals react to form a stable covalent bond. Virtually all free-radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture. The mechanism involves, in order, initiation, chain propagation, and then chain termination. Initiation may be achieved by adding a stable free radical, one that shows little or no tendency for self-combination, directly to the reactants, but a separate initiation step is still involved because these stable radicals are typically inorganic ions or metals. A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions, the most effective of which is redox initiation. This method has found wide application for initiating polymerization reactions and has industrial importance, e.g., in low-temperature emulsion polymerizations. Besides the very short induction period (almost negligible), a lower energy of activation (40–80 kJ/mol) allows the redox polymerization to be carried out under milder conditions than thermal polymerization. This lowers the possibility of side chain reactions giving high molecular weight polymers with a high yield.

[0105] The term "redox initiator" or "redox initiator system" refers to chemicals (e.g., oxidant and reductant) which react by means of a redox reaction to form a radical, which can then initiate a free-radical polymerization reaction. Unlike thermal initiators (e.g., azo initiators), which require high temperatures, redox initiators provide a reliable source of free radicals under mild conditions (e.g., temperatures below 25 °C, below zero °C, or below -2 °C). Redox initiators for free-radical

polymerization are known in principle to those skilled in the art. Suitable examples of "redox initiator systems include ammonium persulfate and ammonium iron(II) sulfate (APS/FAS); tert-butyl hydroperoxide and sodium sulfite (tBHP/SS); Fe(II)/Fe(III)-hydrogen peroxide systems, Fe(II)/Fe(III)-alkyl hydroperoxides systems, alkyl hydroperoxides-sulfite systems, peroxides-thiosulfate systems, alkyl hydroperoxides-sulfinates systems; alkyl hydroperoxides-hydroxymethanesulfinate systems, and t-butyl hydroperoxide-sodium hydroxymethanesulfinate systems. Preferably, tBHP/SS or APS/FAS systems are used. Oxidant and reductant may be added separately or together (i.e., premixed) as individual compounds or as solutions. Redox initiator systems may be added shortly before, simultaneous with, or after addition of monomers, azo initiators, additives, and optional stabilizers. Redox initiator systems are not regenerable, and may consumed; therefore, time between redox initiator addition and monomer addition must be minimized. Preferably redox initiators are added simultaneous with or after monomers are added to the reactor. In certain embodiments the redox initiators are added after adjusting the pH to a range of 7-9, 7-8, 7.1-7.8, or 7.25-7.75 and after cooling to a redox initiation temperature of less than 25 °C. Redox initiators may be added before or after placing the reaction under an inert gas (i.e., inertizing), such as N2, Ar, or He. Preferably, the reaction environment is inertized under inert gas prior to addition of redox initiators. Reductants may also be added to reduce molecular oxygen in the solution.

[0106] Typically, redox initiators are not added until immediately before the polymerization. Preference is given to using a solution, for example an aqueous solution, of the redox initiators. They can be metered in, for example, during or after the charging of the polymerization reactor. Advantageously, the redox initiators can be metered into the monomer feed of the polymerization reactor during the charging of the reactor. In order to assure rapid mixing of the redox initiators, the monomer feed can advantageously be equipped with a static mixer. Under adiabatic conditions, heat generated by the redox initiated polymerization causes the reaction temperature to increase, thereby providing enough heat to cause homolytic bond dissociation in azo initiators, which may be present in solution. Preferably a maximum temperature (Tmax) is reached that is above 100 °C, more preferably, from 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, 100 to 110 °C, or 100 to 105 °C. Thus, after initiation with redox initiators, the onset of the polymerization releases heat, such that, after the rise in temperature, the azo initiator ultimately also begins to break down to form free radicals, essentially causing a thermal initiated polymerization to occur.

[0107] The term "redox initiation temperature" is the reaction temperature at which the redox initiator is added. Suitable redox initiation temperatures range from-10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C.

[0108] The term "equilibrium redox initiator product" "oxidant × reductant" may be calculated using the initial concentrations of redox initiators present (e.g., ammonium persulfate and ammonium iron(II) sulfate (APS/FAS); tert-butyl hydroperoxide and sodium sulfite (tBHP/SS)) in the kinetic rate expression for each redox reaction. The equilibrium redox initiator product has units of $[(\mu mol/kg)^2]$.

[0109] The term "stabilizers" refers to compounds commonly added to polymerization reactions for prevention of polymer degradation by molecular oxygen. It is common practice to add to the polymer solutions stabilizers or combinations of stabilizers to prevent the degradation of the polymer by molecular oxygen or by further reactions induced by molecular oxygen radicals.

Stabilizers of this kind may be free-radical scavengers. Free-radical scavengers react with free radicals (e.g., oxygen radicals, or other unwanted free radicals formed by UV light or other redox processes) such that the free radical is no longer able to attack and chemically degrade the polymer. Examples of stabilizers of this kind include sulfur compounds, for example 2-mercaptobenzothiazole, or sterically hindered amines. WO 2010/133258 A1 and literature cited therein give an overview of the use of various stabilizers in polymer solutions for prevention of free-radical degradation by molecular oxygen for tertiary mineral oil production. The reactivity thereof with respect to the free radicals which occur in the free-radical polymerization must not be so great that they significantly influence the polymerization. Suitable stabilizers therefore have only low reactivity under the conditions of the polymerization or are inert with respect to the free radicals which occur in the course of polymerization. Examples of stabilizers comprise one or more radical scavengers, including but not limited to, thiourea, N,N'-dimethylthiourea, N,N'-diethylthiourea, N,N'-diphenylthiourea, thiocyanates, tetramethylthiuram disulfide, 2-mercaptobenzothiazole (MBT) and salts thereof, e.g., sodium MBT (Na 2-MBT), 2-mercaptobenzimidazole and salts thereof, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate 2,2'-dithiobis(benzothiazole), 4,4'-thiobis(6-t-butyl-m-cresol), dicyandiamide, cyanamide, paramethoxyphenol, 2,6-di-t-butyl-4-methylphenol, butylhydroxyanisole, 8-hydroxyquinoline, 2,5-di(t-amyl)hydroquinone, 5-hydroxy-1,4-naphthoquinone, dimedone, propyl-3,4,5-trihydroxybenzoate, ammonium N-nitrosophenylhydroxylamine, 4-hydroxy-2,2,6,6-tetramethyoxylpiperidine, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, 1,2,2,6,6-pentamethyl-4-piperidinol, or any combination of the foregoing. Stabilizers can be optionally added at any point in the polymerization process, e.g., before, during, or after polymerization. In present embodiments, stabilizers may be optionally added directly to the aqueous monomer solution at any time prior to during or after monomer addition. Single or multiple stabilizers may be added. Stabilizers may also be added before or after cooling, before or after pH adjustment, and before or after redox initiation. More than one stabilizer may be added together or successively in a single dose or multiple doses. In a preferred embodiment, the stabilizer (e.g., MBT or Na 2-MBT) is added directly to the aqueous solution of ethylenically unsaturated monomers prior to adjusting pH, prior to cooling, and prior to redox initiation.

[0110] The term “azo initiators” refers to compounds commonly added to polymerization reactions to form free radicals by homolytic bond cleavage (heat or light initiated) to form free radicals that participate in initiation of polymerization. According to the invention, the aqueous solution further comprises at least one azo initiator, which has a 10 h half-life in water of 40° C to 90° C, preferably 50° C. to 75° C. The 10-hour half-life temperature of azo initiators is a parameter known to those skilled in the art which describes the behavior of initiators. The values describe the temperature at which, after 10 h in each case, half of the amount of Initiator originally present has broken down. Corresponding values can be taken, for example, from the data sheets for azo initiators. On the basis of the 10 h t half-life of 40° C. to 75° C., the initiators do not decompose, or at least do not do so at a significant rate, at room temperature. The values are based on a solution in water.

[0111] In order to obtain high molecular weight polymers with high viscosity, it is desirable to initiate the polymerization at minimum temperature. Exemplary initiation temperatures range from -10 °C to room temperature (e.g., about 25 °C).Preferably cooler temperatures, such as -10 °C to 10 °C, or -6 °C to +3 °C are used for initiation. After redox initiation, the heat of polymerization

released heats up the mixture. On attainment of a sufficient temperature, the azo initiator begins to break down to form radicals and likewise initiates the polymerization.

[0112] Examples of suitable azo initiators include azobisisobutyronitrile (AIBN), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2-azobis(2-methylpropionamidine) dihydrochloride; 2,2'-azobis(*N*-(2-carboxyethyl)-2-methylpropionamidine hydrate; 2,2'-azobis{ 2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propene} dihydrochloride; and 2,2'-azobis(l-imino-l-pyrrolidino-2-ethylpropane) dihydrochloride. The azo initiators are preferably fully water-soluble, but it is sufficient that they are soluble in the monomer solution in the desired amount. AIBN (azobis(isobutyronitrile)), for example, is barely water-soluble, but is soluble in the aqueous solution optionally comprising 25 to 45% by weight of monomers. Azo initiators may be added before or after cooling, before or after pH adjustment, and before, simultaneous with, or after redox initiation, preferably simultaneous with or before redox initiation. Single or multiple azo initiators may be added. More than one azo initiator may be added together or successively in a single dose or multiple doses. In a preferred embodiment, the azo initiator (e.g., AIBN) is added directly to the aqueous solution of ethylenically unsaturated monomers prior to adjusting pH, prior to cooling, and prior to redox initiation.

