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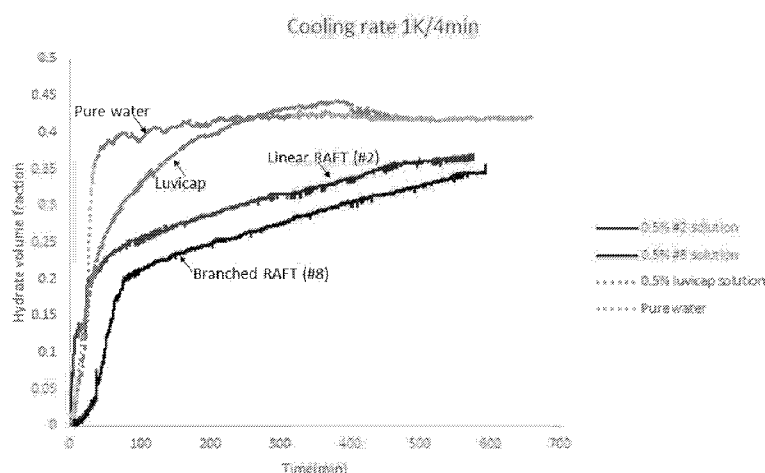


Figure 1

(57) Abstract: A process for inhibiting the formation of gas hydrates in a hydrocarbon fluid comprising adding to the hydrocarbon fluid a hydrate inhibitor which is a polymer comprising covalently bound thereto at least one trithiocarbonate or dithiocarbamate residue of a RAFT agent comprising a trithiocarbonate or a dithiocarbamate group.

PROCESS FOR INHIBITING HYDRATE FORMATION IN HYDROCARBON PRODUCTION

[0001] **Field**

[0002] The invention relates to a process and composition for inhibiting the formation of hydrocarbon hydrates and in particular for inhibiting the formation of hydrocarbon hydrates in the production of oil and gas.

[0003] **Background**

[0004] The following discussion of the background to the invention is intended to facilitate an understanding of the invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was published, known or part of the common general knowledge in Australia or any other country as at the priority date of any one of the claims of this specification.

[0005] Hydrocarbon hydrates are nonstoichiometric crystalline compounds, consisting of host water and guest hydrocarbon molecules. Hydrocarbon hydrates form at lower temperatures and high pressure and cause considerable problems in the oil and gas industry. The formation of hydrocarbon hydrates may result in a disruption in hydrocarbon transport through blockages in infrastructure such as conduits used to transport hydrocarbons. The blockages occur due to the growth and agglomeration of hydrate particles which ultimately turn into a solid hydrate plug which can result in loss of production, shut down of mining facilities and an increased risk of explosion or release of hydrocarbons to the environment.

[0006] In order to reduce the risk of hydrate plug formation the industry has used chemical inhibitors which are added to the hydrocarbon flow particularly in conditions of low temperature and/or high pressure. Conventionally vast quantities of thermodynamic inhibitors have been required such as methanol, ethanol, propanol and monoethylene glycol (MEG). These thermodynamic inhibitors shift the hydrate equilibrium curve such that formation of the hydrates shifts towards higher pressures and lower temperatures. Thus less harsh operating conditions can be used such that

they are outside of the hydrate formation conditions (20 ~ 40wt%). These thermodynamic inhibitors are typically recycled but the process is complicated and exerts a number of technological challenges. Alternative materials exist for hydrate prevention including kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). KHIs are water-soluble polymers that delay the formation of hydrate crystals. Anti-agglomerants (AAs) are surfactants, which suspend the water phase as small droplets, which ensures that the droplets are converted to small hydrate particles when the temperature decreases below the hydrate equilibrium condition. The hydrate particles are well dispersed in the liquid phase thus preventing hydrate blockage in subsea flowlines.

[0007] More recently there have been proposals to use more effective polymeric hydrate inhibitors such as those described by Kelland in the review 'History of the Development of Low Dosage Hydrate Inhibitors', *Energy & Fuels*, Vol 20, No3 (2006) and US 5880319, US2014/0256599, WO 2008/023989, US 8211469 and US 2013/0098623. While polymeric hydrate inhibitors are generally active at much lower concentrations than conventional inhibitors they are generally more expensive.

[0008] Some recent attempts have been made to make polymeric inhibitors by RAFT (reverse addition-fragmentation chain transfer polymerisation) so as to achieve low molecular, well controlled polymers. The RAFT process involves use of chain transfer agents which control the addition of monomer units and these chain transfer agents are often removed after the preparation of the polymer so as to reduce perceived odour, colour and in some case allow subsequent end group functionality.

[0009] There is still a need to improve the activity of hydrate inhibitors, to provide a more cost effective, more economical hydrate inhibitor, or provide an inhibitor that could be used to complement the current thermodynamic inhibitors so as to reduce the amount of the conventional thermodynamic inhibitors and limit recycling costs.

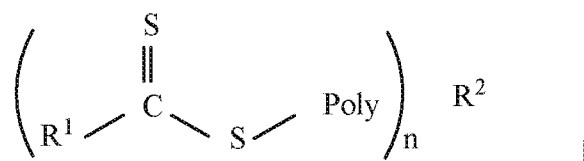
[0010] **Summary**

[0011] There is provided a process for inhibiting the formation of hydrates in a hydrocarbon fluid comprising adding to the fluid a hydrate inhibitor which is a polymer comprising covalently bound thereto at least one a trithiocarbonate or dithiocarbamate residue of a RAFT agent comprising a trithiocarbonate or dithiocarbamate group.

[0012] In a preferred embodiment there is provided a process for inhibiting the formation of hydrates in a hydrocarbon fluid comprising adding to the fluid a hydrate inhibitor which is a polymer comprising one or more monomers selected from the group consisting of optionally substituted N-vinyl lactams, N-alkylacrylamides, N,N-dialkylacrylamides, N,N-dialkylmethacrylamides, N-alkylmethacrylamides, vinyl-N-alkylacetamides, N-alkylaminoalkylacrylate, N,N-dialkylaminoalkylacrylate, N-alkylaminoalkylmethacrylate, N,N-dialkylaminoalkylmethacrylate, hydroxyethylmethacrylate, hydroxyethylacrylate, vinyl acetate, vinyl alcohol, acrylic acid, 2-isopropenyloxazoline and acrylamide alkyl sulfonic acids, wherein the polymer has covalently bound thereto at least one a trithiocarbonate or dithiocarbamate residue of a RAFT agent comprising a trithiocarbonate or dithiocarbamate group.

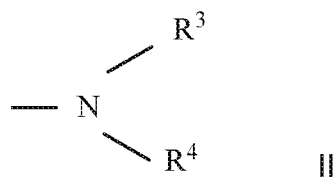
[0013] The hydrate inhibitor may be in a range of polymer architectural forms such as a linear, branched, hyperbranched or star polymer forms.

[0014] In one set of embodiments the hydrate inhibitor is of formula I



wherein

R¹ is selected from the group consisting of optionally substituted alkylthio, optionally substituted arylalkylthio, optionally substituted heteroarylalkylthio, or the group of formula II:



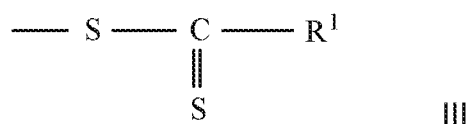
wherein

R³ and R⁴ are independently selected from the group consisting of optionally substituted alkyl, optionally substituted carbocyclic, optionally substituted heterocyclic, optionally substituted aryl, optionally substituted heteroaryl, and the group wherein R³

and R⁴ link to form an optionally substituted heterocyclic ring or optionally substituted heteroaryl of 5 or 6 ring members;

n is an integer of at least 1 preferably from 1 to 20 such as 1 to 8;

R² is selected from the group consisting of hydrogen, optionally substituted alkyl, optionally substituted carbocyclic, optionally substituted heterocyclic, optionally substituted aryl, optionally substituted heteroaryl and the group of formula III:

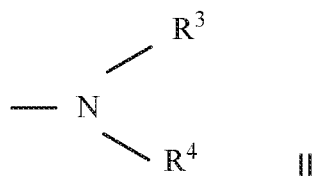


wherein R¹ is as herein before defined; and

Poly is a polymer comprising one or more monomers selected from the group consisting of optionally substituted N-vinyl lactams, N-alkylacrylamides, N,N-dialkylacrylamides, N-alkylmethacrylamides, N,N-dialkylmethacrylamides, vinyl-N-alkylacetamides, N-alkylaminoalkylacrylate, N,N-dialkylaminoalkylacrylate, N-alkylaminoalkylmethacrylate, N,N-dialkylaminoalkylmethacrylate, hydroxyethylmethacrylate, hydroxyethylacrylate, vinyl acetate, vinyl alcohol, acrylic acid, 2-isopropenyloxazoline and acrylamide alkyl sulfonic acids.

