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Sullivan et al.

(54) **TRIGGERING POLYMERIZATION ON-DEMAND FOR WATER CONTROL DOWNHOLE**

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(57) **ABSTRACT**

Methods of sealing a subterranean formation including introducing a trigger-able fluid, the trigger-able fluid containing an ethylenically unsaturated monomer, into a subterranean formation, and using an electromagnetic trigger unit having a electromagnetic source to initiate polymerization of the ethylenically unsaturated monomer after at least a portion of the trigger-able fluid has permeated into the subterranean formation.

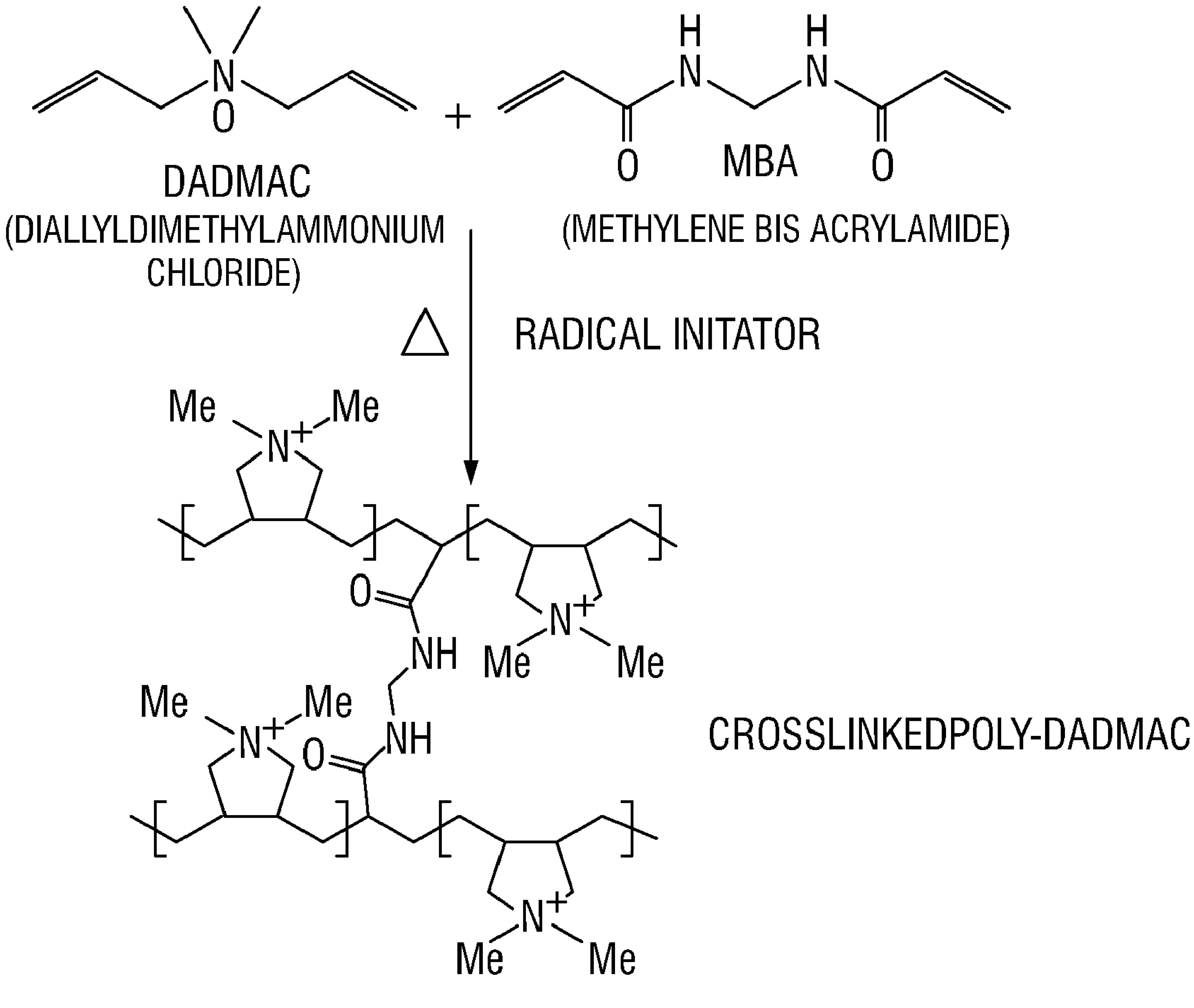
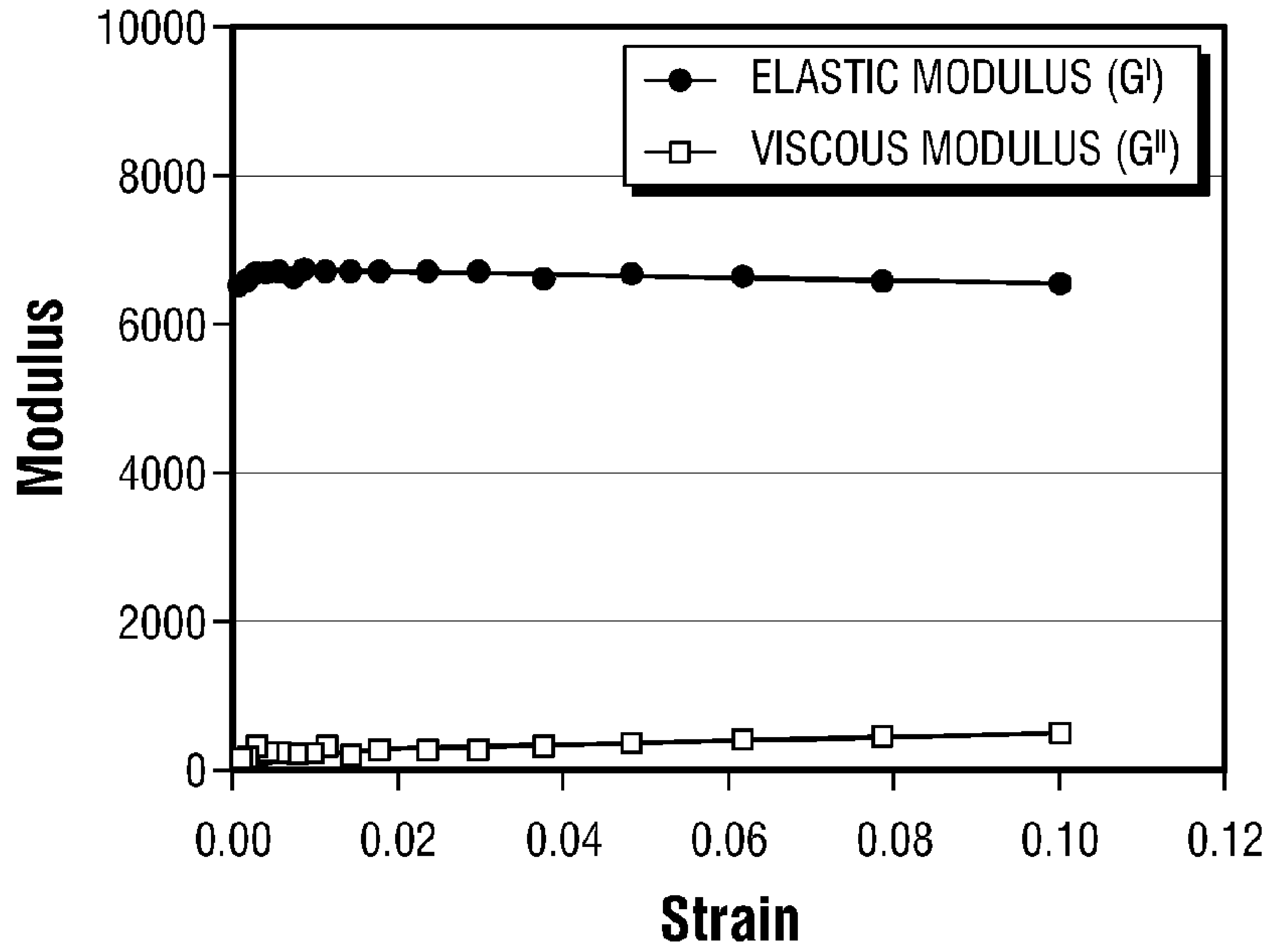
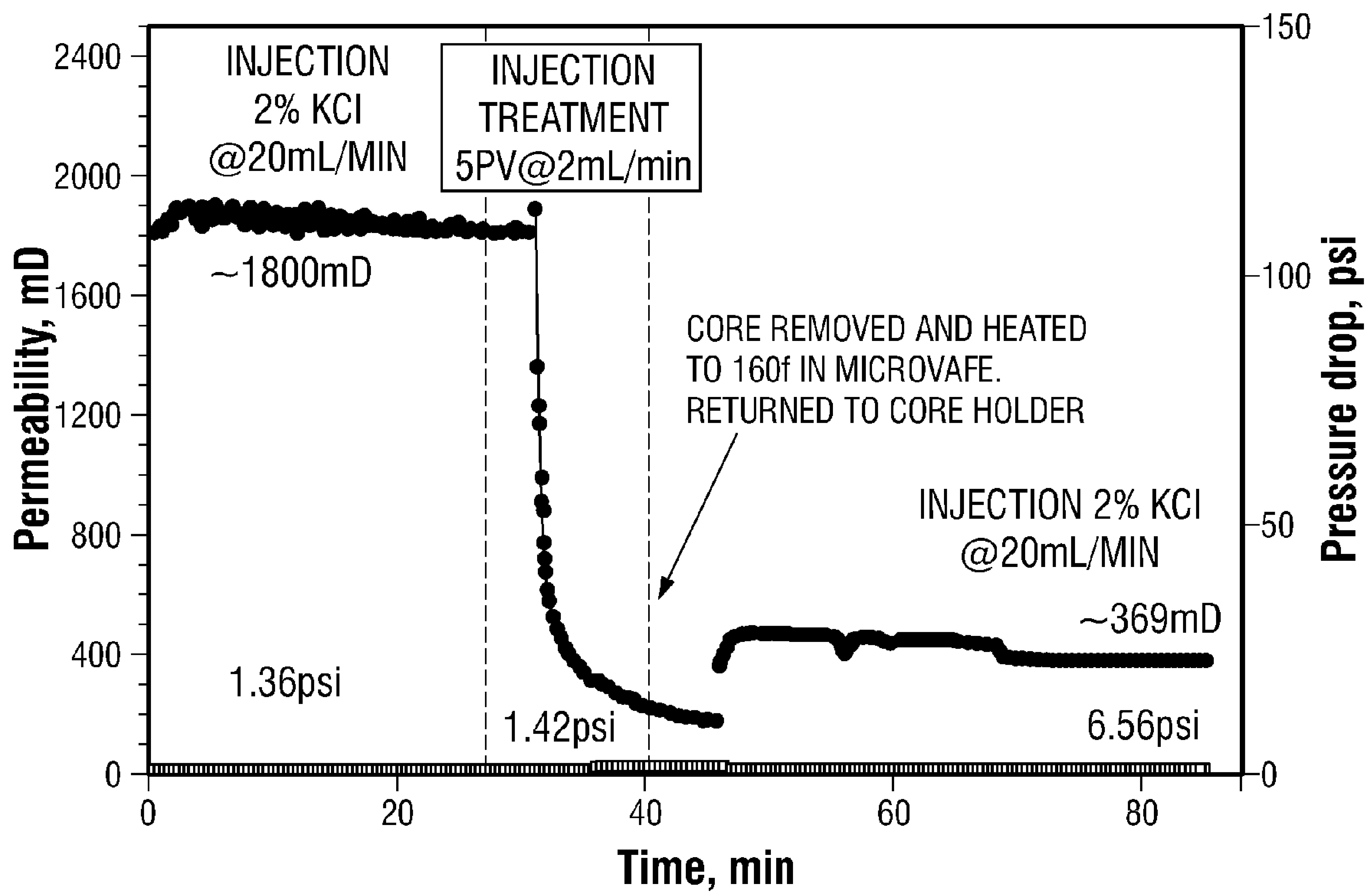