[0113] The term “chelators” refer to chelating agents which bond to multivalent metals from solution by chelation, thereby preventing the metals from engaging in deleterious reactions. Chelation is a type of bonding of ions and molecules to metal ions. It involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central metal atom. Suitable chelators diethylenetriaminepentaacetic acid (pentetic acid), ethylenediaminetetraacetic acid (EDTA) and salts thereof, 2,2’,2’’,2’’’-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid (DOTA), phosphoric acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof, which may be added before or after cooling, before or after pH adjustment, and before, simultaneous with, or after redox initiation, preferably simultaneous with or before redox initiation. Single or multiple chelators may be added. Multiple chelators may be added together or successively in a single dose or multiple doses. In a preferred embodiment, the chelator (e.g., pentetic acid) is added directly to the aqueous solution of ethylenically unsaturated monomers prior to adjusting pH, prior to cooling, and prior to redox initiation.

[0114] The term “chaotropic agents” refers to molecules in water solution that can disrupt the hydrogen bonding network between water molecules (i.e., exerts chaotropic activity). This has an effect on the stability of the native state of other molecules in the solution, mainly macromolecules (e.g., polymers) by weakening the hydrophobic effect and preventing higher order polymer structures from forming and to prevent aggregation. A chaotropic agent is a structure disrupting additive, general examples of which might include, surfactants, low molecular weight polymers, urea, some salts, etc. One might also think of a chaotropic agent as an additive that induces or increases the “chaos” or entropy in a system. Suitable examples of chaotropic agents for preventing aggregation during gel polymerization include urea, thiourea, alcohols, glycerol, guanidine, and guanidinium halide salts, which may be added before or after cooling, before or after pH adjustment, and before, simultaneous with, or after redox initiation, preferably simultaneous with or before redox initiation. Single or multiple chaotropic agents may be added. Multiple chaotropic agents may be added together or successively in a single dose or multiple doses. In a preferred

embodiment, the chaotropic agent (e.g., urea) is added directly to the aqueous solution of ethylenically unsaturated monomers prior to adjusting pH, prior to cooling, and prior to redox initiation.

[0115] The term "chain transfer agents" refer to molecules that participate in chain termination reactions in polymerization and which affect the final molecular weight of the polymer and may also result in branching. In the conventional free radical polymerization, the control of the polymer chain length is difficult to attain. The classical method of controlling molecular weight is the addition of chain transfer agents to the polymerization medium to lower the molecular weight of the polymer strands and to prevent aberrantly long polymer chains from forming. Such aberrantly long strands may contribute to improper solubility of the final polymer. Suitable chain transfer agents include hypophosphorous acid and salts thereof, sodium hypophosphite, sodium formate, pentamethyldisilane (PMDS), isopropyl alcohol, n-butyl mercaptan, chloroform, carbon tetrachloride, carbon tetrabromide, bromotrichloromethane, 4-methylbenzenethiol, and 4,4'-thiobisbenzenethiol, which may be added before or after cooling, before or after pH adjustment, and before, simultaneous with, or after redox initiation, preferably simultaneous with or before redox initiation. Single or multiple chain transfer agents may be added. Multiple chain transfer agents may be added together or successively in a single dose or multiple doses. In a preferred embodiment, the chain transfer agent (e.g., sodium hypophosphite) is added directly to the aqueous solution of ethylenically unsaturated monomers prior to adjusting pH, prior to cooling, and prior to redox initiation.

[0116] The term "adiabatic conditions" or "essentially adiabatic conditions" refer to conditions which allow little to no heat to escape the polymerization reaction. "Adiabatic" is understood by the person skilled in the art to mean that there is no exchange of heat with the environment. This ideal is naturally difficult to achieve in practical chemical engineering. In the context of this invention, "adiabatic" shall consequently be understood to mean "essentially adiabatic", meaning that the reactor is not supplied with any heat from the outside during the polymerization, i.e., is not heated, and the reactor is not cooled during the polymerization. An adiabatic reactor is properly insulated to allow minimal heat to flow in or out of the reactor. It will be clear to the person skilled in the art that—according to the internal temperature of the reactor and the ambient temperature—certain amounts of heat can be released or absorbed via the reactor wall because of temperature gradients, but this effect naturally plays an ever lesser role with increasing reactor size. Exothermic gel polymerization reactions performed under essentially adiabatic conditions will generate heat and, since the heat is unable to escape, the reaction temperature will increase. The solution is polymerized without stirring and the reactor is typically neither heated nor cooled. This gives rise to a solid polymer gel, which is dried and ground to give granules or powder.

[0117] The term "inertized atmosphere" or "inert gas atmosphere" are phrase generally known in the art to mean under an atmosphere comprising sufficiently high concentration of inert gasses (e.g., N_2, argon, helium, or the like) and sufficiently low in reactive gasses (e.g., less than 300 ppb, 200 ppb, or 100 ppb O_2) to allow for a redox initiated polymerization reaction to occur.

[0118] As used herein, the phrases "% by wt." denotes grams / kilograms of dry mass of additive per dry mass of solids in the formulation, solution, or slurry, multiplied by 100%.

DESCRIPTION OF THE INVENTION

[0119] The present invention generally relates to compositions and methods for preparation of high reaction temperature dry polyacrylamide (DPAM) polymers. In particular, the disclosure provides methods for adiabatic redox initiated free-radical polymerization of reaction mixtures comprising at least acrylamide monomers, optionally free-radical scavenger stabilizers, azo initiators, and redox initiators under pH and initial temperature conditions that allow the heat of polymerization to increase to reaction temperatures to above 100 °C (Tmax > 100 °C). Gel polymerization under these conditions produces DPAMs with improved standard viscosity and water solubility.

[0120] Considerable effort has been directed toward adiabatic free-radical gel polymerization methods for preparing high reaction temperature DPAMs (i.e., produced at high temperatures (Tmax) exceeding 100 °C) with high molecular weight, good solubility (low residual insoluble gel and high viscosity (SV 6-7.5 mPas)). However, such efforts have been unsuccessful due to unwanted side reactions at Tmax greater than 100 °C and possible ultra-high molecular weight polymer strand formation during polymerization at high monomer concentration. Such phenomena cause undesirable amounts of insolubles in the final produced DPAM.

[0121] It is generally known by those skilled in the art that polymer solubility will gradually decrease as maximum polymerization temperature (Tmax) is increased. Several patent publications (e.g., US 5633329, US 5296577, US 10233272 B2) indicate that at reaction temperatures exceeding 100 °C, polymers having good solubility and high SV cannot be produced.

[0122] It is therefore an object of the present invention to provide a process for preparing polyacrylamides by means of gel polymerization, in which the polymerization can be performed up to and exceeding temperatures of 100 °C, that provide industrial scale production of dry polyacrylamide type polymer having high standard viscosity (SV 6-7.5 mPas) and good solubility (i.e., less than 0.5% by wt insolubles).

[0123] Previous in-house development has further demonstrated a clear decrease in SV as the total mass % of monomer solids (M solids, % by wt) was increased in polymerization reaction mixtures at Tmax ranging from 100 - ~130 °C). High M solids (i.e., sufficient to produce enough energy by exothermic heat of polymerization to heat a redox initiated reaction mixture from a redox initiation temperature of less than 25 °C to a maximum reaction temperature (Tmax) of greater than 100° C) is very beneficial for achieving high molecular weight polymers and is therefore a preferred reaction condition.

[0124] It is therefore also an object of the present invention to provide a process for preparing polyacrylamides by gel polymerization using high M solids sufficient to produce enough heat to achieve a Tmax of greater than 100 °C, to provide industrial scale production of dry polyacrylamide type polymer having high standard viscosity (SV 6-7.5 mPas), and good solubility (i.e., less than 0.5% by wt insolubles).

[0125] The inventive process for preparing acrylamide polymer of the present invention comprises polymerizing acrylamide monomer alone or a monomer mixture composed of acrylamide monomer and a monomer capable of copolymerizing with acrylamide monomer in the presence of an azo series initiator in an aqueous medium having a pH of 7 or higher at a reaction temperature range

increasing to above 100 °C, and then drying the resulting material. By carefully balancing the combination of M solids, reaction mixture pH, initiation temperature, redox initiator chemistry and concentration, additives, and thermal initiator chemistry in the polymerization recipe.

[0126] By preparing the polymer according to the invention at increased M solids sufficient to produce enough heat to achieve a Tmax of greater than 100 °C it was surprisingly found that the earlier SV vs. M solids correlation was overcome and polymers of SV >6 mPas with good solubility have been produced. The improvement is remarkable and fulfills the quality requirements for SV and % insoluble of e.g., EOR, friction reduction, and the like. The present method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization also provides a means for improving manufacturing capacity.

[0127] According to the invention gel polymerization is effected at higher than usual monomer solids and higher than usual reaction temperature (Tmax > 100 °C) surprisingly resulting in DPAMs with SV>6 mPas and good solubility under balanced reaction conditions.

[0128] The present invention generally relates to compositions and methods for preparation of high reaction temperature dry polyacrylamide (DPAM) polymers. In particular, the disclosure provides methods for adiabatic redox initiated free-radical polymerization of reaction mixtures comprising at least acrylamide monomers, optional free-radical scavenger stabilizers, azo initiators, and redox initiators under initial pH and redox initiation temperature conditions that allow heat of polymerization to increase reaction temperatures to above 100 °C (Tmax > 100 °C). Gel polymerization under these conditions produces DPAMs with improved standard viscosity, improved water solubility, and little to no residual insolubles.