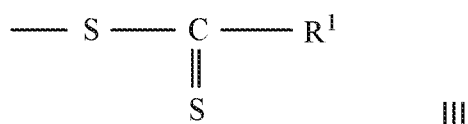
[0015] In a preferred set of embodiments formula I substituents include

R¹ is selected from the group consisting of optionally substituted C₁₋₂₂ alkyl thio; optionally substituted aryl(C₁₋₆ alkyl)thio; and optionally substituted heteroaryl(C₁₋₆ alkyl)thio wherein the optional substituents are selected from the group consisting of carboxy, C₁₋₆ alkoxy-carbonyl, amino, C₁₋₆ alkyl-amino, di-(C₁₋₆ alkyl)amino, oxo, halo, sulfonate, phosphate and quaternary ammonium; and wherein R¹ may be the group of formula II



wherein R^3 and R^4 are independently selected from the group consisting of cycloaliphatic of 4 to 6 ring members optionally substituted with from 1 to 3 C_{1-4} alkyl; heterocyclic of 4 to 6 ring members comprising one or more carbon and 1 to 3 heteroatoms selected from nitrogen and oxygen optionally substituted with 1 to 3 C_{1-4} alkyl; aryl optionally substituted with 1 to 3 C_{1-4} alkyl; heteroaryl of 5 or 6 ring members comprising one or more carbon and 1 to 3 heteroatoms selected from nitrogen; and the group wherein R^3 and R^4 link to form a heterocyclic or heteroaryl ring of 5 or 6 ring members comprising one or more carbon and from 1 to 3 nitrogen atoms wherein the heterocyclic or heteroaryl ring is optionally substituted by 1 to 3 substituents selected from halo and C_{1-4} alkyl;

R^2 is selected from the group consisting of C_{1-12} alkyl optionally substituted with from 1 to 3 substituents selected from the group consisting of carboxyl, cyano; cycloaliphatic of 4 to 6 ring members optionally substituted by 1 to 3 C_{1-4} alkyl; heterocyclic of 4 to 6 constituent ring members comprising 1 to 3 heteroatoms selected from nitrogen and oxygen; aryl optionally substituted with 1 to 3 C_{1-4} alkyl; heteroaryl optionally substituted with 1 to 3 C_{1-4} alkyl; and the group of formula III:



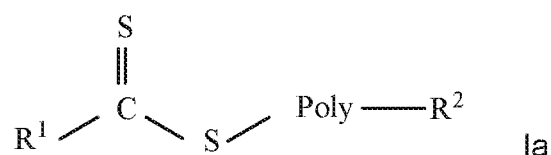
where R^1 is as herein defined; and

Poly is a polymer comprising one or more monomers selected from the group consisting of N-vinyl lactams of 5 to 9 constituent ring atoms optionally substituted with from 1 to 3 C_{1-6} alkyl; isopropenyl-2-oxazoline; N-(C_{1-6} alkyl) acrylamides; N,N-di(C_{1-6} alkyl) acrylamides, N-(C_{1-6} alkyl)methacrylamide; N,N-di(C_{1-6} alkyl)methacrylamides; vinyl-N-(C_{1-6} alkyl)alkyl acetamides; N-(C_{1-6} alkyl)alkylaminoalkylacrylate; N,N-di(C_{1-6} alkyl)aminoalkylacrylate; N-(C_{1-6} alkyl)aminoalkylmethacrylate; N,N-di(C_{1-6} alkyl)aminoalkylmethacrylate; hydroxyethylmethacrylate; hydroxyethylacrylate; vinyl acetate; and acrylamide (C_{1-6} alkyl) sulfonic acids.

[0016] In embodiments where R^1 is of formula II it is generally preferred that at least one of R^3 and R^4 is other than alkyl or that R^3 and R^4 together form an optionally substituted heterocyclic or heteroaryl ring.

[0017] The integer n is at least one. But may be much greater than 1 in the case of branched, star and hyperbranched polymers. In one set of embodiments n is 1 or 2.

[0018] In a preferred set of embodiments n is 1 and the hydrate inhibitor of formula I has the formula Ia:



[0019] In a further set of embodiments n in formula I is 3 to 20.

[0020] Processes for preparation of branched, star and hyperbranched polymers comprising a multiplicity of RAFT agent residues selected from the group of trithiocarbonate and dithiocarbamate groups are known in the art and may be used to prepare suitable branched, star and hyperbranched hydrate inhibitors for use in accordance with the process of the invention.

[0021] In a further embodiment, the hydrate inhibitor in accordance with the invention may also be used to inhibit the corrosion of a material such as ferrous metal, for example steel such as stainless steel, the various alloy steels and carbon steel. In such an embodiment, when the hydrate inhibitor is added to a fluid, it decreases the rate of corrosion of a ferrous metal material in contact with the fluid. Accordingly there is provided a process as herein described wherein the hydrocarbon fluid is in contact with a metal, particularly ferrous metal, and the hydrate inhibitor comprising the RAFT agent is present in an amount sufficient to inhibit corrosion of the metal.

[0022] Detailed Description

[0023] The method of inhibiting hydrate formation utilises polymeric inhibitors which are characterised at least in part by the presence of one or more covalently bound

groups selected from trithiocarbonate and dithiocarbamate groups which are preferably located at the terminus of a polymer chain.

[0024] The hydrate inhibitor used in accordance with the invention may be described as a conjugate of the polymer and at least one RAFT agent residue which is a trithiocarbonate, dithiocarbamate group or may include a plurality of groups selected from trithiocarbonate and dithiocarbamate groups.

[0025] In one set of embodiments the hydrate inhibitor is a linear polymer and comprises one or two RAFT agent residues selected from trithiocarbonate and dithiocarbamate groups, typically at the polymer terminal.

[0026] The polymeric hydrate inhibitors may also be in the form of star, branched or hyperbranched polymers. Such polymers may comprise cross linking monomer units. Accordingly in one set of embodiments the monomers include one or more cross linking agents providing a branched or hyperbranched architecture comprising a multiplicity of the RAFT agent residues, generally at the terminals of the polymer chains. Examples of cross linking agents may be selected from multiolefinic compounds, that is, compounds containing two or more carbon-carbon double bonds prior to polymerisation.

[0027] Specific examples of multiolefinic cross linking agents include divinyl benzene and derivatives of divinyl benzene and monomers containing two or more olefinic groups selected from allyl, acrylate, methacrylate, acrylamide and methacrylamide functional groups. The cross linkers may be diacrylates, dimethacrylates, allyl acrylates; diallyl ethers and di- and tri-allyl amines. Specific examples of cross linkers are disclosed in US6545095. Preferred cross linkers include ethylene glycol diacrylate, ethylene glycol dimethacrylate, polyethylene glycol diacrylate (preferably comprising from 2 to 6 glycol units), propylene glycol dimethacrylate, polyethyleneglycol dimethacrylate (preferably comprising from 2 to 6 glycol units), C₁₋₄ alkylene bis acrylamides such as methylene bis acrylamide, polypropylene glycol dimethacrylate (preferably comprising from 2 to 6 glycol units), polypropylene glycol diacrylate (preferably comprising from 2 to 6 glycol units).

[0028] Suitable star polymers comprising a multiplicity of RAFT agent residues selected from trithiocarbonate and dithiocarbamate groups may be prepared from multifunctional RAFT chain transfer agents prepared by known methods such as disclosed by O'Reilly et al *Polymers* 2009,1, 3-15.

[0029] Hyperbranched polymers comprising a multiplicity of terminal RAFT agent residues may also be prepared using trithiocarbonate and dithiocarbamate based RAFT agent inimers. RAFT agent inimers contain a polymerisable group, generally a carbon-carbon double bond in this case these polymerisable groups are present in addition to the trithiocarbonate and dithiocarbamate groups.

[0030] A wide range of trithiocarbonate and dithiocarbamate RAFT agents including RAFT agent inimers are known to those skilled in the art of polymer science and examples of such agents are available from commercial chemical suppliers including Sigma-Aldrich and Boron Molecular.