DADMAC
(DIALLYLDIMETHYLAMMONIUM CHLORIDE)
MBA
(METHYLENE BIS ACRYLAMIDE)
RADICAL INITATOR
CROSSLINKEDPOLY-DADMAC

FIG. 1



ELASTIC MODULUS (G')
VISCOUS MODULUS (G'')
Modulus
10000
8000
6000
4000
2000
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Strain

FIG. 2



INJECTION
2% KCl
@20mL/MIN
INJECTION
TREATMENT
5PV@2mL/min
~1800mD
CORE REMOVED AND HEATED
TO 160f IN MICROVAFE.
RETURNED TO CORE HOLDER
INJECTION 2% KCl
@20mL/MIN
~369mD
1.36psi
1.42psi
6.56psi
Permeability, mD
Pressure drop, psi
2400
2000
1600
1200
800
400
0
150
100
50
0
0
20
40
60
80
Time, min

FIG. 3

TRIGGERING POLYMERIZATION ON-DEMAND FOR WATER CONTROL DOWNHOLE

CROSS REFERENCE

[0001] This application claims the benefit of a related U.S. Provisional Application Ser. No. 61/487,424, which was filed on May 18, 2011, entitled "TRIGGERING GELATION ON-DEMAND FOR WATER CONTROL DOWNHOLE," to Sullivan et al., the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Hydrocarbons (oil, natural gas, etc.) are obtained from a subterranean geologic formation (a "reservoir") by drilling a well that penetrates the hydrocarbon-bearing formation. This provides a partial flow path for the hydrocarbon to reach the surface. This flow path is through the formation rock—such as sandstone, chalk, limestone, carbonates, sand--which may have pores of sufficient size, connectivity, and number to provide a conduit for the hydrocarbon to move through the formation. During the process of obtaining hydrocarbons, undesirable materials, such as water, may also travel through the formation in the vicinity of the wellbore and ultimately enter the wellbore. The presence of water may be an issue in numerous formations, including but not limited to sand, sandstone, chalk, limestone, etc. The rate at which the water appears in the wellbore may be slowed through the use of various technologies directed to preventing undesirable materials from entering the wellbore. Conventional water shut off techniques range from mechanical to chemical treatment strategies.

SUMMARY

[0003] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0004] In some embodiments, the present disclosure relates to methods of sealing a subterranean formation, including permeating at least a portion of a subterranean formation with a trigger-able fluid, which includes an ethylenically unsaturated monomer. The methods of the present disclosure also include exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit comprising an electromagnetic radiation source to initiate polymerization of the ethylenically unsaturated monomer.