[0129] In one aspect, the present invention provides a method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization, the method comprising:

[0130] (a) providing or producing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers capable of copolymerizing with acrylamide;

[0131] (b) optionally adding one or more stabilizers;

[0132] (c) optionally adding one or more additives, including but not limited to, one or more chelators, and optionally, one or more chaotropic agents, one or more chain transfer agents, or any combination thereof;

[0133] (d) adding one or more azo initiators;

[0134] (e) adjusting the pH to a range of 7-9, 7-8, 7.1-7.8, or 7.25-7.75;

[0135] (f) cooling to a redox initiation temperature of less than 25 °C;

[0136] (g) adding one or more redox initiators, thereby producing a redox initiated reaction mixture;

[0137] (h) allowing a gel polymerization to occur under essentially adiabatic conditions, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) of greater than 100° C; and

[0138] (i) maintaining said Tmax for a curing time, thereby providing a high reaction temperature polyacrylamide gel.

[0139] In certain preferred embodiments, the total % monomer content (M solids) is greater than 36% by wt, the pH ranges from 7.25-7.5, the redox initiator system comprises tert-butyl hydroperoxide and sodium sulfite (tBHP/SS) and is added at high enough redox dosage level to initiate polymerization. Further improvements in solubility may be achieved by addition of hypophosphite or urea.

[0140] In some exemplary embodiments the method further comprises, after step (i) drying, and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM as a homopolymer, copolymer, or terpolymer.

[0141] Adiabatic redox initiated free-radical gel polymerizations may be performed without agitation in any suitable adiabatic polymerization reactor system capable of being pressurized to prevent boiling of the reaction mixtures wherein temperature exceeded 100 °C.

[0142] In some exemplary embodiments of the method said gel polymerization:

[0143] (a) occurs under an atmosphere comprising nitrogen, argon, helium, or a combination thereof; and/or

[0144] (b) occurs under a high pressure which is greater than atmospheric pressure and is maintained optionally by heating by said exothermic heat of polymerization or by pressurizing with an inert gas, including but not limited to, nitrogen, argon, helium, or any combination thereof, and further wherein said high pressure is sufficient to prevent boiling of the aqueous reaction mixture when subjected to temperatures greater than 100 °C.

[0145] Prior to addition of redox initiator system, the reaction mixtures may be cooled to a redox initiation temperature that is suitable to prevent thermal initiation by the azo initiator.

[0146] In some exemplary embodiments the method comprises one or more of the following:

[0147] (a) said redox initiation temperature ranges from -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C;

[0148] (b) said final reaction temperature ranges from 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, 100 to 110 °C, or 100 to 105 °C;

[0149] (c) after addition of said one or more redox initiators, said final reaction temperature is reached over a time ranging from 5-120 min, 10-90, 20-90, or 20-60 min; and

[0150] (d) said curing time ranges from 10-240 min, 30-180 min, or 60-120 min.

[0151] In some exemplary embodiments of the method, said one or more additional monomers comprise:

[0152] (a) one or more ethylenically, preferably water-soluble, unsaturated nonionic monomers, including but not limited to, methacrylamide; N-alkylacrylamides, including but not limited to, N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, and N-butylacrylamide; N,N-dialkylacrylamides, including, but not limited to, N,N-dimethylacrylamide and N,N-diethylacrylamide; N-alkyl methacrylamides; alkyl acrylates; hydroxyalkyl acrylates and methacrylates, including but not

limited to, hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxymethyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, and 4-hydroxybutyl methacrylate; dihydroxyalkyl acrylates and methacrylates, including but not limited to, 2,3-dihydroxypropyl acrylate, 3,4-dihydroxybutyl acrylate, 2,3-dihydroxypropyl methacrylate (DHPMA), and 3,4-dihydroxybutyl methacrylate; alkyl acrylates, including but not limited to, methyl methacrylate; acrylonitrile; N-vinylmethylacetamide, N-vinylmethylformamide; N-vinyl acetate, glyoxalated acrylamides, and vinyl pyrrolidone; and

[0153] (b) one or more ethylenically unsaturated anionic monomers, including but not limited to, acrylic acid, methacrylic acid; sulfonic acids, phosphonic acids, maleic acid, itaconic acid, vinyl sulfonic acid, acrylamido tertiary butyl sulfonic acid (ATBS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl phosphonic acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof; and

[0154] (c) any combination of the foregoing.

[0155] In some exemplary embodiments of the method, said aqueous solution of ethylenically unsaturated monomers comprises:

[0156] (a) acrylamide,

[0157] (b) acrylamide and acrylic acid, or

[0158] (c) acrylamide, acrylic acid, and ATBS.

[0159] In some exemplary embodiments of the method comprises one, two, three or all four of the following:

[0160] (a) said one or more optional stabilizers comprise one or more radical scavengers, including but not limited to, thiourea, N,N'-dimethylthiourea, N,N'-diethylthiourea, N,N'-diphenylthiourea, thiocyanates, tetramethylthiuram disulfide, 2-mercaptobenzothiazole (MBT) and salts thereof, 2-mercaptobenzimidazole and salts thereof, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate 2,2'-dithiobis(benzothiazole), 4,4'-thiobis(6-t-butyl-m-cresol), dicyandiamide, cyanamide, paramethoxyphenol, 2,6-di-t-butyl-4-methylphenol, butylhydroxyanisole, 8-hydroxyquinoline, 2,5-di(t-amyl)hydroquinone, 5-hydroxy-1,4-naphthoquinone, dimedone, propyl-3,4,5-trihydroxybenzoate, ammonium N-nitrosophenylhydroxylamine, 4-hydroxy-2,2,6,6-tetramethyoxylpiperidine, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, 1,2,2,6,6-pentamethyl-4-piperidinol, or any combination of the foregoing;

[0161] (b) said one or more additives comprise:(i) said one or more chelators, including but not limited to, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid (EDTA) and salts thereof, 2,2',2'',2'''-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid (DOTA), phosphoric acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof; (ii) said one or more chaotropic agents, including but not limited to, urea, thiourea, alcohols, glycerol, guanidine, and guanidinium halide salts; (iii) said one or more chain transfer agents, including but not limited to, hypophosphorous acid and salts thereof, sodium hypophosphite, sodium formate, pentamethyldisilane (PMDS), isopropyl alcohol, n-butyl mercaptan, chloroform, carbon

tetrachloride, carbon tetrabromide, bromotrichloromethane, 4-methylbenzenethiol, and 4,4'-thiobisbenzenethiol; or (iv) any combination of the foregoing;

[0162] (c) said one or more azo initiators are selected from the group consisting of azobisisobutyronitrile (AIBN), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2-azobis(2-methylpropionamidine) dihydrochloride; 2,2'-azobis(N-(2-carboxyethyl)-2-methylpropionamidine hydrate; 2,2'-azobis{ 2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propene} dihydrochloride; and 2,2'-azobis(l-imino-l-pyrrolidino-2-ethylpropane) dihydrochloride; or

[0163] (d) said one or more redox initiators are selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS); tert-butyl hydroperoxide and sodium sulfite (tBHP/SS); Fe(II)/Fe(III)-hydrogen peroxide systems, Fe(II)/Fe(III)-alkyl hydroperoxides systems, alkyl hydroperoxides-sulfite systems, peroxides-thiosulfate systems, alkyl hydroperoxides-sulfinates systems; alkyl hydroperoxides-hydroxymethanesulfinate systems, and t-butyl hydroperoxide-sodium hydroxymethanesulfinate systems.

[0164] In some exemplary embodiments of the method:

[0165] (a) said one or more optional stabilizers comprise sodium 2-mercaptobenzothiazole (Na-2-MBT);

[0166] (b) said one or more azo initiators comprise AIBN; and

[0167] (c) said one or more redox initiators comprise ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) or tert-butyl hydroperoxide and sodium sulfite (tBHP/SS).

[0168] In some exemplary embodiments of the method, said one or more additives comprise:

[0169] (a) diethylenetriaminepentaacetic acid;

[0170] (b) diethylenetriaminepentaacetic acid and urea;

[0171] (c) diethylenetriaminepentaacetic acid and sodium hypophosphite; or

[0172] (d) diethylenetriaminepentaacetic acid, sodium hypophosphite, and urea.

[0173] In some exemplary embodiments of the method, said redox initiated reaction mixture comprises one or more of the following:

[0174] (a) a total monomer concentration ranging from 30-60%, 32-55%, 32-50%, or 36-42% by wt based on all components therein, wherein said total monomer concentration is sufficient to heat said redox initiated reaction mixture from said redox initiation temperature to said Tmax of greater than 100° C, wherein said redox initiated reaction mixture is heated by said exothermic heat of polymerization;

[0175] (b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

[0176] (c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

[0177] (d) optionally a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein; and

[0178] (e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) ranging from 50-6000, 100-5000, 200-5000, 500-5000, 1000-5000, 1000-3000 [(μmol/kg)^2].

[0179] In some exemplary embodiments of the method:

[0180] (a) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of tBHP/SS ranges from 750-5000 [(μmol/kg)^2], the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt; or

[0181] (b) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of APS/FAS ranges from 50-400 [(μmol/kg)^2], and the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt.