[0031] Specific examples of trithiocarbonate and dithiocarbamate groups, which are present as the group $R^1-C(S)S$ in formula I include:

(i) (optionally substituted C_{2-22} alkyl)thiocarbonothioylthio such as (unsubstituted C_{2-22} alkyl)thiocarbonothioylthio such as (dodecylthio)carbonothioylthio-, (carboxy- C_{2-22} alkyl)thiocarbonothioylthio such as ((2-carboxyethyl)thio)carbonothioylthio- and (substituted C_{2-22} alkyl) carbonothioylthio- comprising one or more substituents selected from amino ($-NH_2$), C_{1-6} alkylamino and di- $(C_{1-6}alkyl)amino$, oxo ($=O$), carboxy and $(C_{1-6}alkoxy)-carbonyl$ such as ((1-carboxyethyl)thio)carbonothioylthio- and (3-amino-3-oxopropylthio)carbonothioylthio- ;

(ii) (Optionally substituted-heteroaryl)carbamoylethioylthio, including unsubstituted heteroaryl)carbamoylethioylthio such as methyl(4-pyridyl)carbamoylethioylthio;

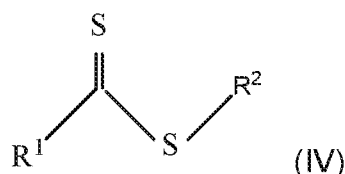
(iii) Nitrogen containing heteroarylcarbodithioate (dithiocarbamates) optionally substituted with 1 to 3 substituents such as halo and/or C_{1-6} alkyl such as

3,5-dimethyl-1H-pyrazole-carbodithioate and 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate; and

(iv) (optionally substituted aryl)thio carbonothioyl)thio-, including (optionally substituted phenyl) thiocarbonothioyl)thio- such as (benzylthio)carbonothioyl)thio-.

[0032] In one set of embodiments the group R^1 in formula I is selected from the group consisting of 3,5-dimethylpyrazol-1-yl, diphenylamino, hydroxycarbonylethylthio and laurylthio.

[0033] The RAFT agent used to provide the trithiocarbonate or dithiocarbamate residue may be of formula IV



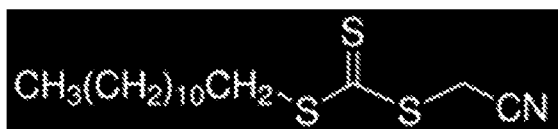
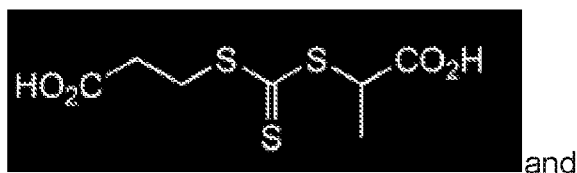
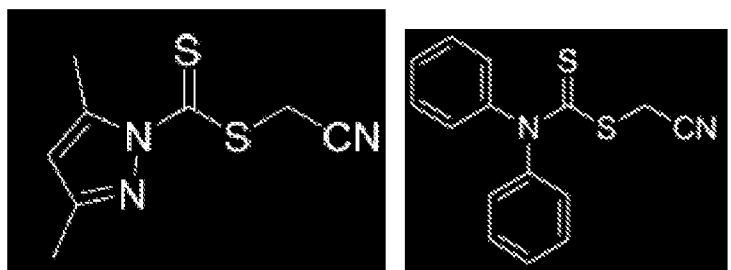
wherein R^1 and R^2 are defined above.

[0034] Examples of RAFT agent inimers which may be used to prepare hyperbranched polymers comprising terminal groups selected from trithiocarbonate and dithiocarbamate groups may be selected from compounds of formula (IV) wherein R^2 comprises a polymerisable group such as vinyl benzene, acrylyloxy(C_{1-6} alkyl) wherein the alkyl is optionally substituted and methacrylyloxy(C_{1-6} alkyl) wherein the alkyl is optionally substituted. Many examples of RAFT agent inimers are provided in the literature such as 2-(3-(benzylthiocarbonothioylthio)propanoyloxy)ethyl acrylate, butyl (4-vinylbenzyl) carbonotrithioate, 4-vinylbenzyl 3,5-dimethyl-1H-pyrazolecarbodithioate, 4-vinylbenzyl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate and S-1-dodecyl-S'-(α,α' -dimethyl- α'' -methyl acetate)trithiocarbonate (DDMMAT)

[0035] Examples of specific preferred RAFT agents may be selected from the group consisting of

2-(((dodecylthio)carbonothioyl)thio)propanoic acid,
 methyl 4-cyano-4-(dodecylthiocarbonothioylthio)pentanoate,
 4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoic acid,
 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid,
 2-cyanobutan-2-yl dodecyl carbonotrithioate,
 cyanomethyl dodecyl trithiocarbonate,
 bis(4-chloro-3,5-dimethyl-1H-pyrazolesulfanylthiocarbonyl)disulfide,
 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate,
 2-cyanobutanyl-2-yl 3,5-dimethyl-1H-pyrazole-1-carbodithioate,
 benzyl 3,5-dimethyl-1H-pyrazole-1-carbodithioate,
 bis(3,5-dimethyl-1H-pyrazol-1-ylthiocarbonyl)disulfide,
 cyanomethyl (3,5-dimethyl-1H-pyrazole)-carbodithioate,
 2-cyanopropan-2-yl methyl(4-pyridinyl)carbamoyldithioate,
 bis(Methyl-pyridin-4-yl-amino-thiocarbonyl)disulphide,
 cyanomethyl methyl(phenyl)carbamodithioate,
 3-(((1-carboxyethyl)thio)carbonothioyl)thio)propanoic acid,
 4-((3-amino-3-oxopropylthio)carbonothioylthio)-4-cyanopentanoic acid,
 4-(((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid,
 dibenzyl trithiocarbonate and
 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate.

[0036] In a more preferred embodiment particularly significant improvement in hydrate inhibition activity is provided by trithiocarbonate or dithiocarbamate residues of a RAFT agent of formula selected from the group consisting of:



[0037] The polymer of the current invention preferably comprises random or block copolymers of one or more monomers selected from optionally substituted N-vinyl lactams, N-alkylacrylamides, N-alkylmethacrylamides, N,N-dialkylacrylamides, N,N-dialkylmethacrylamides, vinyl-N-alkylacetamides, N-alkylaminoalkylacrylate, N,N-dialkylaminoalkylacrylate, N-alkylaminoalkylmethacrylate, N,N-dialkylaminoalkylmethacrylate, hydroxyethylmethacrylate, hydroxyethylacrylate, vinyl acetate, 2-isopropenyloxazoline and acrylamide alkyl sulfonic acids

[0038] In a preferred set of embodiments the polymer comprises at least one segment comprising a poly(alkylacrylamide) or poly(alkylmethacrylamide) wherein the alkyl group is preferable C₁₋₆ alkyl. Specific examples of poly(alkylacrylamide) and poly(alkylmethacrylamide) include poly(N-isopropylacrylamide), poly(N-isobutylacrylamide), poly(N-isopentylacrylamide), poly(N-isopropylmethacrylamide), poly(N-isobutylmethacrylamide) and poly(N-isopentylmethacrylamide). Most preferably the polymer comprises at least one segment of poly(N-isopropylacrylamide) or poly(N-isopropylmethacrylamide).

[0039] In a further embodiment the polymeric hydrate inhibitor comprises a copolymer comprising vinyl lactam monomer residues such as vinylcaprolactam.

[0040] In a further embodiment the polymeric hydrate inhibitor comprises a copolymer comprising vinyl pyrrolidone monomer residues.

[0041] In a further preferred embodiment the copolymer has monomers selected from the group of N-vinyl lactams, N-alkylacrylamides, vinyl-N-alkylacetamides and 2-isopropenyloxazoline.

[0042] In one set of embodiments the weight average molecular weight of the polymer is in the range of from 500 to 1,000,000 and preferably from 500 to 500,000 and more preferably from 500 to 200,000 such as 500 to 100,000, 500 to 50,000 or 5000 to 20,000. RAFT polymerisation generally has the advantage of allowing good control over molecular weight with low polydispersity.

[0043] The method generally comprises addition of the polymeric hydrate inhibitor into a hydrocarbon fluid. The polymeric hydrate inhibitor may be added neat or may be added as a solution or dispersion in a suitable carrier. Examples of liquid carriers may be selected from the group consisting of water, brine, seawater, methanol, ethanol, propanol, isopropanol, monoethylene glycol and mixtures thereof. If desired the polymeric hydrate inhibitor may be added to the hydrocarbon fluid in admixture with or contemporaneously with a conventional thermodynamic hydrate inhibitor such as methanol, ethanol, propanol, isopropanol, monoethylene glycol and mixtures thereof. The polymeric kinetic hydrate inhibitor in combination with the conventional thermodynamic hydrate inhibitor will generally provide much more effective control of hydrate formation and/or will allow a significant reduction in the use of the conventional hydrate inhibitor.