[0005] In other embodiments, described herein is a method of controlling water in a subterranean formation that includes: introducing a trigger-able fluid containing one or more ethylenically unsaturated monomers into a wellbore that penetrates a water-bearing subterranean formation such that at least some of the trigger-able fluid permeates a portion of the water-bearing subterranean formation. After at least a portion of the trigger-able fluid has permeated the water-bearing subterranean formation, polymerization of the ethylenically unsaturated monomer of the trigger-able fluid that permeated the water-bearing subterranean formation is initiated, thus exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit positioned in the wellbore. The trigger-able fluid may include diallyldimethyl ammonium chloride (DADMAC), methylene bis acrylamide, an inhibitor, and an initiator, such as, for example, water-soluble initiators, a persulfate, an ammonium persulfate, an organic peroxides, an inorganic peroxide, an azo initiator, a 2,2'-azobis(2-amidinopropane)dihydrochloride, a nitroxide, or a disulfide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The manner in which the objectives of the present disclosure and other desirable characteristics may be obtained is explained in the following description and attached drawings in which:

[0007] FIG. **1** illustrates that the polymerization reaction of diallyldimethyl ammonium chloride (DADMAC) in the presence of methylene bis acrylamide (MBA) forms a crosslinked poly-DADMAC.

[0008] FIG. **2** is a graphic representation of a rheology analysis of the crosslinked poly-DADMAC that was performed using parallel plate geometry; and

[0009] FIG. **3** is a graphic representation of a permeability analysis of a trigger-able fluid containing DADMAC, MBA, and ammonium persulfate (without an inhibitor) before, during and after exposure to electromagnetic radiation (microwave).

DETAILED DESCRIPTION

[0010] In the following description, numerous details are set forth to provide an understanding of the present disclosure. However, it may be understood by those skilled in the art that the methods of the present disclosure may be practiced without these details and that numerous variations or modifications from the described embodiments may be possible.

[0011] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation-specific decisions may be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited. In the summary and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary and this detailed description, it should be understood that a range listed or described as being useful, suitable, or the like, is intended to include support for any conceivable sub-range within the range at least because every point within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each possible number along the continuum between about 1 and about 10. Thus, even if a specific data points within the range, or even no data points within the range, are explicitly identified or refer to a few specific, it is to be understood that inventors appreciate and understand that any conceivable data point within the range is to be considered to have been specified, and that inventors possessed knowledge of the entire range and each conceivable point and sub-range within the range.

[0012] The present disclosure relates generally to sealing hydrocarbon-bearing rock formations and/or controlling fluids in hydrocarbon-bearing rock formations to minimize flow of an unacceptable amount of material/fluid (such as water), into a predetermined area, such as into a wellbore. Additionally, the present disclosure relates to the servicing of oil and/or gas wells, including methods useful in downhole applications (such as, for example, an annular gel packer, or a flexible isolation plug, or water and/or gas shut-off agents) where "on-demand" formation of a material capable of maintaining at least a temporary seal is performed by the injection of a trigger-able fluid into a subterranean geologic formation and exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit.

[0013] The present disclosure also relates to methods of controlling water in a subterranean formation, such as subterranean formations found in oil fields. The methods of the present disclosure may comprise introducing a trigger-able fluid comprising one or more ethylenically unsaturated monomers into a subterranean formation. For example, the trigger-able fluid may be introduced or injected or conveyed into a subterranean formation by way of a wellbore that penetrates a subterranean formation, such as a water-bearing subterranean formation.

[0014] The subject matter of the present application also relates to well servicing methods that may be applied at any time in the life cycle of a reservoir or field to enhance the value of oil and gas assets through reduced water handling cost, improved hydrocarbon productivity and/or higher recovery factors. As used herein, the term "field" includes land based (surface and sub-surface) and sub-seabed applications. The term "oilfield," as used herein, includes hydrocarbon oil and gas reservoirs, and formations or portions of formations where hydrocarbon oil and gas are expected but may ultimately contain water, brine, or some other composition.

[0015] As used herein, the phrase "trigger-able fluid" means, for example, a composition comprising an ethylenically unsaturated monomer that may be substantially inert to any produced fluids (gases and liquids) and other fluids injected into the wellbore or around the wellbore, such as workover fluids, which is able to be triggered to polymerize and seal at least a portion of the area exposed to electromagnetic radiation and optionally areas immediately adjacent to the area exposed to electromagnetic radiation. In embodiments, the trigger-able fluid may be a flowable solution having a very low viscosity that can be readily pumped or otherwise handled. For example, the viscosity of the trigger-able fluid may be from about 1 cP to about 10,000 cP, or be from about 1 cP to about 1,000 cP, or be from about 1 cP to about 100 cP.

[0016] The trigger-able fluids suitable for use in the methods of the present disclosure comprise an ethylenically unsaturated monomer. An "ethylenically unsaturated monomer," as the term is used herein, is a compound that has at least two terminal ethylenically unsaturated double bonds as terminal groups. In embodiments, polymers resulting from the polymerization of the ethylenically unsaturated monomer may comprise a crosslinkable moiety. In embodiments, the ethylenically unsaturated monomer may comprise a crosslinkable moiety other than the two terminal ethylenically unsaturated double bonds.

[0017] Suitable ethylenically unsaturated monomers that may be used include acrylate monomers; methacrylate monomers; acrylamide monomers; methacrylic acid; methacrylamide; hydroxyethylacrylate; maleic acid; diallyldiethyl ammonium chloride; diallyldipropyl ammonium chloride quaternary or acid salts of dialkylaminoalkyl acrylates and methacrylates such as dimethylaminoethylacrylate methyl chloride quaternary salt (DMAEAMCQ), dimethylaminoethylmethacrylate methyl chloride quaternary salt (DMAEMMCQ), dimethylaminoethylacrylate hydrochloric acid salt, dimethylaminoethylacrylate sulfuric acid salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt (DMAEABCQ) and dimethylaminoethylacrylate methyl sulfate quaternary salt; the quaternary or acid salts of dialkylaminoalkylacrylamides and methacrylamides such as dimethylaminopropyl acrylamide hydrochloric acid salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, dimethylaminopropyl methacrylamide sulfuric acid salt, methacrylamidopropyl trimethyl ammonium chloride and acrylamidopropyl trimethyl ammonium chloride; N,N-diallyldialkyl ammonium halides such as diallyldimethyl ammonium chloride (DADMAC); methylene bis-acrylamide; urea; vinyl acetic acid; styrene sulfonic acid; N,N-dimethyl-N-acryloyloxyethyl-N-(3-sulfopropyl)-ammonium betaine; N,N-dimethyl-N-acrylamidopropyl-N-(2-carboxymethyl)-ammonium betaine; N,N-dimethyl-N-acrylamidopropyl-N-(3-sulfopropyl)-ammonium betaine; N,N-dimethyl-N-acrylamidopropyl-N-(2-carboxymethyl)-ammonium betaine; 2-(methylthio)ethyl methacryloyl-S-(sulfopropyl)-sulfonium betaine; 2-[(2-acryloylethyl)dimethylammonio]ethyl 2-methyl phosphate; 2-(acryloyloxyethyl)-2'-(trimethylammonium)ethyl phosphate; [(2-acryloylethyl)dimethylammonio]methyl phosphonic acid; 2-methacryloyloxyethyl phosphorylcholine; 2-[(3-acrylamidopropyl)dimethylammonio] ethyl 2'-isopropyl phosphate); 1-vinyl-3-(3-sulfopropyl) imidazolium hydroxide; (2-acryloxyethyl)carboxymethyl methylsulfonium chloride; 1-(3-sulfopropyl)-2-vinylpyridinium betaine; N-(4-sulfobutyl)-N-methyl-N,N-diallylamine ammonium betaine; N,N-diallyl-N-methyl-N-(2-sulfoethyl)ammonium betaine; salts thereof, or mixtures thereof In embodiments, the ethylenically unsaturated monomer may comprise one or more N,N-diallyldialkyl ammonium halides, where the alkyl group comprises from about 1 to about 20 carbon atoms, such as N,N-diallyldialkyl ammonium halides, where the alkyl group comprises from about 1 to about 8 carbon atoms. In specific embodiments, the N,N-diallyldialkyl ammonium halide is DADMAC. The concentration of ethylenically unsaturated monomer in the trigger-able fluid may be from about 40 wt % to about 95 wt %, such as from about 50 wt % to about 85 wt %, or from about 55 wt % to about 75 wt %.