[0182] In some exemplary embodiments of the method, said high reaction temperature DPAM comprises one or more of the following:

[0183] (a) a standard viscosity (SV) ranging from 6.0-7.5 mPas, 6.5-7.4 mPas, or 7.0-7.2 mPas, determined using a Brookfield viscometer DV1MLV with a UL adapter and a ULA-DIN-Y spindle at 25 °C ± 0.2 °C and 60 rpm;

[0184] (b) a high water solubility as determined by residual insoluble gel content ranging from 0-0.5% by wt, 0-0.2% by wt, 0-0.1% by wt, or 0-<0.1% by wt, determined by dissolving 1 g of said high reaction temperature DPAM in 1 L of water at 25 °C and then filtering through a 300 μm aperture;

[0185] (c) a higher standard viscosity (SV) and higher water solubility compared to a DPAM polymer prepared using the same monomers and same high temperature (Tmax > 100 °C) method with the exceptions of lower monomer concentration and lower pH; or

[0186] (d) any combination of the foregoing.

[0187] In another aspect, the present invention provides a method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization, the method comprising:

[0188] (a) providing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers selected from the group consisting of acrylic acid and salts thereof, acrylamido tertiary butyl sulfonic acid (ATBS) and salts thereof, or a combination of acrylic acid and sodium ATBS;

[0189] (b) adding 2-mercaptobenzothiazole (MBT) or salts thereof;

[0190] (c) adding diethylenetriaminepentaacetic acid;

[0191] (d) adding azobisisobutyronitrile (AIBN);

[0192] (e) adjusting the pH to a range of 7-8, 7.1-7.8, or 7.25-7.75;

[0193] (f) cooling to a redox initiation temperature ranging from less than 25 °C, -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to +3 °C;

[0194] (g) adding one or more redox initiators selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) system; tert-butyl

hydroperoxide and sodium sulfite (tBHP/SS) system, thereby producing a redox initiated reaction mixture;

[0195] (h) allowing a gel polymerization to occur under essentially adiabatic conditions and under a high pressure inert gas atmosphere, wherein said high pressure is sufficient to prevent boiling, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) ranging from greater than 100° C, 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, or 100 to 110 °C, wherein said gel polymerization occurs;

[0196] (i) maintaining said Tmax for a curing time ranging from 10-240 min, 30-180 min, or 60-120 min, thereby providing a high reaction temperature polyacrylamide gel; and

[0197] (j) optionally drying and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM;

[0198] wherein said high reaction temperature DPAM is a homopolymer, copolymer, or terpolymer.

[0199] In some exemplary embodiments of the method, said redox initiated reaction mixture comprises one or more of the following:

[0200] (a) a total monomer concentration ranging from 32-50%, or 36-42% by wt based on all components therein;

[0201] (b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

[0202] (c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

[0203] (d) optionally a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein;

[0204] (e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of tBHP/SS ranging from 750-5000, 1000-5000, or 1000-3000 [$(\mu mol/kg)^2$] or an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of APS/FAS ranging from 50-1000, 50-600, or 50-400 [$(\mu mol/kg)^2$]; or

[0205] (f) any combination of the foregoing.

[0206] In another aspect, the present invention provides a composition comprising a high reaction temperature dry polyacrylamide (DPAM), obtainable or obtained by a method according to any of the foregoing.

[0207] The methods and compositions illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein and/or any element specifically disclosed herein. Exemplary embodiments of the invention and its advantages are further disclosed in the following examples.

EXAMPLES

[0208] The examples provided herein are for illustrative purposes so that the invention may be more fully understood. These examples should not be construed as limiting the invention in any way.

[0209] GENERAL METHODS

[0210] Laboratory Reactor Set-Up and Gel Polymerization

[0211] Adiabatic redox initiated free-radical gel polymerizations were performed in a cryogenic flask that was placed in a pressurizable chamber to prevent boiling of the reaction mixtures wherein temperature exceeded 100 °C. The pressure chamber was modified in-house from a pressure pot for spray painting (Paint Pressure Tank 10 Liter No Agitator, manufacturer Protima and distributed by Pressurepots.co.uk). Modifications were done for additional safety features and obtaining temperature measurement inside the pot.

[0212] Polymerization reagents (e.g., monomers, azo initiators, additives, including but not limited to, chelating agents, stabilizers, and/or chain transfer agents) were added to the cryogenic flask. The pH was adjusted and the mixtures were cooled and purged with N_2 gas. Redox initiators were added and the polymerizations were visually inspected to verify initiation of the polymerization by observation of gel strings and/or temperature increase.

[0213] The pressure chamber was then closed and pressurized with N_2 gas to prevent boiling as reaction temperatures increased above 100 °C. Heat generated by the polymerization reaction caused the reaction temperature to increase to a maximum temperature (Tmax) above 100 °C. After reaching Tmax, the reactions continued at Tmax for a desired maturation time (i.e., reaction time), and then the chamber pressure was reduced to atmospheric pressure. Resulting polymer gels were cooled, comminuted, dried, and milled according to standard processing and drying procedures. The resulting polymers were evaluated for gel content and standard viscosity (SV).

[0214] Determination of Gel Content

[0215] The resulting polymer (1 g) of was dissolved in 1 L of tap water at 25° C (concentration: 1000 ppm). The solution was filtered through a stainless steel sieve aperture (300 µm) and the amount of polymer gel remaining on the sieve was dried and weighed. Insoluble polymer residue weight-% was calculated.

[0216] Determination of Standard Viscosity (UL Viscosity):

[0217] The standard viscosity was determined in each case. The resulting polymer was dispersed in deionized water and stirred until the polymer was dissolved. Then NaCl solution was added so that the polymer concentration was 0.1 % and the NaCl concentration was 1.0 M. The UL viscosity (standard viscosity, SV) was determined at 25 ± 0.2 °C using a Brookfield viscometer DV1MLV with a UL adapter and a ULA-DIN-Y spindle at 60 rpm.

Example 1: Preparation of a high reaction temperature DPAM copolymer

[0218] pH 7.25

[0219] Initiation temperature: -3 °C.

[0220] Monomer concentration: 36.5% by weight

[0221] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0222] Adiabatic redox initiated free-radical gel polymerization was performed according to the General Methods. To a glass beaker with magnetic stirrer was added 82.1 g of distilled water and

then successively, 267.4 g of acrylamide (49.9% aqueous solution), 170.0 g of a 35% aqueous solution of sodium acrylate (SODAC), 15.9 mg of chelating agent diethylenetriaminepentaacetic acid, pentasodium salt (pentetic acid sodium salt, as 40% aqueous solution), 0.38 g of free-radical oxygen scavenging stabilizer sodium 2-mercaptobenzothiazole (Na-2-MBT, as 50% aqueous solution) and 185.0 mg of azo initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) dispersed in small amount of monomer solution. AIBN has a $t_{1/2}$ of 10 h in toluene at 67 °C.

[0223] The monomer solution was adjusted to pH 7.25 with a 50% sulfuric acid solution and then cooled to a temperature of −5 °C.

[0224] The cooled monomer solution was transferred to a cryogenic flask fitted with a temperature sensor and the solution was purged by bubbling with N_2 gas for 20 minutes. The initiation temperature after purging was -3 °C. Thereafter, redox initiation (tBHP/SS) was achieved by addition of 4 mL of a 0.043% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.056% aqueous sodium sulfite (SS) solution.

[0225] After mixing, the cryogenic flask was placed in a pressure chamber. After visualization of proper initiation of the polymerization (gel strings / temperature increase), the N_2 purging was removed. The chamber was closed and then pressurized with N_2 gas. The temperature rose from -3 °C to a Tmax of 104 °C within 50 min. After Tmax was observed, the gel was matured at Tmax for another 2 h and then the N_2 pressurization was removed.

[0226] After cooling, the resulting solid polymer gel block was comminuted using a meat grinder (LM-10/P, Koneteollisuus Oy, Finland) and the gel granules obtained were dried in a fluidized bed dryer at 95 °C (FBD95) for 30 min. A white, hard granular material was obtained, which was converted to a coarse powder with particle size < 1000 µm by means of a centrifugal mill.

[0227] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 2: Second preparation of a high reaction temperature DPAM copolymer

[0228] pH 7.25

[0229] Initiation temperature: -3 °C.

[0230] Monomer concentration: 36.5% by weight

[0231] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0232] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using less redox initiator.

[0233] Redox initiation (tBHP/SS) was achieved by addition of 2.4 mL of 0.051% aqueous solution of t-butyl hydroperoxide (tBHP) and 3.2 mL of a 0.057% aqueous sodium sulfite (SS) solution.

[0234] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

[0235] **Table 1**: Polymerization conditions and results for high reaction temperature DPAMs.