[0044] The amount of the polymeric hydrate inhibitor added to the hydrocarbon fluid will depend on the nature and conditions such as pressure and temperature under which the hydrocarbon fluid is transported and the amount of water present in the hydrocarbon fluid. The amount will generally be chosen to be effective to inhibit hydrate formation such that plug formation is avoided. The amount is typically in the range of from 0.01 % to 5% by weight based on the weight of water in the hydrocarbon fluid and preferably in the range of from 0.01 % to 3% such as 0.01 % to 2% by weight based on the weight of water in the hydrocarbon fluid.

[0045] The polymeric hydrate inhibitor may be used in controlling the formation of hydrocarbon hydrates in a range of hydrocarbons. Examples of hydrocarbons in which hydrate formation is a particular problem include, but are not limited to, crude oil, methane, ethane, propane, isobutane, butane, neopentane, ethylene, propylene, isobutylene, cyclopropane, cyclobutane, cyclopentane, cyclohexane, acetylene, methylacetylene and benzene.

[0046] The process using the polymeric hydrate inhibitors is particularly useful in inhibiting formation of gas hydrates.

[0047] The hydrate inhibitors of the invention also generally have the further particularly desirable attribute of acting as corrosion inhibitors. Generally it has been the practice to use corrosion inhibitors in combination with hydrate inhibitors. Corrosion inhibitors are in some cases needed to compensate for corrosive effect of compositions containing the hydrate inhibitor and in some cases the hydrate inhibitors (particularly those of the KHI type) have been found to interact with and counteract the corrosion inhibitor. Examples of known corrosion inhibitors include primary, secondary or tertiary amines or quaternary ammonium salts, preferably amines or salts containing at least one hydrophobic group, benzalkonium halides, preferably benzyl hexyldimethyl ammonium chloride.

[0048] The RAFT group comprising a trithiocarbonate or dithiocarbamate present in the hydrate inhibitors provides both hydrate inhibition and metal corrosion inhibition in a single additive.

[0049] Accordingly there is provided a method of inhibiting hydrate formation and inhibiting corrosion produced by a hydrocarbon fluid comprising water in contact with metals, particularly ferrous metals, the method comprising adding to the hydrocarbon fluid a polymer having covalently bound thereto a trithiocarbonate or dithiocarbamate RAFT agent. The polymer may be added in an amount sufficient to inhibit corrosion of the metal component.

[0050] The amount necessary to inhibit corrosion of the metal component will depend on the metal present in the metal component, nature and proportion of components in the fluid and the conditions such as temperature and pressure under

which the fluid is in contact with the metal. The amount will generally be at least 0.01% based on the water content of the fluid, preferably at least 0.1% in the range of from. In one set of embodiments the amount of inhibitor is in the range of from 0.01 % to 5% by weight based on the weight of water in the hydrocarbon fluid and preferably in the range of from 0.01 % to 3% such as 0.01 % to 2% by weight based on the weight of water in the hydrocarbon fluid.

[0051] The corrosion inhibition provided by the hydrate inhibitors is particularly useful in pumping hydrocarbon fluid in metal (particularly ferrous metal) conduit under conditions of temperature and pressure which would, in the absence of the hydrate inhibitor, lead to formation of hydrocarbon hydrates.

[0052] The polymeric hydrate inhibitor may be prepared by RAFT mediated polymerisation using a RAFT agent selected from trithiocarbonate and dithiocarbamate RAFT agents such as those described above.

[0053] The polymerisation process is generally a radical polymerisation in accordance with the procedures and conditions described in detail in the literature. Examples of reviews of the RAFT mediated polymerisation process are described in review papers such as Moad et al "Living Free Radical Polymerisation by the RAFT Process" *Aust. J. Chem.* 2012, 65(8) 985-1076. Approaches to star and hyperbranched polymers using S-(4-vinyl)benzyl S'-propyltrithiocarbonate (VBPT) are described by Zhang et al. *Macromolecules*, 2011, 44 (7), pp 2034–2049.

[0054] **Terms**

[0055] With regards to the definitions provided herein, unless stated otherwise, or implicit from context, the defined terms and phrases include the provided meanings. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired by a person skilled in the relevant art. The definitions are provided to aid in describing particular embodiments, and are not intended to limit the claimed invention, because the scope of the invention is limited only by the claims. Furthermore, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0056] Throughout the description and the claims of this specification the word "comprise" and variations of the word, such as "comprising" and "comprises" is not intended to exclude other additives, components, integers or steps.

[0057] "Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C₁–C₁₄ alkyl, more preferably a C₁–C₁₀ alkyl, most preferably C₁–C₆ unless otherwise noted. Examples of suitable straight and branched C₁–C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like.

[0058] "Alkoxy" refers to an alkyl-O- group in which alkyl is as defined herein. Preferably the alkoxy is a C₁–C₆ alkoxy. Examples include, but are not limited to, methoxy and ethoxy.

[0059] Suitable examples of heterocyclyl groups may include aziridinyl, oxiranyl, thiiranyl, azetidiny, oxetanyl, thietanyl, 2H-pyrrolyl, pyrrolidinyl, pyrrolinyl, piperidyl, piperazinyl, morpholinyl, indolinyl, imidazolidinyl, imidazoliny, pyrazolidinyl, thiomorpholinyl, dioxanyl, tetrahydrofuranyl, tetrahydropyranyl, tetrahydropyrrolyl, tetrahydrothiophenyl, pyrazolinyl, dioxalanyl, thiazolidinyl, isoxazolidinyl, dihydropyranyl, oxaziny], thiazinyl, thiomorpholinyl, oxathianyl, dithianyl, trioxanyl, thiadiazinyl, dithiazinyl, trithianyl, azepinyl, oxepinyl, thiepinyl, indenyl, indanyl, 3H-indolyl, isoindolinyl, 4H-quinolaziny, chromenyl, chromanyl, isochromanyl, pyranyl and dihydropyranyl. A heterocyclyl group may be optionally substituted by one or more optional substituents as herein defined.

[0060] The term "heteroaryl" includes monocyclic heteroaryl, wherein one or more carbon atoms are replaced by a heteroatom so as to provide an aromatic residue. Preferred heteroaryl have 3-20 ring atoms, e.g. 3-10. Particularly preferred heteroaryl are 5-6 and 9-10 membered bicyclic ring systems. Suitable heteroatoms include, O, N, S and P, particularly O, N and S. Where two or more carbon atoms are replaced, this may be by two or more of the same heteroatom or by different heteroatoms. Suitable examples of heteroaryl groups may include pyridyl, pyrrolyl, thienyl, imidazolyl, furanyl, benzothienyl, isobenzothienyl, benzofuranyl, isobenzofuranyl, indolyl, isoindolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, quinolyl,

isoquinolyl, phthalazinyl, 1,5-naphthyridinyl, quinoxalyl, quinazolinyl, quinolinyl, oxazolyl, thiazolyl, isothiazolyl, isoxazolyl, triazolyl, oxadiazolyl, oxatriazolyl, triazinyl, and furazanyl. A heteroaryl group may be optionally substituted by one or more optional substituents as herein defined.

[0061] The term "carbocyclyl" includes any of non-aromatic monocyclic (preferably C₃₋₈). The rings may be saturated, e.g. cycloalkyl, or may possess one or more double bonds (cycloalkenyl) and/or one or more triple bonds (cycloalkynyl). Particularly preferred carbocyclyl moieties are 5- 6-membered or 9-10 membered ring systems. Suitable examples include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclopentenyl, cyclohexenyl, cyclooctenyl, cyclopentadienyl, cyclohexadienyl, cyclooctatetraenyl, indanyl, decalyl and indenyl. A carbocyclyl group may be optionally substituted by one or more optional substituents as herein defined.

[0062] As used herein, the term "acyloxy" refers to an "acyl" group wherein the "acyl" group is in turn attached through an oxygen atom. Examples of "acyloxy" include hexylcarbonyloxy (heptanoyloxy), cyclopentylcarbonyloxy, benzoyloxy, 4-chlorobenzoyloxy, decylcarbonyloxy (undecanoyloxy), propylcarbonyloxy (butanoyloxy), octylcarbonyloxy (nonanoyloxy), biphenylcarbonyloxy (eg 4-phenylbenzoyloxy), naphthylcarbonyloxy (eg 1-naphthoyloxy) and the like.