[0018] In embodiments, the ethylenically unsaturated monomer polymerizes with itself upon exposure to electromagnetic radiation (without the assistance of an additional chemical initiator or compound that is capable of converting electromagnetic radiation into chemical energy in the form of a reactive initiating species).

[0019] The trigger-able fluid may further comprise an initiator or activator. For example, if the ethylenically unsaturated monomer is chosen such that it will not auto-polymerize upon exposure to electromagnetic radiation, the trigger-able fluid may further comprise a compound that is capable of converting electromagnetic radiation into chemical energy in the form of a reactive initiating species, such as a water-soluble initiator, to start the polymerization reaction of the ethylenically unsaturated monomer upon exposure of the compound to electromagnetic radiation. Specifically, for trigger-able fluids in which the ethylenically unsaturated monomer does not auto-polymerize by exposure to electromagnetic radiation, the trigger-able fluid may further comprises an initiator and/or activator that initiates or catalyzes (upon being exposed to electromagnetic radiation) the formation of a polymer from the ethylenically unsaturated monomer.

[0020] Suitable initiators include tert-butyl peroxybenzoate; a persulfate, such as ammonium persulfate; an organic or inorganic peroxide; an azo initiator, such as 2,2'-azobis(2-amidinopropane)dihydrochloride; a nitroxide; or a disulfide. The concentration of the initiator may be from about 0.0001 wt % to about 5 wt % of the trigger-able fluid.

[0021] In embodiments, the trigger-able fluid further comprises a cross-linking agent. The phrase "cross-linking agent" refers, for example, to a compound or mixture that assists in the formation of a three dimensional polymerized structure of the ethylenically unsaturated monomer under at least some downhole conditions, such as after exposure of the trigger-able fluid to electromagnetic radiation. After the ethylenically unsaturated monomer is polymerized, suitable cross-linking agents for the methods of the present disclosure would be capable of crosslinking polymer molecules (comprised of the polymerized ethylenically unsaturated monomer) to form a three-dimensional network. Suitable organic crosslinking agents include, but are not limited to, aldehydes, dialdehydes, phenols, substituted phenols, ethers, and a second ethylenically unsaturated monomer, such as methylene bis acrylamide, capable of crosslinking the polymerized first ethylenically unsaturated monomer and having a different chemical structure (from the first ethylenically unsaturated monomer, which would be the major component of such a composition) and present in an amount less than about 10% of the total weight of the trigger-able fluid. Suitable inorganic crosslinking agents include, but are not limited to, polyvalent metals, chelated polyvalent metals, and compounds capable of yielding polyvalent metals. The concentration of the cross-linking agent in the trigger-able fluid may be from about 0.001 wt % to about 10 wt %, such as about 0.005 wt % to about 2 wt %, or about 0.01 wt % to about 1 wt %.

[0022] Optionally, agents to accelerate or delay initiation may be included in the trigger-able fluid. Suitable agents to accelerate or delay initiation include analogues of ferricyanide, such as sodium nitroferricyanide, quinines, ammonium salts of N-nitroso N-phenylhydroxylamine, nitrides (such as TEMPO), tetramethylthiuram disulfide, hydrazyls, Fe^{3+} and Cu^{2+} complexes. For example, when potassium ferricyanide, $K_3[Fe(CN)_6]$, is used, the start of the polymerization process can be delayed to a higher temperature with the appropriate inhibitor.

[0023] While the trigger-able fluids of the present disclosure are described herein as comprising the above-mentioned components, it should be understood that the trigger-able fluids of the present disclosure may optionally comprise other chemically different materials. In embodiments, the trigger-able fluid may further comprise stabilizing agents, surfactants, diverting agents, or other additives. Additionally, a trigger-able fluid may comprise a mixture of two or more ethylenically unsaturated monomers, various crosslinking agents, and/or other additives, such as fibers or fillers, provided that the other components chosen for the mixture are compatible with the intended use of forming a polymerized structure that at least partially seals a portion of a subterranean formation, such as a water bearing portion of a subterranean formation, permeated by the trigger-able fluid. Furthermore, the trigger-able fluid may comprise buffers, pH control agents, and various other additives added to promote the stability or the functionality of the trigger-able fluid. The trigger-able fluid may be based on an aqueous or non-aqueous solution. The components of the trigger-able fluid may be selected such that they may or may not react with the subterranean formation that is to be sealed.

[0024] In this regard, the trigger-able fluid may include components independently selected from any solids, liquids, gases, and combinations thereof, such as slurries, gas-saturated or non-gas-saturated liquids, mixtures of two or more miscible or immiscible liquids, and the like, as long as such additional components allow for the polymerization of the ethylenically unsaturated monomer upon exposure to electromagnetic radiation. For example, the trigger-able fluid may comprise organic chemicals, inorganic chemicals, and any combinations thereof Organic chemicals may be monomeric, oligomeric, polymeric, crosslinked, and combinations, while polymers may be thermoplastic, thermosetting, moisture setting, elastomeric, and the like. Inorganic chemicals may be metals, alkaline and alkaline earth chemicals, minerals, and the like.

[0025] Fibrous materials may also be included in the trigger-able fluid. Suitable fibrous materials may be woven or nonwoven, and may be comprised of organic fibers, inorganic fibers, mixtures thereof and combinations thereof The trigger-able fluid may be polymerized around the fibers upon exposure to electromagnetic radiation from the electromagnetic trigger unit, or otherwise supported by the fibers in such as way that the trigger-able fluid does not easily come loose from the fibers, but is able to itself interact with, or cause a sealing effect upon exposure to the electromagnetic trigger.

[0026] Stabilizing agents can be added to slow the degradation of the polymerized structure after its formation downhole. Typical stabilizing agents include buffering agents, such as agents capable of buffering at pH of about **8.0** or greater (such as water-soluble bicarbonate salts, carbonate salts, phosphate salts, or mixtures thereof, among others); and chelating agents (such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid (HEDTA), or hydroxyethyliminodiacetic acid (HEIDA), among others). Buffering agents may be added to the consolidating fluid to at least about 0.05 wt %, such as from about 0.05 wt % to about 10 wt %, and from about 0.1 wt % to about 2 wt %, based upon the total weight of the trigger-able fluid. Chelating agents may be added to the consolidating fluid to at least about 0.75 mole per mole of metal ions expected to be encountered in the downhole environment, such as at least about 0.9 mole per mole of metal ions, based upon the total weight of the trigger-able fluid.