Example No.	pH	Redox pair	OX*RED [(µmol/kg)^2]	Monomers	Monomer Total wt%	Chain transfer agent ($NaPO_2H_2$)	Redox Initiation T °C	SV norm 88%, mPas	Gel content (wt% of dry polymer)
1	7.25	tBHP/SS	1330	69% AMD, 31 SODAC	36.5	No	-3	7.0	0
2	7.25	tBHP/SS	760	69% AMD, 31 SODAC	36.5	No	-3	7.2	0.1
3	7.25	APS/FAS	240	69% AMD, 31 SODAC	36.5	No	-3	7.2	0.2
4	7.5	tBHP/SS	1280	69% AMD, 31 SODAC	36.5	No	-3	7.1	<0.1
5	7.5	APS/FAS	240	69% AMD, 31 SODAC	36.5	No	-3	7.3	0.5
6	7.75	tBHP/SS	4930	69% AMD, 31 SODAC	36.5	No	-3	7.1	<0.1
7	7.5	tBHP/SS	3180	69% AMD, 31 SODAC	41.5	No	+3	6.1	0
8	7.25	tBHP/SS	1330	69% AMD, 31 SODAC	36.5	Yes	-3	6.7	0
9	7.5	tBHP/SS	2270	61% AMD, 39 SODAC	37.0	No	-3	7.2	0
10	7.5	APS/FAS	240	69% AMD, 31 SODAC	36.5	Yes	-3	7.0	0
C1	6.25	tBHP/SS	250	69% AMD, 31 SODAC	36.5	No	-2	6.4	0.2
C2	6.75	tBHP/SS	450	69% AMD, 31 SODAC	36.5	No	-2	6.4	0
C3	6.95	tBHP/SS	1250	69% AMD, 31 SODAC	36.5	No	-2	6.4	0
C4*	6.85	tBHP/SS	1020	69% AMD, 31 SODAC	41.5	No	+5	5.2	0
C5**	7.25	tBHP/SS	1330	69% AMD, 31 SODAC	36.5	Yes	-3	6.1	0
C6#	7.75	tBHP/SS	1280	69% AMD, 31 SODAC	36.5	No	-3	-	-

** Clearly shorter dissolution time compared to other data points.*

*** Without Na-2-MBT*

 # No polymerization observed.

Example 3: Third preparation of a high reaction temperature DPAM copolymer

[0236] pH 7.25

[0237] Initiation temperature: -3 °C.

[0238] Monomer concentration: 36.5% by weight

[0239] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate

[0240] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a different redox initiator. Redox initiation (APS/FAS) was achieved by addition of 2.4 mL of 0.074% aqueous solution of ammonium persulfate (APS) and 2.4 mL of a 0.127% aqueous ammonium iron(II) sulfate hexahydrate (FAS) solution.

[0241] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 4: Fourth preparation of a high reaction temperature DPAM copolymer

[0242] pH 7.5

[0243] Initiation temperature: -3 °C.

[0244] Monomer concentration: 36.5% by weight

[0245] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0246] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a higher pH and less redox initiator. Redox initiation (tBHP/SS) was achieved by addition of 2.4 mL of 0.051% aqueous solution of t-butyl hydroperoxide (tBHP) and 2.4 mL of a 0.127% aqueous sodium sulfite (SS) solution.

[0247] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 5: Fifth preparation of a high reaction temperature DPAM copolymer

[0248] pH 7.5

[0249] Initiation temperature: -3 °C.

[0250] Monomer concentration: 36.5% by weight

[0251] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0252] Adiabatic redox initiated free-radical polymerization was performed according to **Example 3** using a higher pH. Redox initiation (APS/FAS) was achieved by addition of 2.4 mL of 0.074% aqueous solution of ammonium persulfate (APS) and 2.4 mL of a 0.127% aqueous ammonium iron(II) sulfate hexahydrate (FAS) solution.

[0253] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 6: Sixth preparation of a high reaction temperature DPAM copolymer

[0254] pH 7.75

[0255] Initiation temperature: -3 °C.

[0256] Monomer concentration: 36.5% by weight

[0257] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0258] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a higher pH and more redox initiator. Redox initiation (tBHP/SS) was achieved by addition of 4 mL of 0.051% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.178% aqueous sodium sulfite (SS) solution.

[0259] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 7: Seventh preparation of a high reaction temperature DPAM copolymer

[0260] pH 7.5

[0261] Initiation temperature: +3 °C.

[0262] Monomer concentration: 41.5% by weight

[0263] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0264] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a higher pH, a higher initiation temperature, higher monomer concentration, and more redox initiator.

[0265] To a glass beaker with magnetic stirrer was added 23.3 g of distilled water and then successively, 303.3 g of acrylamide (49.9% aqueous solution), 192.8 g of a 35% aqueous solution of sodium acrylate (SODAC), 15.9 mg of chelating agent diethylenetriaminepentaacetic acid, pentasodium salt (pentetic acid sodium salt, as 40% aqueous solution), 0.43 g of free-radical oxygen scavenging stabilizer sodium 2-mercaptobenzothiazole (Na-2-MBT, as 50% aqueous solution) and 185.0 mg of azo initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) dispersed in small amount of monomer solution. AIBN has a $t_{1/2}$ of 10 h in toluene at 67 °C.

[0266] The monomer solution was adjusted to pH 7. 5 with a 50% sulfuric acid solution and then cooled to a temperature of +1 °C.

[0267] The cooled monomer solution was transferred to a cryogenic flask fitted with a temperature sensor and the solution was purged by bubbling with N_2 gas for 20 minutes. The initiation temperature after purging was +3 °C. Thereafter, redox initiation (tBHP/SS) was achieved by addition of 2.4 mL of a 0.068% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.142% aqueous sodium sulfite (SS) solution.

[0268] After mixing, the cryogenic flask was placed in a pressure chamber. After visualization of proper initiation of the polymerization (gel strings / temperature increase), the N_2 purging was removed. The chamber was closed and then pressurized with N_2 gas. The temperature rose from +3 °C to a Tmax of 127 °C within 20 min. After Tmax was observed, the gel was matured at Tmax for another 2 h and then the N_2 pressurization was removed.

[0269] After cooling, the resulting solid polymer gel block was comminuted using a meat grinder (LM-10/P, Koneteollisuus Oy, Finland) and the gel granules obtained were dried in a fluidized bed

dryer at 95 °C (FBD95) for 30 min. A white, hard granular material was obtained, which was converted to a coarse powder with particle size < 1000 µm by means of a centrifugal mill.

[0270] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 8: Eighth preparation of a high reaction temperature DPAM copolymer

[0271] pH 7.25

[0272] Initiation temperature: -3 °C.

[0273] Monomer concentration: 36.5% by weight

[0274] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0275] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** with the addition of a chain transfer agent.

[0276] To a glass beaker with magnetic stirrer was added 81.8 g of distilled water and then successively, 267.4 g of acrylamide (49.9% aqueous solution), 170.0 g of a 35% aqueous solution of sodium acrylate (SODAC), 15.9 mg of chelating agent diethylenetriaminepentaacetic acid, pentasodium salt (pentetic acid sodium salt, as 40% aqueous solution), 0.38 g of free-radical oxygen scavenging stabilizer sodium 2-mercaptobenzothiazole (Na-2-MBT, as 50% aqueous solution), 0.26 g of chain transfer agent sodium hypophosphite (0.2 % aqueous solution), and 185.0 mg of azo initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) dispersed in small amount of monomer solution. AIBN has a $t_{1/2}$ of 10 h in toluene at 67 °C.

[0277] The monomer solution was adjusted to pH 7.25 with a 50% sulfuric acid solution and then cooled to a temperature of −5 °C.

[0278] The cooled monomer solution was transferred to a cryogenic flask fitted with a temperature sensor and the solution was purged by bubbling with N_2 gas for 20 minutes. The initiation temperature after purging was -3 °C. Thereafter, redox initiation (tBHP/SS) was achieved by addition of 4 mL of a 0.043% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.056% aqueous sodium sulfite (SS) solution.

[0279] After mixing, the cryogenic flask was placed in a pressure chamber. After visualization of proper initiation of the polymerization (gel strings / temperature increase), the N_2 purging was removed. The chamber was closed and then pressurized with N_2 gas. The temperature rose from -3 °C to a Tmax of 107 °C within 50 min. After Tmax was observed, the gel was matured at Tmax for another 2 h and then the N_2 pressurization was removed.

[0280] After cooling, the resulting solid polymer gel block was comminuted using a meat grinder (LM-10/P, Koneteollisuus Oy, Finland) and the gel granules obtained were dried in a fluidized bed dryer at 95 °C (FBD95) for 30 min. A white, hard granular material was obtained, which was converted to a coarse powder with particle size < 1000 µm by means of a centrifugal mill.

[0281] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 9: Ninth preparation of a high reaction temperature DPAM copolymer

[0282] pH 7.5

[0283] Initiation temperature: -3 °C.

[0284] Monomer concentration: 37% by weight

[0285] Monomer ratio: 61% by weight of acrylamide and 39% by weight of sodium acrylate.

[0286] Adiabatic redox initiated free-radical gel polymerization was performed according to the General Methods. To a glass beaker with magnetic stirrer was added 62.9 g of distilled water and then successively, 240.1 g of acrylamide (49.9% aqueous solution), 216.4 g of a 35% aqueous solution of sodium acrylate (SODAC), 15.9 mg of chelating agent diethylenetriaminepentaacetic acid, pentasodium salt (pentetic acid sodium salt, as 40% aqueous solution), 0.39 g of free-radical oxygen scavenging stabilizer sodium 2-mercaptobenzothiazole (Na-2-MBT, as 50% aqueous solution) and 185.0 mg of azo initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) dispersed in small amount of monomer solution. AIBN has a $t_{1/2}$ of 10 h in toluene at 67 °C.

[0287] The monomer solution was adjusted to pH 7. 5 with a 50% sulfuric acid solution and then cooled to a temperature of −5 °C.

[0288] The cooled monomer solution was transferred to a cryogenic flask fitted with a temperature sensor and the solution was purged by bubbling with N_2 gas for 20 minutes. The initiation temperature after purging was -3 °C. Thereafter, redox initiation (tBHP/SS) was achieved by addition of 3.2 mL of a 0.051% aqueous solution of t-butyl hydroperoxide (tBHP) and 3.2 mL of a 0.127% aqueous sodium sulfite (SS) solution.