[0063] As used herein, the term "alkoxycarbonyl" refers to an "alkoxy" group attached through a carbonyl group. Examples of "alkoxycarbonyl" groups include butylformate, sec-butylformate, hexylformate, octylformate decylformate, cyclopentylformate and the like. As used herein, the term "arylalkyl" refers to groups formed from straight or branched chain alkanes substituted with an aromatic ring. Examples of arylalkyl include phenylmethyl (benzyl), phenylethyl and phenylpropyl.

[0064] As used herein, the term "alkylaryl" refers to groups formed from aryl groups substituted with a straight chain or branched alkane. Examples of alkylaryl include methylphenyl and isopropylphenyl.

[0065] Preferred optional substituents include alkyl, (e.g. C₁₋₆ alkyl such as methyl, ethyl, propyl, butyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl), hydroxyalkyl

(e.g. - hydroxymethyl, hydroxyethyl, hydroxypropyl), alkoxyalkyl (e.g. methoxymethyl, methoxyethyl, methoxypropyl, ethoxymethyl, ethoxyethyl, ethoxypropyl etc.) alkoxy (e.g. C₁₋₆ alkoxy such as methoxy, ethoxy, propoxy, butoxy, cyclopropoxy, cyclobutoxy), halo, trifluoromethyl, trichloromethyl, tribromomethyl, hydroxy, phenyl (which itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), benzyl (wherein benzyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyC₁₋₆ alkyl, alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), phenoxy (wherein phenyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), benzyloxy (wherein benzyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), amino, alkylamino (e.g. C₁₋₆ alkyl, such as methylamino, ethylamino, propylamino etc), dialkylamino (e.g. C₁₋₆ alkyl, such as dimethylamino, diethylamino, dipropylamino), acylamino (e.g. NHC(O)CH₃), phenylamino (wherein phenyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), nitro, formyl, -C(O)-alkyl (e.g. C₁₋₆ alkyl, such as acetyl), O-C(O)-alkyl (e.g. C₁₋₆ alkyl, such as acetyloxy), benzoyl (wherein the phenyl group itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxyl, hydroxyC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), replacement of CH₂ with C=O, CO₂H, CO₂alkyl (e.g. C₁₋₆ alkyl such as methyl ester, ethyl ester, propyl ester, butyl ester), CO₂phenyl (wherein phenyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxylC₁₋₆ alkyl, C₁₋₆ alkoxy, haloC₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆alkyl, and amino), CONH₂, CONHphenyl (wherein phenyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy, hydroxyl C₁₋₆ alkyl, C₁₋₆ alkoxy, halo C₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), CONHbenzyl (wherein benzyl itself may be further substituted e.g., by C₁₋₆ alkyl, halo, hydroxy hydroxyl C₁₋₆ alkyl, C₁₋₆ alkoxy, halo C₁₋₆ alkyl, cyano, nitro OC(O)C₁₋₆ alkyl, and amino), CONHalkyl (e.g. C₁₋₆ alkyl such as methyl ester, ethyl ester, propyl ester, butyl amide) CONdialkyl (e.g. C₁₋₆ alkyl) aminoalkyl (e.g., H₂N-C₁₋₆ alkyl, C₁₋₆ alkylHN-C₁₋₆ alkyl and (C₁₋₆ alkyl)₂N-C₁₋₆ alkyl-), thioalkyl (e.g., HS C₁₋₆ alkyl-), carboxyalkyl (e.g., HO₂CC₁₋₆ alkyl-), carboxyesteralkyl

(e.g., C_{1-6} alkylO₂CC₁₋₆ alkyl-), amidoalkyl (e.g., $H_2N(O)CC_{1-6}$ alkyl-, $H(C_{1-6}$ alkyl)N(O)CC₁₋₆ alkyl-), formylalkyl (e.g., OHC_{1-6} alkyl-), acylalkyl (e.g., C_{1-6} alkyl(O)CC₁₋₆ alkyl-), nitroalkyl (e.g., O_2NC_{1-6} alkyl-), sulfoxidealkyl (e.g., $R(O)SC_{1-6}$ alkyl, such as C_{1-6} alkyl(O)SC₁₋₆ alkyl-), sulfonylalkyl (e.g., $R(O)_2SC_{1-6}$ alkyl- such as C_{1-6} alkyl(O)₂SC₁₋₆ alkyl-), sulfonamidoalkyl (e.g., $H_2RN(O)SC_{1-6}$ alkyl, $H(C_{1-6}$ alkyl)N(O)SC₁₋₆ alkyl-), triarylmethyl, triarylamino, oxadiazole, and carbazole.

[0066] The invention will now be described with reference to the following examples. It is to be understood that the examples are provided by way of illustration of the invention and that they are in no way limiting to the scope of the invention.

[0067] **EXAMPLES**

[0068] **Brief Description of Drawings**

[0069] In the attached drawings:

[0070] **Figure 1** is a graph showing the change in hydrate volume fraction over time at 1K/min cooling rate for RAFT based poly-N-isopropylacrylamide linear (sample 2) and branched (sample 8) compared to system without inhibitor (pure water). Leading commercial KHI (Iuvicap) shown as well as polyvinylpyrrolidone control polymers. The pure water case shows a higher hydrate volume fraction and fast hydrate formation as evidenced by the steep increase in hydrate volume fraction in the early stages of formation. For the RAFT-based polymers the overall hydrate fraction is lower and there is a delay in formation.

[0071] **Figures 2(a) and 2(b)** are graphs showing the change in hydrate volume fraction at different cooling rates for RAFT based poly-N-isopropylacrylamide branched (sample 8, **Figure 2(a)** left image) and linear (sample 2, **Figure 2(b)** right image). At slower cooling rates the inhibitors prevent significant hydrate formation as can be seen at 1K/60mins there is minimal hydrate volume fraction after 200 mins.

[0072] **Figure 3** includes three photographs (a), (b) and (c) comprising hydrate formation using cyclopentane as a hydrate forming molecule for a week inhibitor (polyacrylamide-co-acrylic acid, left photo (a)) compared to a RAFT based linear polymer (sample 3, centre image photo (b)), and a RAFT based branched polymer

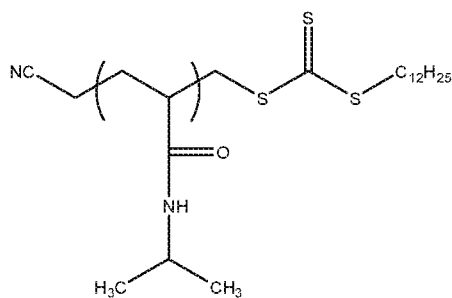
(sample 9, right image photo (c)). Inhibitor concentration decreases from left to right for each image. Amount of hydrate in the RAFT cases is decreased substantially even at low inhibitor concentrations which is indicative of strong hydrate inhibition.

[0073] **Figure 4 is a column chart** comparing corrosion as measured by % weight loss from carbon steel in the presence of various corrosion inhibitors. RAFT based samples are #1 (linear), #3 (linear) and #7 (branched) compared to non RAFT-based (PNIPAM) and other optimized corrosion inhibitors (PNIPAM-co-AA and PNIPAM-APIM-20), corrosion inhibitor group shown (APIM) and control (blank). As can be seen, RAFT based polymers compete with those where typical corrosion inhibition groups are included.

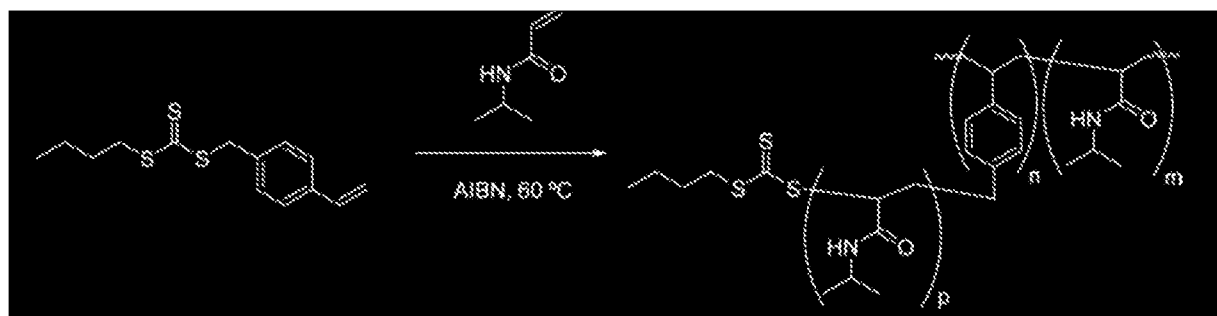
[0074] **Procedure**

[0075] N-isopropylacrylamide (NIPAM) monomer, RAFT agent, and azoisobutyronitrile (AIBN) were weighed in a 20mL reaction vessel and they were dissolved in dioxane (please see below for amounts). The mixture was degassed nitrogen for 1 hour and then heated to 60 °C for 19 hours. The final polymers were purified by precipitation from the monomer/solvent mixture into hexane and dried under vacuum until constant weight.