[0027] Surfactants can be added to promote dispersion or emulsification of components of the trigger-able fluid, or to provide foaming of the polymer upon its formation downhole. Suitable surfactants include alkyl polyethylene oxide sulfates, alkyl alkylolamine sulfates, modified ether alcohol sulfate sodium salts, or sodium lauryl sulfate, among others. A surfactant may be added to the trigger-able fluid in an amount in the range of about 0.01 wt % to about 10 wt %, such as about 0.1 wt % to about 2 wt %.

[0028] Diverting agents may be added to improve penetration of the trigger-able fluid into lower-permeability areas when treating a zone with heterogeneous permeability. The use of diverting agents in formation treatment applications is known, such as given in Reservoir Stimulation, 3rd edition, M. Economides and K. Nolte, eds., Section 19.3.

[0029] In embodiments, the components of the trigger-able fluid may be selected so that the morphology of the polymerized structure, which forms by polymerizing the trigger-able fluid, may be tuned to provide the desired sealing function. Such morphologies of the polymerized trigger-able fluid system may include, for example, a gelled material such as an elastic gel, a rigid gel, etc.; a slurried material; an elastic solid; a rigid solid; a brittle solid; a foamed material, and the like. In embodiments, the components of the trigger-able fluid may be selected such that polymerization occurs at a temperature above the bottom hole static temperature (BHST), such as at least 20° C. above BHST, or at least 50° C. above BHST.

[0030] For example, in embodiments, the polymerized structure formed may be a gel that is substantially non-rigid after polymerization. A polymerized trigger-able fluid that is a non-rigid gel will substantially return to its starting condition after compression with a linear strain of at least about 10%, such as at least about 25%, or greater than about 50%. Non-rigidity of which can be determined by any techniques known to those of ordinary skill in the art. The storage modulus G' of polymerized trigger-able fluid system, as measured according to standard protocols given in U.S. Pat. No. 6,011,075, the disclosure of which is hereby incorporated by reference in its entirety, may be about 150 dynes/cm^2 to about 500,000 dynes/cm^2, such as from about 1000 dynes/cm^2 to about 200,000 dynes/cm^2, or from about 10,000 dynes/cm^2 to about 150,000 dynes/cm^2.

[0031] In the methods of the present disclosure, after the trigger-able fluid is prepared, it can be injected or conveyed into a subterranean formation to substantially seal at least a portion of the subterranean formation upon polymerization of one or more of the components of the trigger-able fluid (by exposure to electromagnetic radiation). In embodiments, at least some of the trigger-able fluid permeates a portion of the subterranean formation, such as a water-bearing subterranean formation.

[0032] In embodiments, the ethylenically unsaturated monomer does not substantially polymerize under the subterranean conditions (downhole conditions) until the trigger-able fluid and/or the ethylenically unsaturated monomer itself is exposed to electromagnetic radiation from the electromagnetic trigger unit comprising an electromagnetic radiation source. In other words, polymerization of the ethylenically unsaturated monomer does not substantially occur until the trigger-able fluid is exposed to electromagnetic radiation. For example, at least 80% of the ethylenically unsaturated monomer remains unreacted, such as at least 95%, or as at least 99% of the ethylenically unsaturated monomer remains unreacted until the trigger-able fluid is exposed to electromagnetic radiation, such as electromagnetic radiation generated by an electromagnetic trigger unit positioned in the wellbore in the vicinity of the subterranean formation to be sealed.

[0033] The phrase "in the vicinity," for example, as used in the phrase "an electromagnetic trigger unit positioned in the wellbore in the vicinity of a subterranean formation to be sealed," means within a distance that is close enough to allow for an effective amount of the respective electromagnetic radiation generated by the electromagnetic trigger unit to penetrate the subterranean formation to be sealed and convert a component of the trigger-able fluid (such as, for example, the ethylenically unsaturated monomer and/or initiator) into a reactive initiating species to trigger the polymerization reaction of the ethylenically unsaturated monomer. The term "vicinity," may also represent a distance that is close enough such that the intensity of the respective electromagnetic radiation generated by the electromagnetic trigger unit is sufficient to convert a component of the trigger-able fluid that has permeated a water bearing subterranean formation (such as, for example, the ethylenically unsaturated monomer and/or initiator) into a reactive initiating species to trigger the polymerization reaction of the ethylenically unsaturated monomer such that the triggered polymerization reaction at least partially seals, and may completely seal, at least a portion of the water bearing subterranean formation through which trigger-able fluid is dispersed.

[0034] The portion of the subterranean formation in which the trigger-able is permeated may be referred to herein as a "treated zone." In embodiments, for a predetermined vertical region (depending on the vertical depth of the region to be treated), the treated zone may be a volume extending at least about 15 cm from the outer wall of the wellbore, such as a volume extending at least about 30 cm from the outer wall of the wellbore, or a volume extending at least about 50 cm from the outer wall of the wellbore.

[0035] In embodiments, the trigger-able fluid systems are introduced into the subterranean material surrounding a wellbore by flowing the trigger-able fluid system into the wellbore. A "wellbore" may be any type of well, including, but not limited to, a producing well, a non-producing well, an injection well, a fluid disposal well, an experimental well, an exploratory well, and the like. Wellbores may be vertical, horizontal, deviated some angle between vertical and horizontal, and combinations thereof, for example a vertical well with a non-vertical component. In embodiments, the one or more monomer components of the trigger-able fluid do not polymerize until after their introduction into the wellbore, such as injection and/or permeation into the subterranean formation.

[0036] Methods in accordance with the present disclosure may comprise triggering one or more components of a trigger-able fluid to initiate a polymerization reaction of one or more of the components of the trigger-able fluid. The terms "triggering" and "triggered," as used herein, include exposing the trigger-able fluid to an electromagnetic radiation source and optionally any other mechanical, physical, chemical, thermal and other means to activate, initiate, catalyze, or otherwise induce or cause the trigger-able fluid or a component thereof to transform from a substantially inert composition to a sealing composition.

[0037] In embodiments, the polymerized composition that is formed following the triggered polymerization reaction at least partially seals, and may completely seal, at least a portion of a subterranean formation through which trigger-able fluid systems are dispersed. For example, the polymerization of the trigger-able fluid of the present disclosure may be conducted such that the permeability of the subterranean formation substantially decreases. In embodiments, upon polymerization of the trigger-able fluid of the present disclosure, the permeability of the subterranean formation, such as a water bearing subterranean formation, may decrease by at least about 80%, such as at least about 90%, or by at least about 99%.

[0038] In the methods of the present disclosure, triggering the trigger-able fluid may comprise applying an electromagnetic trigger, such as a microwave, optionally in combination with one or more other techniques, such as mechanical, physical, chemical, thermal initiation, and the like. For example, the methods of the present disclosure may comprise flowing one or more trigger-able fluid systems into a subterranean material to be sealed, such as a subterranean formation immediately adjacent to a wellbore, and polymerizing one or more of the components of the trigger-able fluid by exposing the trigger-able fluid to an effective amount, such as, for example, from about 200 W to about 2000 W, from about 500 W to about 1500 W and from about 750 W to about 1000 W, of electromagnetic radiation (produced by an electromagnetic trigger unit placed in close proximity to the medium to be sealed) suitable to polymerize one or more of the components of the trigger-able fluid system, thereby effectively sealing the material occupied by the trigger-able fluid.