[0289] After mixing, the cryogenic flask was placed in a pressure chamber. After visualization of proper initiation of the polymerization (gel strings / temperature increase), the N_2 purging was removed. The chamber was closed and then pressurized with N_2 gas. The temperature rose from -3 °C to a Tmax of 110 °C within 60 min. After Tmax was observed, the gel was matured at Tmax for another 2 h and then the N_2 pressurization was removed.

[0290] After cooling, the resulting solid polymer gel block was comminuted using a meat grinder (LM-10/P, Koneteollisuus Oy, Finland) and the gel granules obtained were dried in a fluidized bed dryer at 95 °C (FBD95) for 30 min. A white, hard granular material was obtained, which was converted to a coarse powder with particle size < 1000 µm by means of a centrifugal mill.

[0291] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Example 10: Tenth preparation of a high reaction temperature DPAM copolymer

[0292] pH 7.5

[0293] Initiation temperature: -3 °C.

[0294] Monomer concentration: 36.5% by weight

[0295] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0296] Adiabatic redox initiated free-radical polymerization was performed according to **Example 5** with the addition of a chain transfer agent e.g., 0.26 g of sodium hypophosphite (0,2 % aqueous solution) and 0.13 g of orthophosphoric acid (75% aqueous solution) were added to reaction mixture prior redox initiation.

[0297] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 1: Preparation of a first comparative copolymer

[0298] pH 6.25

[0299] Initiation temperature: -1 °C.

[0300] Monomer concentration: 36.5% by weight

[0301] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0302] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a lower pH and less redox initiator. Redox initiation (tBHP/SS) was achieved by addition of 4 mL of 0.018% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.026% aqueous sodium sulfite (SS) solution.

[0303] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 2: Preparation of a second comparative copolymer

[0304] pH 6.75

[0305] Initiation temperature: -2 °C.

[0306] Monomer concentration: 36.5% by weight

[0307] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0308] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a lower pH and less redox initiator. Redox initiation (tBHP/SS) was achieved by addition of 4 mL of 0.024% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.034% aqueous sodium sulfite (SS) solution.

[0309] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 3: Preparation of a third comparative copolymer

[0310] pH 6.95

[0311] Initiation temperature: -2 °C.

[0312] Monomer concentration: 36.5% by weight

[0313] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0314] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a lower pH and less redox initiator. Redox initiation (tBHP/SS) was achieved by addition of 2.8

mL of 0.043% aqueous solution of t-butyl hydroperoxide (tBHP) and 4 mL of a 0.076% aqueous sodium sulfite (SS) solution.

[0315] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 4: Preparation of a fourth comparative copolymer

[0316] pH 6.85

[0317] Initiation temperature: +5 °C.

[0318] Monomer concentration: 41.5% by weight

[0319] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0320] Adiabatic redox initiated free-radical polymerization was performed according to **Example 1** using a lower pH, a higher initiation temperature, higher monomer concentration, and less redox initiator.

[0321] To a glass beaker with magnetic stirrer was added 23.3 g of distilled water and then successively, 303.3 g of acrylamide (49.9% aqueous solution), 192.8 g of a 35% aqueous solution of sodium acrylate (SODAC), 38.9 mg of chelating agent diethylenetriaminepentaacetic acid, pentasodium salt (pentetic acid sodium salt, as 40% aqueous solution), 0.43 g of free-radical oxygen scavenging stabilizer sodium 2-mercaptobenzothiazole (Na-2-MBT, as 50% aqueous solution) and 312.0 mg of azo initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) dispersed in small amount of monomer solution. AIBN has a $t_{1/2}$ of 10 h in toluene at 67 °C.

[0322] The monomer solution was adjusted to pH 6.85 with a 50% sulfuric acid solution and then cooled to a temperature of +4 °C.

[0323] The cooled monomer solution was transferred to a cryogenic flask fitted with a temperature sensor and the solution was purged by bubbling with N_2 gas for 20 minutes. The initiation temperature after purging was +5 °C. Thereafter, redox initiation (tBHP/SS) was achieved by addition of 2 mL of a 0.072% aqueous solution of t-butyl hydroperoxide (tBHP) and 2 mL of a 0.103% aqueous sodium sulfite (SS) solution.

[0324] After mixing, the cryogenic flask was placed in a pressure chamber. After visualization of proper initiation of the polymerization (gel strings / temperature increase), the N_2 purging was removed. The chamber was closed and then pressurized with N_2 gas. The temperature rose from +5 °C to a Tmax of 133 °C within 15 min. After Tmax was observed, the gel was matured at Tmax for another 2 h and then the N_2 pressurization was removed.

[0325] After cooling, the resulting solid polymer gel block was comminuted using a meat grinder (LM-10/P, Koneteollisuus Oy, Finland) and the gel granules obtained were dried in a fluidized bed dryer at 95 °C (FBD95) for 30 min. A white, hard granular material was obtained, which was converted to a coarse powder with particle size < 1000 µm by means of a centrifugal mill.

[0326] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 5: Preparation of a fifth comparative copolymer of 69% by weight of acrylamide and 31% by weight of sodium acrylate

[0327] pH 7.25

[0328] Initiation temperature: -3 °C.

[0329] Monomer concentration: 36.5% by weight

[0330] Adiabatic redox initiated free-radical polymerization was performed according to **Example 8** without Na-2-MBT.

[0331] Insoluble gel content and standard viscosity (SV) were determined according to the General Methods. Polymerization conditions and results are summarized in **Table 1**.

Comparative Example 6: Preparation of a sixth comparative copolymer

[0332] pH 7.75

[0333] Initiation temperature: -3 °C.

[0334] Monomer concentration: 36.5% by weight

[0335] Monomer ratio: 69% by weight of acrylamide and 31% by weight of sodium acrylate.

[0336] Adiabatic redox initiated free-radical polymerization was performed according to **Example 4** using a higher pH. Polymerization did not initiate and gel strings / temperature increase were not observed.

[0337] Polymerization conditions are summarized in **Table 1**.

Commentary on the Experiments:

[0338] An exemplary graph of SV (UL Viscosity) vs. pH of reaction for high reaction temperature DPAMs prepared according to **Examples 1-6** and **Comparative Examples 1-3** is provided in **FIG 1**.

[0339] These results indicate a clear stepwise increase in standard viscosity when pH is increased from below 7 to 7.25-7.75, with the highest SV achieved by polymerization at a pH of 7.5. As shown by **Table 1**, residual insoluble gel content for all DPAMs was suitable for applications requiring good solubility, e.g., EOR (i.e., 0.5 wt % or less), with the majority of DPAMs having little to no insoluble content.

[0340] It was surprisingly found that polymerization using the inventive methods of **Examples 1-6** provided high reaction temperature DPAMs with suitable SV values for use in EOR applications such as polymer flooding and other industrial applications, including but not limited to as thickeners, flocculants, strengtheners for paper, for enhanced oil recovery, for tailings treatment, wastewater treatment, drinking water treatment, and for mining applications. By preparing the polymer according to the invention at increased M solids (i.e., total monomer content greater than 36% by wt) it was surprisingly found that the earlier SV vs. M solids correlation was overcome and polymers of SV >7.0 mPas with good solubility have been produced. The improvement is remarkable and fulfills the quality requirements for SV and % insolubles. The present method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization also provide a means for improving manufacturing capacity.

[0341] An exemplary graph of SV (UL Viscosity) vs. maximun reaction temperature (Tmax) for high reaction temperature DPAMs prepared at varying pH, redox level, and monomer concentration including **Examples 1-10** and **Comparative Examples 1-6** is provided in **FIG 2**. Data points only with good solubility are shown, i.e., insoluble content ≤ 0.5 wt%. The lines are added to denote the maximum viscosity achieved. Dashed line denotes the maximum viscosity obtained for process products pH < 7. Dotted line denotes the maximum viscosity obtained for process products pH > 7. Parameter summary for data points: Monomer solids 35.5 – 41.5 wt% ; Redox Initiation Temp -6 °C - +8 °C; Tmax 100-137 °C; pH 5.75-7.75 (triangles pH > 7); Na-2-MBT 0-7000 ppm of M solids % by wt; Fluid Bed Drying @ 95 °C for 30 min.

[0342] These results indicate a clear increase in standard viscosity when polymerization was performed at pH >7 across all maximum reaction temperatures (100-137 °C). As shown by **Table 1**, residual insoluble gel content for all DPAMs was suitable for applications requiring good solubility (i.e., 0.5 wt % or less), with the majority of DPAMs having little to no insoluble content. These results are highly surprising in light of the industry wide failure to produce highly water soluble DPAMs with high SV at reaction temperatures higher than 100 °C. Without being bound to theory, it can be rationalized that the present methods for producing high reaction temperature DPAMs provide optimal conditions to minimize the frequency of unwanted side reactions. Increasing the pH to values between 7.2 and 7.8 increases the degree of ionization and thus causes the acrylic acid units to have a negative charge. This creates repulsions between the elongating polymer strands, especially at the ends of the elongating strands where additional monomers are added. Anionic monomer units being charged produces repulsion at the end of growing chains, thereby preventing side reactions, which otherwise increase at high temps.