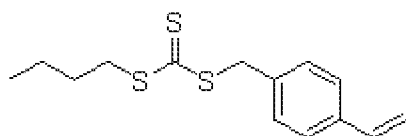
Linear PNIPAM is of formula



Branched PNIPAM using inimer



[0076] **Synthesis of RAFT agent Inimer Agent: butyl (4-vinylbenzyl) carbonotrithioate for the purpose of generating branched polymers**



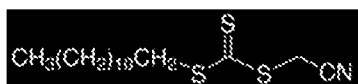
[0077] RAFT Agent Inimer synthesized using a procedure described previously (J. Phys. Chem. B 2013, 117, 10504–10512).

[0078] n-Butanethiol (5.4 g, 6.4 mL, 0.06 mol), carbon disulfide (9.1 g, 7.3 mL, 0.120 mol), and chloroform (50 mL) were added to a flask purged with argon. Triethylamine (12.5 g, 17.3 mL, 0.124 mol) was then added dropwise with stirring. The solution became orange as the addition proceeded with the formation of the intermediate triethylammonium S-n-butyl trithiocarbonate salt. The solution was left to stir at room temperature for 2.5 hours. 1-Chloromethyl-4-vinylbenzene (9.16 g, 8.45 mL, 0.06 mol) was then added dropwise, and the solution was left to stir under argon. Volatiles were removed under rotavaporation, poured into deionized water, and extracted with CHCl_3 . The organic layer was washed 2× with the following: deionized water, 1 M HCl, and brine. This was then dried over anhydrous MgSO_4 , filtered and the solvent removed to leave behind a yellow oil (16.96 g, yield ~99%). The crude compound was further purified on silica column chromatography running a gradient from hexane to 5% DCM in hexane to obtain a pure fraction (14 g, yield = 83%, NMR purity of ~95%). ^1H NMR (400 MHz, CDCl_3): δ 0.94 (tr, CH_3 , 3H), 1.43 (m, CH_2 , 2H), 1.67 (m, CH_2 , 2H), 3.37 (tr, CH_2 , 2H), 4.59 (s, CH_3 , 2H), 5.24 (d, $\text{CH}=\text{CHH}$, 1H), 5.73 (d, $\text{CH}=\text{CHH}$, 1H), 6.68 (q, $\text{CH}=\text{CH}_2$, 1H), 7.28–7.36 (q, aromatic CH, 4H). ^{13}C NMR

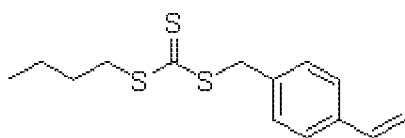
(400 MHz, CDCl₃): δ 13.6, 22.1, 30.1, 36.8, 41.1, 114.2, 126.5, 129.5, 134.7, 136.3, 137.1, 223.3.

[0079] General RAFT procedure: An effective RAFT polymerisation is carried out by introducing an organic compound that can participate in the process of reversible addition – fragmentation (RAFT agent) to a classical free radical polymerization (see Living and controlled polymerisation, synthesis, characterisation, and properties of the respective polymers and copolymers, J. Jagur-Grodzinski, Nova Science Publishers). Typically a monomer, RAFT agent, and a free radical initiator (e.g., azoisobutyronitrile, AIBN) are weighed in a reaction vessel and are dissolved in an appropriate solvent. The mixture is degassed with nitrogen for 1 hour to remove oxygen and then heated to the desired reaction temperature (60°C for AIBN). The final polymers are purified by precipitation from the monomer/solvent mixture into hexane and dried under vacuum until constant weight.

[0080] **Linear RAFT Agent** (cyanomethyldodecyltrithiocarbonate)



Branched RAFT Agent (butyl (4-vinylbenzyl) carbonotrithioate)

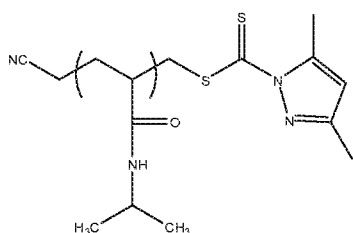


[0081] **Synthesis of Linear PNIPAM with different RAFT agents**

(BM1481 and BM1429 available from Boron Molecular)

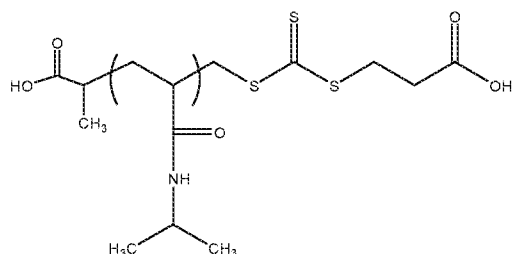
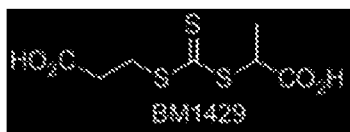
[0082] Initiator was Vazo-67, temp=100 degrees C, time=2hrs, >99% conversion. The synthesis of JG320 was carried out in 1,4-dioxane and JG321 used acetonitrile.

1. **Sample JG320** - ratio of monomer : RAFT agent : initiator = 70:1:0.1,
Theoretical MW = 8100
RAFT agent = BM1481



2. **Sample JG321** - ratio of monomer : RAFT agent : initiator = 70:1:0.1, Th MW = 8200

RAFT agent = BM1429



[0083] **Stock Solution A** was prepared by dissolving 15.1746g of NIPAM monomer and 0.022021 g of AIBN in 24.27 g of dioxane.

[0084] **Stock solution B** (linear RAFT agent) was prepared by dissolving 0.5603g of RAFT agent (cycanmethyldodecyltrithiocarbonate) in 10 g of dioxane.

3. **Stock solution C** (branching RAFT agent) was prepared by dissolving 0.5555g of RAFT agent (butyl (4-vinylbenzyl) carbonotrithioate) in 10g of dioxane.

[0085] **Table 1.** Amounts Added (1-6 are for linear polymers, 7-12 are for branched)

	Reactant Vial amounts added				
Reactor	A (NIPAM)	B (RAFT Agent linear)	C (RAFT agent branch)	D (solvent)	Total vol
1	2.602	0.266	0	1.153	4.021
2	2.602	0.533	0	0.901	4.036
3	2.602	0.640	0	0.800	4.042
4	2.602	0.800	0	0.648	4.050
5	2.602	0.906	0	0.547	4.055
6	2.602	1.066	0	0.396	4.064
7	2.602	0	0.237	1.180	4.019
8	2.602	0	0.474	0.957	4.033
9	2.602	0	0.569	0.867	4.038
10	2.602	0	0.711	0.732	4.045
11	2.602	0	0.806	0.642	4.050
12	2.602	0	0.949	0.507	4.058

[0086] **Table 2.** Molecular Weights of Resulting polymers (1-6 are for linear polymers, 7-12 are for branched)

Sample from Reactor	RAFT ratio (linear)	Mw	Mn	PDI	Notes
1	5	36733	34289	1.07	Low dispersity
2	10	18887	17634	1.07	Low dispersity
3	12	15900	14997	1.06	Low dispersity
4	15	123989	12311	1.05	Low dispersity
5	17	10339	9767	1.05	Low dispersity
6	20	9074	8555	1.06	Low dispersity
7	5	80002	53460	1.50	v. broad Mw distribution
8	10	52049	35151	1.48	v. broad Mw distribution
9	12	46189	30818	1.49	v. broad Mw distribution
10	15	38799	26347	1.49	v. broad Mw distribution
11	17	30949	21017	1.47	v. broad Mw distribution
12	20	44680	28909	1.54	Solvent lost during synthesis

[0087] Gas Hydrate Testing

[0088] A high pressure autoclave equipped with a magnetic stirrer coupling was used to study hydrate formation. This provides information regarding the hydrate onset time, growth rate, and hydrate fraction by measuring pressure, temperature, and torque changes during hydrate formation. A synthetic natural gas mixture was used in all of the experiments according to Table 3.