[0039] Methods of the present disclosure may be used to seal or reduce the flow of an unacceptable amount of water (or other undesired material) into or near the wellbore. The phrase unacceptable amount of water (or other undesired material) may be determined on a case-by-case basis. As used herein, the terms "seal", "sealed" and "sealing" mean at least the ability to substantially prevent fluids, such as fluids comprising an unacceptable amount of water, to flow through the area of the trigger-able fluid that was polymerized after initiation of the polymerization by exposure to electromagnetic radiation. The terms "seal", "sealed" and "sealing" may also mean the ability to substantially prevent fluids from flowing between the medium where the trigger-able fluid was polymerized and whatever surface it is sealing against, for example an open hole, a sand face, a casing pipe, and the like.

[0040] After at least a portion of the trigger-able fluid has permeated the subterranean formation, such as water-bearing subterranean formation, the methods of the present disclosure may comprise initiating polymerization of the ethylenically unsaturated monomer (such as the ethylenically unsaturated monomer of the trigger-able fluid that permeated the formation) to form a polymerized structure and seal the subterranean formation. As discussed above, a subterranean formation is sealed if part or a majority of subterranean formation has been treated with the trigger-able fluid and this treated zone has been exposed to an effective amount of electromagnetic radiation to polymerize one or more of the components of the trigger-able fluid and reduce the permeability of the subterranean formation. For example, upon polymerization of the trigger-able fluid of the present disclosure by exposure to an effective amount of electromagnetic radiation, the permeability of the subterranean formation may decrease by at least about 80%, such as by at least about 90%, or by at least about 99%. In embodiments, for a predetermined vertical region (depending on the vertical depth of the region to be sealed), the sealed zone may be a volume extending at least about 15 cm from the outer wall of the wellbore, such as a volume extending at least about 30 cm from the outer wall of the wellbore, or a volume extending at least about 50 cm from the outer wall of the wellbore.

[0041] In the methods of the present disclosure, initiating the polymerization of the ethylenically unsaturated monomer may be accomplished by exposing the trigger-able fluid to electromagnetic radiation. In embodiments, an electromagnetic trigger unit positioned in the wellbore in the vicinity of the water-bearing subterranean formation into which the trigger-able fluid has permeated may be used to generate the electromagnetic radiation. In embodiments, the electromagnetic trigger unit may be inserted into the wellbore before, during or after the trigger-able fluid is conveyed into the wellbore, such as before, during or after at least a portion of the trigger-able fluid has permeated a water-bearing subterranean formation that the wellbore penetrates. For example, the electromagnetic trigger unit may be lowered into the wellbore by known methods, such as coiled tubing, after the desired volume of trigger-able fluid has been pumped into the wellbore and positioned in the wellbore in the vicinity of the water-bearing subterranean formation into which the trigger-able fluid has permeated. Then, electromagnetic trigger unit may be actuated by any suitable method (such as a wireless communication device or a communication line) to start or stop the generation of electromagnetic radiation. Once the polymerization of the ethylenically unsaturated monomer is substantially completed, such as 75% or the ethylenically unsaturated monomer is polymerized, or 95% or the ethylenically unsaturated monomer is polymerized, or 99.9% or the ethylenically unsaturated monomer is polymerized, the electromagnetic trigger unit may be removed from the wellbore.

[0042] In embodiments, to minimize the possibility that electromagnetic trigger unit becomes trapped in the wellbore once the trigger-able fluid begins polymerizing the electromagnetic trigger unit may be moved in a direction away from the site of polymerization (after the polymerization has been initiated). For example, upon actuation of the electromagnetic trigger unit and generation of electromagnet radiation that is absorbed by the trigger-able fluid (thereby initiating the polymerization of the ethylenically unsaturated monomer deepest part of the water-bearing subterranean formation to be sealed) the electromagnetic trigger unit may be moved in continuous or incremental fashion, while continuously or intermittently generating electromagnetic radiation, toward a more shallow location in wellbore (in a direction away from the bottom or end of the wellbore, or toward the wellbore opening on the surface) at a rate that sufficient to avoid the component of the trigger-able fluid being polymerized around the electromagnetic trigger unit.

[0043] Forms of electromagnetic radiation suitable for the electromagnetic trigger unit may be selected from the group consisting of actinic radiation, microwave, radiowave, electron beam, ultraviolet light, visible light, near infra-red radiation, and gamma radiation. In embodiments, multiple forms of electromagnetic radiation may be used in combination. The electromagnetic radiation suitable for use in the present disclosure may generate radicals, carbocations and bases, to initiate cycloaddition reactions, or bring about thermal reactions.

[0044] Methods of the present disclosure may include those where the electromagnetic radiation is generated by an electromagnetic trigger unit that is positioned in the wellbore. Known sources (such as lamps, antennas, etc.,) for producing the desired form of electromagnetic radiation may be used with the methods of the present disclosure as long as they are designed to be able to withstand the downhole environment. The electromagnetic trigger unit may be inserted into the wellbore either before or after conveying a trigger-able fluid to the subterranean formation to be sealed via a suitable delivery method, such as coiled tubing. In embodiments, the electromagnetic trigger unit may be positioned in the vicinity of the subterranean formation to be sealed with or without a communication line, such as a slickline, micro-line, or micro-wire. In embodiments, the electromagnetic trigger unit may accompany the coiled tubing, either attached to the outside of the coiled tubing, or disposed inside the coiled tubing. Then, after the trigger-able fluid has sufficiently penetrated the medium to be sealed, the electromagnetic trigger unit may be used to generate electromagnetic radiation, such as microwave or other radio-frequencies, to initiate the polymerization of one or more components of the trigger-able fluid.

[0045] An electromagnetic trigger unit is any unit capable of transmitting electromagnetic energy to the trigger-able fluid, such as, for example, a wireline tool.

[0046] In embodiments, a sensor may be attached to a distal end of a communication line that is inserted into the wellbore and data may be collected and used to monitor status of the polymerization reaction, or model subsequent applications of triggering conditions. The measured property for monitoring the progress of the polymerization reaction at or near the medium to be sealed may be any property that may be measured downhole that provides an indication that the polymerization reaction is proceeding, including but not limited to, temperature, pH, amount of precipitate, fluid temperature, depth, presence of water, chemical luminescence, gamma-ray, resistivity, salinity, fluid flow, fluid compressibility, electromagnetic trigger unit location, electromagnetic trigger unit state and electromagnetic trigger unit orientation. In particular embodiments, the parameter being measured may be any parameter that may be adjusted, including but not limited to quantity of polymerizable material in the trigger-able fluid, relative proportions of each component in the trigger-able fluid, the chemical concentration of one or more components in a set of trigger-able fluids, the relative proportion of fluids being pumped in the annulus to fluids being pumped in the coiled tubing, concentration of a catalyst to be released, concentration of a polymer, concentration of other optional components, and/or location of coiled tubing.