[0343] This repulsion serves to minimize unwanted side reactions, thereby minimizing unwanted side reactions between vicinal strands, which causes decreasing molecular weight, branching and in worst case insolubility. In this manner, the present method likely controls the MW distribution and polymer structure. Thus, insoluble gel content is minimized, even at high temperatures.

[0344] It is evident from the data in **Table 1**, that the correct combination of conditions (redox initiation temperature, redox initiator concentration, and pH) is needed to achieve highly soluble DPAMs with good SV characteristics for use in EOR and other industrial applications, including but not limited to as thickeners, flocculants, strengtheners for paper, for enhanced oil recovery, for tailings treatment, wastewater treatment, drinking water treatment, and for mining applications.

[0345] While having described the invention, and exemplary embodiments, this description is not meant to be construed in a limiting sense. Various modifications of the disclosed embodiments as well as alternative embodiments of the invention will become apparent to persons skilled in the art. It is therefore contemplated that the following claims will cover any such modifications or embodiments that fall within the scope of the invention.

CLAIMS

What is claimed is:

1. A method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization, the method comprising:
    (a) providing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers capable of copolymerizing with acrylamide;
    (b) optionally adding one or more stabilizers;
    (c) optionally adding one or more additives, including but not limited to, one or more chelators, and optionally, one or more chaotropic agents, one or more chain transfer agents, or any combination thereof;
    (d) adding one or more azo initiators;
    (e) adjusting the pH to a range of 7-9, 7-8, 7.1-7.8, or 7.25-7.75;
    (f) cooling to a redox initiation temperature of less than 25 °C;
    (g) adding one or more redox initiators, thereby producing a redox initiated reaction mixture;
    (h) allowing a gel polymerization to occur under essentially adiabatic conditions, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) of greater than 100° C; and
    (i) maintaining said Tmax for a curing time, thereby providing a high reaction temperature polyacrylamide gel.
2. The method of **claim 1**, further comprising after step (i), drying, and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM as a homopolymer, copolymer, or terpolymer.
3. The method of **claim 1 or 2**, wherein said gel polymerization:
    (a) occurs under an atmosphere comprising nitrogen, argon, helium, or a combination thereof; and/or
    (b) occurs under a high pressure which is greater than atmospheric pressure and is maintained optionally by heating by said exothermic heat of polymerization or by pressurizing with an inert gas, including but not limited to, nitrogen, argon, helium, or any combination thereof, and further wherein said high pressure is sufficient to prevent boiling of the aqueous reaction mixture when subjected to temperatures greater than 100 °C.
4. The method of **any one of claims 1, 2, or 3**, wherein one, two, three or all four of the following are satisfied:
    (a) said redox initiation temperature ranges from -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C;
    (b) said final reaction temperature ranges from 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, 100 to 110 °C, or 100 to 105 °C;

(c) after addition of said one or more redox initiators, said final reaction temperature is reached over a time ranging from 5-120 min, 10-90, 20-90, or 20-60 min; and

(d) said curing time ranges from 10-240 min, 30-180 min, or 60-120 min.

5. The method of **any one of the foregoing claims**, wherein said one or more additional monomers comprises:

(a) one or more ethylenically unsaturated, preferably water-soluble, nonionic monomers, including but not limited to, (meth)acrylamide; N-alkylacrylamides, including but not limited to, N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, and N-butylacrylamide; N,N-dialkylacrylamides, including, but not limited to, N,N-dimethylacrylamide and N,N-diethylacrylamide; N-alkyl methacrylamides; alkyl acrylates; hydroxyalkyl acrylates and methacrylates, including but not limited to, hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxymethyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, and 4-hydroxybutyl methacrylate; dihydroxyalkyl acrylates and methacrylates, including but not limited to, 2,3-dihydroxypropyl acrylate, 3,4-dihydroxybutyl acrylate, 2,3-dihydroxypropyl methacrylate (DHPMA), and 3,4-dihydroxybutyl methacrylate; alkyl acrylates, including but not limited to, methyl methacrylate; acrylonitrile; N-vinylmethylacetamide, N-vinylmethylformamide; N-vinyl acetate, glyoxalated acrylamides, and vinyl pyrrolidone;

(b) one or more ethylenically unsaturated anionic monomers, including but not limited to, acrylic acid, methacrylic acid; sulfonic acids, phosphonic acids, maleic acid, itaconic acid, vinyl sulfonic acid, acrylamido tertiary butyl sulfonic acid (ATBS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl phosphonic acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof; or

(c) any combination of the foregoing.

6. The method of **any one of the foregoing claims**, wherein said aqueous solution of ethylenically unsaturated monomers comprises:

(a) acrylamide;

(b) acrylamide and acrylic acid; or

(c) acrylamide, acrylic acid, and ATBS.

7. The method of **any one of the foregoing claims**, wherein:

(a) said one or more optional stabilizers comprise one or more radical scavengers, including but not limited to, thiourea, N,N'-dimethylthiourea, N,N'-diethylthiourea, N,N'-diphenylthiourea, thiocyanates, tetramethylthiuram disulfide, 2-mercaptobenzothiazole (MBT) and salts thereof, 2-mercaptobenzimidazole and salts thereof, sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate 2,2'-dithiobis(benzothiazole), 4,4'-thiobis(6-t-butyl-m-cresol), dicyandiamide, cyanamide, paramethoxyphenol, 2,6-di-t-butyl-4-methylphenol, butylhydroxyanisole, 8-hydroxyquinoline, 2,5-di(t-amyl)hydroquinone, 5-hydroxy-1,4-naphthoquinone, dimedone, propyl-3,4,5-trihydroxybenzoate, ammonium N-nitrosophenylhydroxylamine, 4-hydroxy-2,2,6,6-tetramethyoxylpiperidine, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine,

1,2,2,6,6-pentamethyl-4-piperidinol, or any combination of the foregoing;

(b) said one or more additives comprise:

(i) said one or more chelators, including but not limited to, diethylenetriaminepentaacetic acid, ethylenediaminetetraacetic acid (EDTA) and salts thereof, 2,2',2'',2'''-(1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrayl)tetraacetic acid (DOTA), phosphoric acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof;

(ii) said one or more chaotropic agents, including but not limited to, urea, thiourea, alcohols, glycerol, guanidine, and guanidinium halide salts;

(iii) said one or more chain transfer agents, including but not limited to, hypophosphorous acid and salts thereof, sodium hypophosphite, sodium formate, pentamethyldisilane (PMDS), isopropyl alcohol, n-butyl mercaptan, chloroform, carbon tetrachloride, carbon tetrabromide, bromotrichloromethane, 4-methylbenzenethiol, and 4,4'-thiobisbenzenethiol; or

(iv) any combination of the foregoing;

(c) said one or more azo initiators are selected from the group consisting of azobisisobutyronitrile (AIBN), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride; 2,2-azobis(2-methylpropionamidine) dihydrochloride; 2,2'-azobis(*N*-(2-carboxyethyl)-2-methylpropionamidine hydrate; 2,2'-azobis{ 2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propene} dihydrochloride; and 2,2'-azobis(l-imino-l-pyrrolidino-2-ethylpropane) dihydrochloride; and

(d) said one or more redox initiators are selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS); tert-butyl hydroperoxide and sodium sulfite (tBHP/SS); Fe(II)/Fe(III)-hydrogen peroxide systems, Fe(II)/Fe(III)-alkyl hydroperoxides systems, alkyl hydroperoxides-sulfite systems, peroxides-thiosulfate systems, alkyl hydroperoxides-sulfinates systems; alkyl hydroperoxides-hydroxymethanesulfinate systems, and t-butyl hydroperoxide-sodium hydroxymethanesulfinate systems; or

(e) any combination of the foregoing.

8. The method of **any one of the foregoing claims**, wherein:

(a) said one or more optional stabilizers comprise sodium 2-mercaptobenzothiazole (Na-2-MBT);

(b) said one or more azo initiators comprise AIBN; and

(c) said one or more redox initiators comprise ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) or tert-butyl hydroperoxide and sodium sulfite (tBHP/SS).

9. The method of **any one of the foregoing claims**, wherein said one or more additives comprise:

(a) diethylenetriaminepentaacetic acid;

(b) diethylenetriaminepentaacetic acid and urea;

(c) diethylenetriaminepentaacetic acid and sodium hypophosphite; or

(d) diethylenetriaminepentaacetic acid, sodium hypophosphite, and urea.

10. The method of **any one of the foregoing claims**, wherein said redox initiated reaction mixture comprises:

    (a) a total monomer concentration ranging from 30-60%, 32-55%, 32-50%, or 36-42% by wt based on all components therein, wherein said total monomer concentration is sufficient to heat said redox initiated reaction mixture from said redox initiation temperature to said Tmax of greater than 100° C, wherein said redox initiated reaction mixture is heated by said exothermic heat of polymerization;

    (b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

    (c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

    (d) optionally a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein; and

    (e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) ranging from 50-6000, 100-5000, 200-5000, 500-5000, 1000-5000, or 1000-3000 [$(\mu mol/kg)^2$].

11. The method of **any one of the foregoing claims**, wherein:

    (a) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of tBHP/SS ranges from 750-5000 [$(\mu mol/kg)^2$], the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt; or

    (b) the pH ranges from 7.2-7.8, the equilibrium redox initiator product concentration of APS/FAS ranges from 50-400 [$(\mu mol/kg)^2$], and the redox initiation temperature ranges from -4 to 6 °C, -4 to 2 °C, or -4 to -2 °C, and the total monomer concentration ranges from 36-42% by wt.