[0089] **Table 3.** Composition of synthetic natural gas.

Components	Composition (mol%)
CH ₄	84.22
C ₂ H ₆	6.79
C ₃ H ₈	3.12
i-C ₄ H ₁₀	0.41
n-C ₄ H ₁₀	0.59
i-C ₅ H ₁₂	0.04
n-C ₅ H ₁₂	0.02
C ₆ +	0.01
CO ₂	2.19
N ₂	2.59

[0090] A total liquid volume of 30 mL was loaded into the autoclave cell which had an internal volume of 360 mL. The cell was immersed in a temperature-controlled liquid bath connected to an external refrigerated heater. A platinum resistance thermometer monitored the temperature of the liquid phase inside of the autoclave with an uncertainty of 0.15 °C. The pressure was measured by a pressure transducer with an uncertainty of 0.1 bar in a range of 0 - 200 bar. Temperature and pressure were recorded using a data acquisition system.

[0091] The experiment was commenced by loading the 30 ml of liquid phase into the autoclave cell. After purging the cell three times with the natural gas, the autoclave was pressurized to 120 bar at 24 °C while stirring at 600 rpm to saturate the liquid phase with gas. Once the pressure and temperature reached steady-state, the cell

was cooled to 4 °C within 2 hours and kept for 10 hours at the temperature. During this time, torque, pressure and temperature were continuously monitored. Ten experiments were carried out for each system to determine averages for the hydrate onset time, hydrate volume fraction (Figure 1 and 2), subcooling temperature, and the amount of gas consumed, and to obtain improved statistics regarding any trends in hydrate formation and transportability (Table 4). The dissociation of hydrate was carried out at 24 °C for 3 hours to remove the residual hydrate structures.

[0092] In addition, cyclopentane (Cp) was used as an ambient pressure hydrate former (figure 3). Cp was chosen as a model of hydrate because it forms a structure sII hydrate, which is the same structure as the hydrates formed in subsea pipelines. The equilibrium temperature is 7.7 °C and the hydrate is formed at atmospheric pressure.

[0093] The polymer solutions with concentrations of 0.01; 0.05; 0.1; 0.5 to 1.0 % (w/v) were prepared and 1 mL of each solution was frozen using dry ice. Cyclopentane is added in the ratio of 1: 5 (0.2 ml of Cp per sample). Then the vials return to dry ice to ensure the polymer phase is frozen. All samples are quickly added to the sample holder (metal cabinet) that is adjusted to the water bath (glass container) according to Figure 3. The more effective the inhibitor the lower concentration at which hydrate could be inhibited. Figure 3 includes three photographs (a), (b) and (c) comprising hydrate formation using cyclopentane as a hydrate forming molecule (*Method described in detail in Energy Fuels 2016, 30, 5432–5438*) for a week inhibitor (polyacrylamide-co-acrylic acid, left photo (a)) compared to a RAFT based linear polymer (sample 3, centre image photo (b)), and a RAFT based branched polymer (sample 9, right image photo (c)). Inhibitor concentration decreases from left to right (1wt.% and decreases by a factor of half each time) for each image and each image is captured 2 hrs after hydrate formation conditions were reached. Amount of hydrate in the RAFT cases is decreased substantially even at low inhibitor concentrations (right images down to 0.03wt%, right hand vials) there is no hydrate observed at the interface or the vertical section which is indicative of strong hydrate inhibition because the inhibitors are effective at low concentration. For polyacrylamide-co-acrylic acid the image (photograph (a)) shows

dense white hydrate formation at the liquid interface (vial 2 and 3 from left, at high concentrations 0.5wt% and 0.25wt%) and at lower concentration (vial 4, 5 and 6; concentration 0.12wt.%, 0.06wt% and 0.03wt.%) a hydrate film can be seen along the entire vertical section of each vial which is indicative of maximum conversion to hydrate (>50%).

Table 4 Hydrate formation conditions measured for linear RAFT polymer (reactor 2), a commercial, conventional kinetic hydrate inhibitor (luvicap), a branched RAFT polymer (reactor 8) compared to pure water (uninhibited system)

	#2 0.5% solution			Luvicap 0.5% solution			#8 0.5% solution				Pure water
	1K/4min η	1K/30 min	1K/30 min (2nd)	1K/4min η	1K/30 min	1K/60 min	1K/4min	1K/30min	1K/60 min		
Teq(K)	294.09	294.01	294.05	294.13	294.05	293.97	294.15	294.12	294.05		1K/4min
Peq(bar)	117.84	116.16	116.72	118.34	116.33	115.04	118.43	117.99	117.49		
Tonset(K)	282.45	283.61	282.89	282.55	282.63	283.93	283.55	284.15	285.09		289.37
Ponset(bar)	109.14	107.84	108.14	109.68	107.97	107.18	110.61	110.58	110.94		113.88
$\Delta T_{sub}(K)$	11.64	10.40	11.16	11.58	11.43	10.04	10.60	9.97	8.96		4.71
tonset(min)	77.33	358.13	351.30	83.83	353.21	618.17	67.33	309.36	532.77		20.40
Gas Consumption (mol)	0.09	0.08	0.07	0.09	0.08	0.09	0.0671	0.073			
							(1-5)	(1-6)			
Hydrate Volume fraction	0.39	0.36	0.32	0.40	0.38	0.39	0.07963	0.083	0.06		0.12
							(2-5)	(except 5)			
							0.1237	0.3338			
Water Conversion (mol%)	57.39	51.76	45.97	58.87	55.79	57.48	(1-5)	(1-6)	0.28		
							0.3630	0.3753			
							(2-5)	(except 5)			
							44.5399	48.64			
							(1-5)	(1-6)	40.49		74.04
							52.8904	54.86			
							(2-5)	(except 5)			

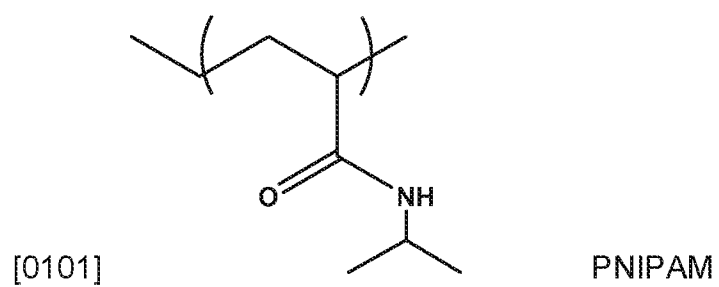
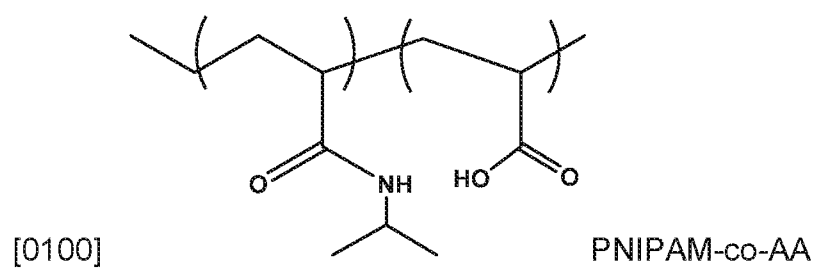
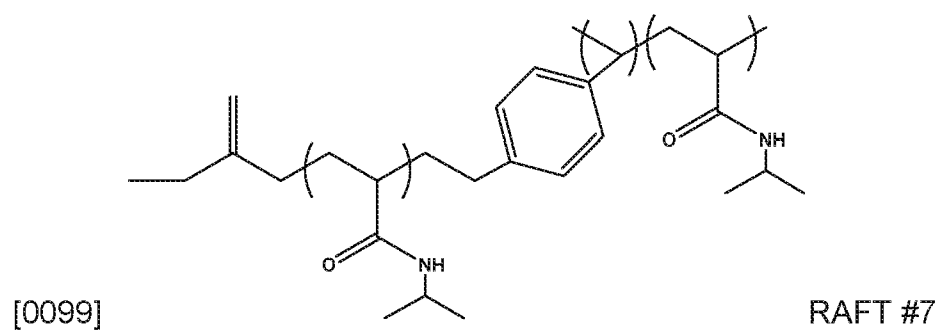
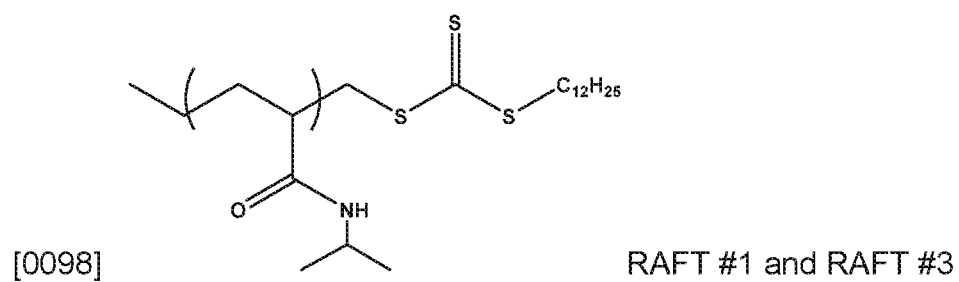
[0094] Corrosion Weight-loss Measurements