[0047] The minimum and maximum time that the trigger-able fluid is exposed to electromagnetic radiation may be a function of, inter alia, type of the electromagnetic radiation employed, the downhole polymerization rate, and the amount of electromagnetic radiation exposure adequate to initiate a sufficient amount of polymerization to obtain the desired reduction of permeability of the subterranean formation. In embodiments, the time that at least a portion of the trigger-able fluid (or the entire volume of the trigger-able fluid pumped into the wellbore) is exposed to electromagnetic radiation may be greater than 1 second, such as from about 5 seconds to about 5 minutes, or from about 10 seconds to about 1 minute, or from about 20 seconds to about 40 seconds.

[0048] The trigger-able fluids of the present disclosure may be suitable for use in numerous subterranean formation types. For example, formations for which sealing with the trigger-able fluids of the present disclosure may be used include sand, sandstone, shale, chalk, limestone, and any other hydrocarbon bearing formation.

[0049] The portion of the wellbore through which the trigger-able fluid is injected into the treated zone can be open-hole (or comprise no casing) or can have previously received a casing. If cased, the casing is desirably perforated prior to injection of the trigger-able fluid. Optionally, the wellbore can have previously received a screen. If it has received a screen, the wellbore can also have previously received a gravel pack, with the placing of the gravel pack optionally occurring above the formation fracture pressure (a frac-pack).

[0050] Techniques for injection of fluids with viscosities similar to those of the trigger-able fluids of the present disclosure are well known in the art and may be employed with the methods of the present disclosure. For example, known techniques may be used in the methods of the present disclosure to convey the trigger-able fluids of the present disclosure into the subterranean formation to be treated.

[0051] In embodiments, the trigger-able fluid may be driven into a wellbore by a pumping system that pumps one or more trigger-able fluids into the wellbore. The pumping systems may include mixing or combining devices, wherein various components, such as fluids, solids, and/or gases maybe mixed or combined prior to being pumped into the wellbore. The mixing or combining device may be controlled in a number of ways, including, but not limited to, using data obtained either downhole from the wellbore, surface data, or some combination thereof Methods of this disclosure may include using a surface data acquisition and/or analysis system, such as described in U.S. Pat. No. 6,498,988, incorporated herein by reference in its entirety. In embodiments, one or more trigger-able fluid is pumped into the wellbore either before or after the electromagnetic trigger is set into position after detecting an unacceptable amount of water or other condition has been detected making desirable to trigger the polymerization of the trigger-able fluid. After the trigger-able fluid has sufficiently permeated the medium to be sealed, the electromagnetic trigger is actuated to trigger the polymerization of the trigger-able fluid or a component thereof. Specific embodiments may comprise sealing the zone of interest (which may be where an unacceptable amount of water or other condition has been detected making desirable to trigger the polymerization of the trigger-able fluid) using the trigger-able fluid optionally with packers, such as straddle cup packers. Packers or similar devices can be used to control flow of the trigger-able fluid into the subterranean formation for which sealing is desired.

[0052] In embodiments, the trigger-able fluid may be injected into the subterranean formation at a pressure less than the fracturing pressure of the formation. For example, the trigger-able fluids will be injected below the formation fracturing pressure of the respective formation.

[0053] The volume of trigger-able fluids to be injected into subterranean formation is a function of the subterranean formation volume to be treated and the ability of the trigger-able fluid of the present disclosure to penetrate the subterranean formation. The volume of trigger-able fluid to be injected can be readily determined by one of ordinary skill in the art. As a guideline, the formation volume to be treated relates to the height of the desired treated zone and the desired depth of penetration. In embodiments, the depth of penetration of the trigger-able fluid may be at least about 15 cm from the outer wall of the wellbore into the subterranean formation, such as the depth of penetration of at least about 30 cm from the outer wall of the wellbore.

[0054] The ability of the trigger-able fluid to penetrate the subterranean formation depends on the permeability of the subterranean formation and the viscosity of the trigger-able fluid. In embodiments, the viscosity of the trigger-able fluid is sufficiently low as to not slow penetration of the consolidating fluid into the subterranean formation. In a low-permeability subterranean formation, the viscosity of the trigger-able fluid is sufficiently low as to not slow penetration of the consolidating fluid into the subterranean formation. For example, in a low-permeability subterranean formation, suitable viscosities may be similar to that of water, such as from about from about 1 cP to about10,000 cP, or be from about 1 cP to about 1,000 cP, or be from about 1 cP to about 100 cP.

[0055] In embodiments, after the trigger-able fluid penetrates the subterranean formation, polymerization occurs after exposure to electromagnetic polymerization, whereby the one or more the components of the trigger-able fluid, including the ethylenically unsaturated monomer, are polymerized. The polymerized structure formed may comprise three-dimensional linkages that effectively blocks permeation of fluids through the sealed region. Thus, the sealed subterranean formation becomes relatively impermeable and any remaining pores in the sealed subterranean formation do not communicate with the wellbore and do not produce water.

[0056] After the subterranean formation has been sealed according to the methods of the present disclosure, it has been rendered relatively impermeable. In embodiments, the permeability of the subterranean formation has been reduced by at least about 90%, such as by at least about 95%, or by at least about 99%. In embodiments, fracturing or perforating through the sealed subterranean formation may be performed to allow communication through the sealed subterranean formation.

[0057] Techniques for hydraulically fracturing a subterranean formation are known to persons of ordinary skill in the art, and will involve pumping the fracturing fluid into the borehole and out into the surrounding formation. The fluid pressure is above the minimum in situ rock stress, thus creating or extending fractures in the formation. In order to maintain the fractures formed in the formation after the release of the fluid pressure, the fracturing fluid can comprise either a proppant, to physically hold the fractures open, or an acid, which can etch the faces of the fracture to provide pores for hydrocarbon production.

[0058] The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the present disclosure.

EXAMPLES

[0059] A trigger-able fluid was prepared by mixing the following components: diallyldimethylammonium chloride (DADMAC; 65% solution in water; 50 mL), methylene bis acrylamide (MBA; 2.5% solution in DI water; 50 mL), ammonium persulfate (used as a radical initiator; 0.06 grams), potassium ferricyanide, $K_3[Fe(CN)_6]$ (used as a inhibitor; 0.018 grams). DADMAC and MBA reacted in the presence of a radical initiator after exposure to electromagnetic radiation to form a crosslinked poly-DADMAC, as illustrated in FIG. **1**. In the present example, the trigger-able fluid was exposed to microwaves generated with a commercial microwave oven source for a period of time sufficient to initiate polymerization of the above components.

[0060] Rheology of the polymerized DADMAC gel used in the example above was performed using parallel plate geometry and is shown in FIG. **2**. For the above polymerized trigger-able fluid, G' is greater than G", which means the gel behaves like a solid.

[0061] Applications: Water Shut-off

[0062] The above example composition was tested for water shut-off on sandstone and synthetic aloxide cores. The initial permeability of a 15.2 cm long core with 2.5 cm diameter was measured by passing a 2% KCl solution through the core at different flow rates between 1 and 3 ml/min while monitoring the differential pressure across the core. The core was isolated in a rubber sleeve during the permability measurement. Then the core was treated with 5 pore volume of the above trigger-able fluid containing DADMAC, MBA, and ammonium persulfate (with or without an inhibitor). The core was subjected to a microwave pulse (20 to 40 seconds). Return permeability was measured against 2% KCl. As illustrated in FIG. **3**, a reduction in permeability of 80% or higher was observed. In the presence of the inhibitor, a higher temperature, thus a longer microwave pulse, was required to cause reduction in permeability.