12. The method of **any one of the foregoing claims**, wherein said high reaction temperature DPAM:

    (a) has a standard viscosity (SV) ranging from 6.0-7.5 mPas, 6.5-7.4 mPas, or 7.0-7.2 mPas, determined using a Brookfield viscometer DV1MLV with a UL adapter and a ULA-DIN-Y spindle at 25 °C ± 0.2 °C and 60 rpm;

    (b) has a high water solubility as determined by residual insoluble gel content ranging from 0-0.5% by wt, 0-0.2% by wt, 0-0.1% by wt, or 0-<0.1% by wt, determined by dissolving 1 g of said high reaction temperature DPAM in 1 L of water at 25 °C and then filtering through a 300 µm aperture;

    (c) has a higher standard viscosity (SV) and higher water solubility compared to a DPAM polymer prepared using the same monomers and same high temperature (Tmax > 100 °C) method with the exceptions of lower pH; or

    (d) any combination of the foregoing.

13. A method for preparing a high reaction temperature dry polyacrylamide (DPAM) by redox initiated free-radical polymerization **according to claim 1**, the method comprising:

    (a) providing an aqueous solution of ethylenically unsaturated monomers comprising water and (i) acrylamide or (ii) acrylamide and one or more additional monomers selected from the group consisting of acrylic acid and salts thereof, acrylamido tertiary butyl

sulfonic acid (ATBS) and salts thereof, or a combination of acrylic acid and sodium ATBS;

(b) adding 2-mercaptobenzothiazole (MBT) or salts thereof;

(c) adding diethylenetriaminepentaacetic acid;

(d) adding azobisisobutyronitrile (AIBN);

(e) adjusting the pH to a range of 7-8, 7.1-7.8, or 7.25-7.75;

(f) cooling to a redox initiation temperature ranging from less than 25 °C, -10 to 25 °C, -10 to 15 °C, -10 to 10 °C, -10 to 5 °C, or -6 to 3 °C;

(g) adding one or more redox initiators selected from the group of redox initiator systems consisting of ammonium persulfate and ammonium iron(II) sulfate (APS/FAS) system; tert-butyl hydroperoxide and sodium sulfite (tBHP/SS) system, thereby producing a redox initiated reaction mixture;

(h) allowing a gel polymerization to occur under essentially adiabatic conditions and under a high pressure inert gas atmosphere, wherein said high pressure is sufficient to prevent boiling, wherein said redox initiated reaction mixture is heated by an exothermic heat of polymerization to a maximum reaction temperature (Tmax) ranging from greater than 100 °C, 100 to 150 °C, 100 to 140 °C, 100 to 130 °C, 100 to 120 °C, or 100 to 110 °C, wherein said gel polymerization occurs;

(i) maintaining said Tmax for a curing time ranging from 10-240 min, 30-180 min, or 60-120 min, thereby providing a high reaction temperature polyacrylamide gel; and

(j) optionally drying and milling said high reaction temperature polyacrylamide gel to form said high reaction temperature DPAM;

wherein the resultant high reaction temperature DPAM is a homopolymer, copolymer, or terpolymer.

14. The method of **claim 13**, wherein said redox initiated reaction mixture comprises one or more of:

(a) a total monomer concentration ranging from 32-50%, or 36-42% by wt based on all components therein;

(b) a mole percent of acrylamide in said total monomer concentration ranging from 1-100%, 35-95%, or 65-85%;

(c) a mole percent of said one or more additional monomers in said total monomer concentration ranging from 0-99%, 5-65%, or 15-35%;

(d) a stabilizer concentration ranging from 0.01-2%, 0.02-1.5%, or 0.05-1.0% by wt based on total weight of monomers therein;

(e) an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of tBHP/SS ranging from 750-5000, 1000-5000, or 1000-3000 [$(\mu mol/kg)^2$] or an equilibrium redox initiator product concentration (e.g., oxidant × reductant) of APS/FAS ranging from 50-1000, 50-600, or 50-400 [$(\mu mol/kg)^2$]; or

(f) any combination of the foregoing.

15. A composition comprising a high reaction temperature dry polyacrylamide (DPAM), obtainable or produced by a method according to **any of the foregoing claims**.

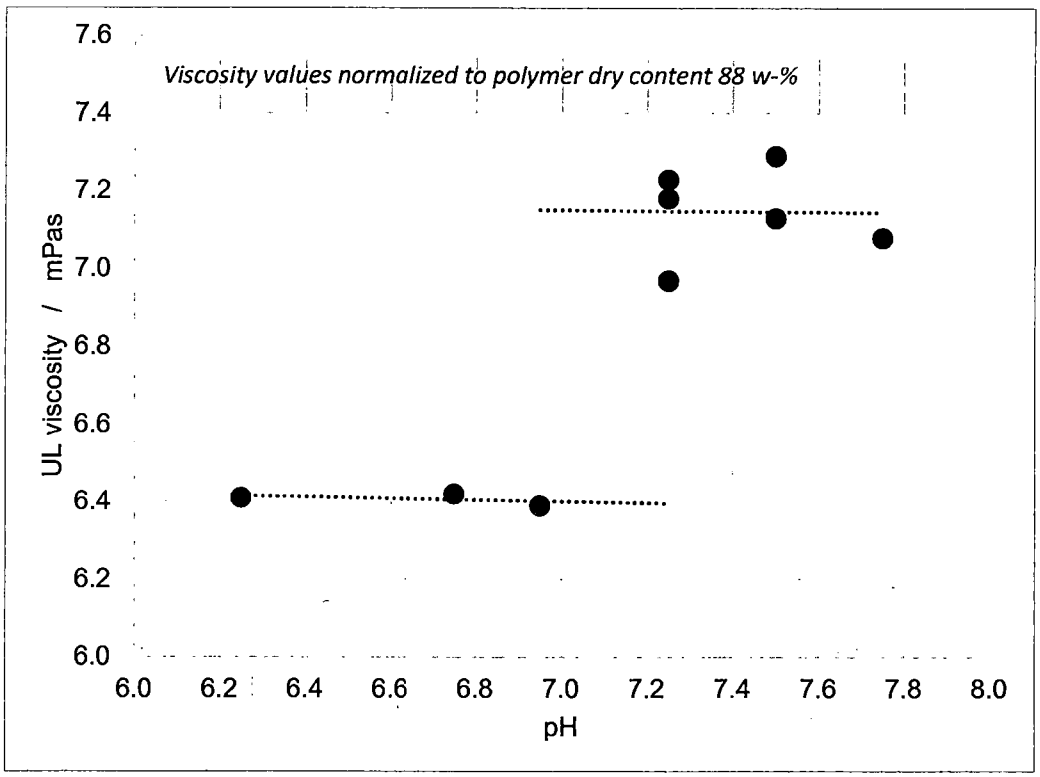
Viscosity values normalized to polymer dry content 88 w-%
UL viscosity / mPas
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
6.0 6.2 6.4 6.6 6.8 7.0 7.2 7.4 7.6 7.8 8.0
pH

FIG 1

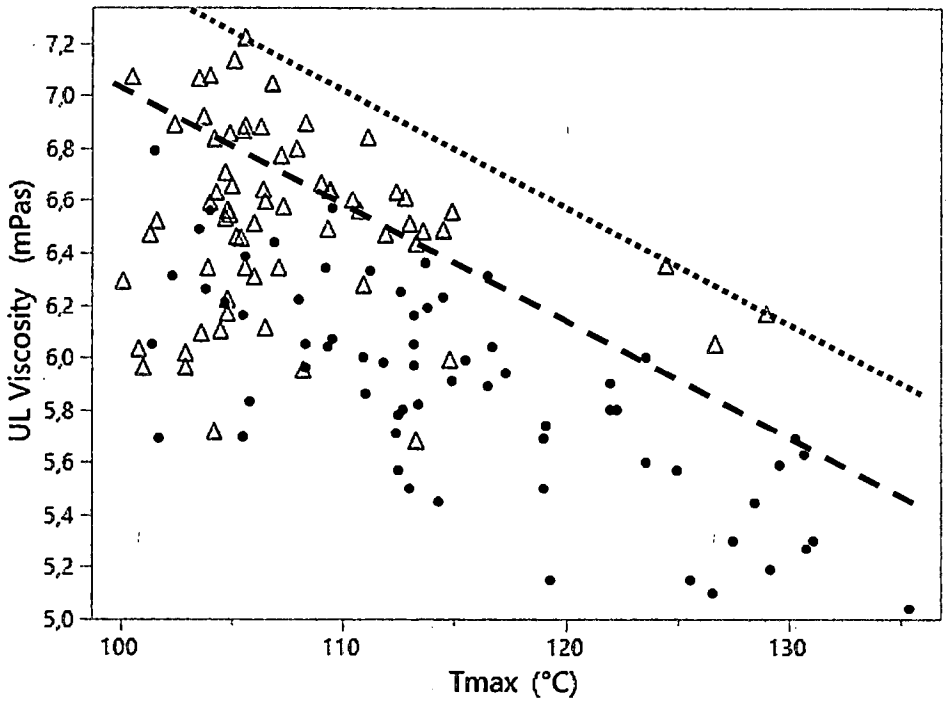
UL Viscosity (mPas)
7,2
7,0
6,8
6,6
6,4
6,2
6,0
5,8
5,6
5,4
5,2
5,0
100
110
120
130
Tmax (°C)

FIG 2