[0063] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from Triggering Polymerization On-Demand For Water Control Downhole. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35 U.S.C. §112, paragraph 6 for any limitations of any of the claims herein, except for those in which the claim expressly uses the words 'means for' together with an associated function.

What is claimed is:

1. A method of sealing a subterranean formation, comprising:

permeating at least a portion of a subterranean formation with a trigger-able fluid, wherein the trigger-able fluid comprises an ethylenically unsaturated monomer; and

following the permeating, exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit comprising an electromagnetic radiation source to initiate polymerization of the ethylenically unsaturated monomer.

2. The method of claim **1**, wherein the ethylenically unsaturated monomer is one or more monomer selected from the group consisting of acrylic acid, acrylamide, methacrylic acid, methacrylamide, hydroxyethylacrylate, maleic acid, N,N-diallyldialkyl ammonium halides, diallyldimethyl ammonium chloride, methylene bis-acrylamide, urea, vinyl acetic acid, styrene sulfonic acid, and salts thereof

3. The method of claim **1**, wherein polymerizing the ethylenically unsaturated monomer forms a polymerized structure that reduces permeability of the subterranean formation permeated by the trigger-able fluid by at least about 80%.

4. The method of claim **1**, wherein polymers resulting from the polymerization of the ethylenically unsaturated monomer comprise a crosslinkable moiety, and

the trigger-able fluid further comprises a cross-linking agent capable of crosslinking the polymers resulting from the polymerization of the ethylenically unsaturated monomer to form a three-dimensional network.

5. The method of claim **4**, wherein the crosslinking agent comprises a functional group selected from the group consisting of an aldehyde, a dialdehyde, a phenol, a substituted phenol, an ether, a polyvalent metal, and a chelated polyvalent metal.

6. The method of claim **4**, wherein the ethylenically unsaturated monomer is diallyldimethyl ammonium chloride, and the crossing-linking agent is methylene bis acrylamide.

7. The method of claim **1**, wherein the trigger-able fluid further comprises:

an agent that delays initiation of the polymerization reaction, and

an initiator selected from the group consisting of water-soluble initiators, a persulfate, an ammonium persulfate, an organic peroxides, an inorganic peroxide, an azo initiator, a 2,2'-azobis(2-amidinopropane)dihydrochloride, a nitroxide, and a disulfide.

8. The method of claim **1**, wherein the electromagnetic radiation is a microwave.

9. The method of claim **3**, wherein the polymerized structure has G' between about 1000 dynes/cm^2 and about 200,000 dynes/cm^2.

10. The method of claim **1**, wherein the portion of the trigger-able fluid that has permeated the water-bearing formation is exposed to electromagnetic radiation for an amount of time in the range of from about 5 seconds to about 5 minutes.

11. The method of claim **1**, wherein the exposing comprises:

lowering the electromagnetic trigger unit into the wellbore to a position in a vicinity of the trigger-able fluid that has permeated at least a portion of the subterranean formation, and

after the electromagnetic trigger unit is in the vicinity of the trigger-able fluid that has permeated at least a portion of the subterranean formation, initiating polymerization of the ethylenically unsaturated monomer by generating electromagnetic radiation with the electromagnetic trigger.

12. A method of controlling water in a subterranean formation, comprising:

introducing a trigger-able fluid comprising one or more ethylenically unsaturated monomers into a wellbore that penetrates a water-bearing subterranean formation, wherein at least some of the trigger-able fluid permeates a portion of the water-bearing subterranean formation; and

after at least a portion of the trigger-able fluid has permeated the water-bearing subterranean formation, initiating polymerization of the ethylenically unsaturated monomer of the trigger-able fluid that permeated the water-bearing subterranean formation by exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit positioned in the wellbore.

13. The method of claim **12**, wherein the ethylenically unsaturated monomer is one or more monomer selected from the group consisting of acrylic acid, acrylamide, methacrylic acid, methacrylamide, hydroxyethylacrylate, maleic acid, N,N-diallyldialkyl ammonium halides, diallyldimethyl ammonium chloride, methylene bis-acrylamide, urea, vinyl acetic acid, styrene sulfonic acid, and salts thereof.

14. The method of claim **12**, wherein polymerizing the ethylenically unsaturated monomer forms a polymerized structure that reduces permeability of the water-bearing subterranean formation permeated by the trigger-able fluid by at least about 80%.

15. The method of claim **12**, wherein polymers resulting from the polymerization of the ethylenically unsaturated monomer comprise a crosslinkable moiety, and

the trigger-able fluid further comprises a cross-linking agent capable of crosslinking the polymers resulting from the polymerization of the ethylenically unsaturated monomer to form a three-dimensional network.

16. The method of claim **15**, wherein the crosslinking agent comprises a functional group selected from the group consisting of an aldehyde, a dialdehyde, a phenol, a substituted phenol, an ether, a polyvalent metal, and a chelated polyvalent metal.

17. The method of claim **15**, wherein the ethylenically unsaturated monomer is diallyldimethyl ammonium chloride, and the crossing-linking agent is methylene bis acrylamide.

18. The method of claim **12**, wherein the trigger-able fluid further comprises:

an agent that delays initiation of the polymerization reaction, and

initiator selected from the group consisting of water-soluble initiators, a persulfate, an ammonium persulfate, an organic peroxides, an inorganic peroxide, an azo initiator, a 2,2'-azobis(2-amidinopropane)dihydrochloride, a nitroxide, and a disulfide.

19. The method of claim **12**, wherein the electromagnetic radiation is a microwave.

20. The method of claim **14**, wherein the polymerized structure has G' between about 1000 dynes/cm^2 and about 200,000 dynes/cm^2.

21. The method of claim **12**, wherein the portion of the trigger-able fluid that has permeated the water-bearing formation is exposed to electromagnetic radiation for an amount of time in the range of from about 5 seconds to about 5 minutes.

22. The method of claim **12**, wherein the electromagnetic trigger unit is positioned in the wellbore in the vicinity of the water-bearing subterranean formation before any of the trigger-able fluid has permeated the water-bearing subterranean formation.

23. The method of claim **12**, wherein the electromagnetic trigger unit is positioned in the wellbore in the vicinity of the water-bearing subterranean formation after at least a portion of the trigger-able fluid has permeated the water-bearing subterranean formation.

24. The method of claim **12**, further comprising removing the electromagnetic trigger unit from the wellbore.

25. A method of controlling water in a subterranean formation, comprising:

introducing a trigger-able fluid into a wellbore that penetrates a water-bearing subterranean formation, the trigger-able fluid comprising:

diallyldimethyl ammonium chloride,

methylene bis acrylamide,

an inhibitor, and

an initiator selected from the group consisting of water-soluble initiators, a persulfate, an ammonium persulfate, an organic peroxides, an inorganic peroxide, an azo initiator, a 2,2'-azobis(2-amidinopropane)dihydrochloride, a nitroxide, and a disulfide, wherein at least some of the trigger-able fluid permeates a portion of the water-bearing subterranean formation; and

after at least a portion of the trigger-able fluid has permeated the water-bearing subterranean formation, initiating polymerization of the diallyldimethyl ammonium chloride of the trigger-able fluid that permeated the water-bearing subterranean formation by exposing the trigger-able fluid to electromagnetic radiation generated by an electromagnetic trigger unit positioned in the wellbore in the vicinity of the water-bearing subterranean formation.

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