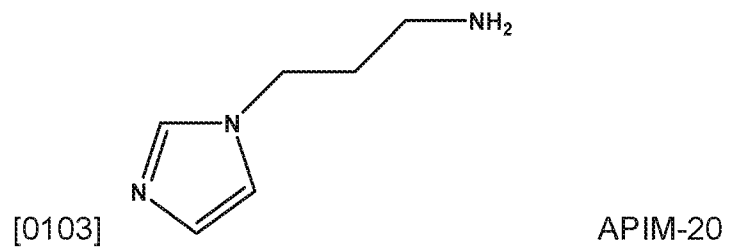
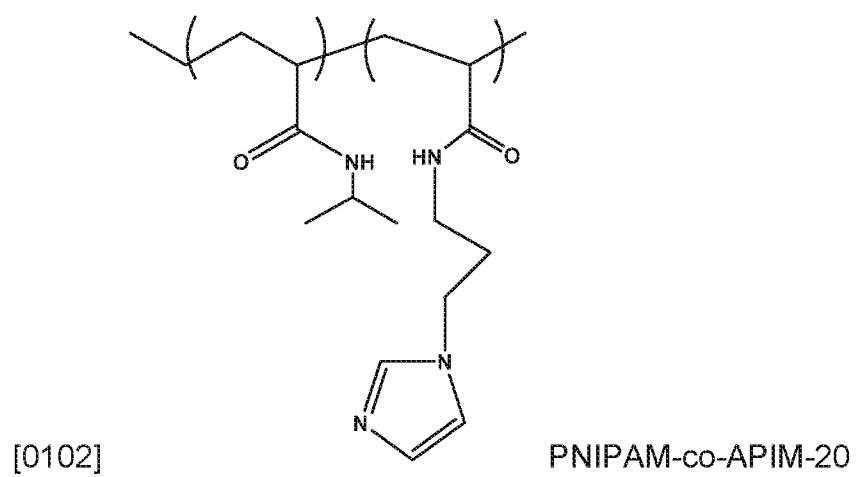
[0095] Carbon steel coupons (13 x 1 mm) were polished and then washed with water and ethanol prior to rinsing and drying with distilled water. The coupons were then exposed to 2M HCl with or without 500 ppm (0.05 wt%) polymer solution for 120 h in open glass vials. At specific time intervals, the coupons were withdrawn from the solutions and weighted after being rinsed by ethanol and distilled water. The immersion tests were repeated 5 times to test the reproducibility. Three RAFT samples were tested (1, 3 and 7) and compared with a non-RAFT polymer (PNIPAM) which is already a reasonable corrosion inhibitor; two optimized PNIPAM structures included that were generated without RAFT (PNIPAM-co-AA and PNIPAM-APIM-20); a known corrosion inhibitor group (APIM) as well as the control with no inhibitor. The results are shown in the Column Chart in Figure 4. As can be seen from the results, RAFT based polymers compete with those where typical corrosion groups are included.

[0096] **Table 5.** Corrosion as measured by weight loss from carbon steel.

Sample	Weight loss %
RAFT #1	1.16
RAFT #3	0.95
RAFT #7	1.28
PNINAM	2.05
PNINAM-co-AA	1.55
PNINAM-APIM-20	0.77
APIM	2.84
Control (blank)	5.34

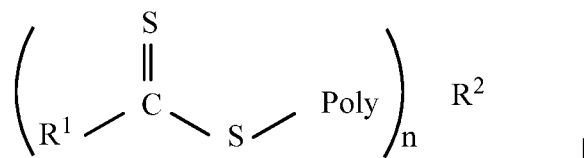
[0097] The structures of the components tested is shown below:





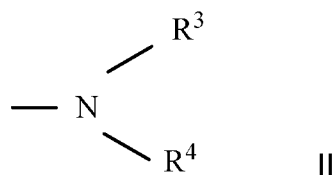
Claims

1. A process for inhibiting the formation of gas hydrates in a hydrocarbon fluid comprising adding to the hydrocarbon fluid a hydrate inhibitor which is a polymer comprising covalently bound thereto at least one trithiocarbonate or dithiocarbamate residue of a RAFT agent comprising a trithiocarbonate or a dithiocarbamate group.
2. A process for inhibiting the formation of gas hydrates in a hydrocarbon fluid comprising adding to the hydrocarbon fluid a hydrate inhibitor which is a polymer comprising one or more monomers selected from the group consisting of optionally substituted N-vinyl lactams, N-alkylacrylamides, N,N-dialkylacrylamides, N-alkylmethacrylamides, N,N-dialkylmethacrylamides, vinyl-N-alkylacetamides, N-alkylaminoalkylacrylate, N,N-dialkylaminoalkylacrylate, N-alkylaminoalkylmethacrylate, N,N-dialkylaminoalkylmethacrylate, hydroxyethylmethacrylate, hydroxyethylacrylate, vinyl acetate, vinyl alcohol, acrylic acid, 2-isopropenyloxazoline and acrylamide alkyl sulfonic acids, wherein the polymer has covalently bound thereto at least one trithiocarbonate or dithiocarbamate residue of a RAFT agent comprising a trithiocarbonate or a dithiocarbamate group.
3. A process according to claim 1 or claim 2 wherein the hydrate inhibitor is in the form of a linear polymer.
4. A process according to claim 1 or claim 2 wherein the hydrate inhibitor is in the form of a star, branched, or hyperbranched polymer comprising covalently bound thereto a plurality of trithiocarbonate or dithiocarbamate residues.
5. A process according to any one of claims 1 to 4 wherein the hydrate inhibitor is of formula I



wherein

R¹ is selected from the group consisting of optionally substituted alkylthio, optionally substituted arylalkylthio, optionally substituted heteroarylalkylthio and the group of formula II:

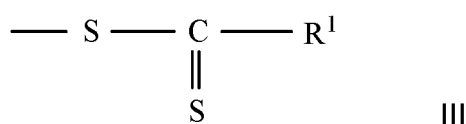


wherein

R³ and R⁴ are independently selected from the group consisting of optionally substituted alkyl, optionally substituted carbocyclic, optionally substituted heterocyclic; optionally substituted aryl, optionally substituted heteroaryl and the group wherein R³ and R⁴ link to form an optionally substituted heterocyclic ring or heteroaryl of 5 or 6 ring members;

n is an integer of at least 1;

R² is selected from the group consisting of hydrogen optionally substituted alkyl, optionally substituted carbocyclic, optionally substituted heterocyclic, optionally substituted aryl, optionally substituted heteroaryl and the group of formula III:

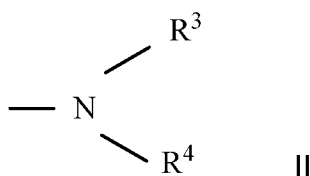


wherein R¹ is as herein before defined; and

Poly is a polymer comprising one or more monomers selected from the group consisting of optionally substituted N-vinyl lactams, N-alkylacrylamides, N,N-dialkylacrylamides, N-alkylmethacrylamides, N,N-dialkylmethacrylamides, vinyl-N-alkylacetamides, N-alkylaminoalkylacrylate, N,N-dialkylaminoalkylacrylate, N-alkylaminoalkylmethacrylate, N,N-dialkylaminoalkylmethacrylate, hydroxyethylmethacrylate, hydroxyethylacrylate, vinyl acetate, 2-isopropenyloxazoline and acrylamide alkyl sulfonic acids.

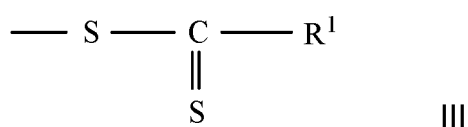
6. A process according to claim 5, wherein in formula I

R^1 is selected from the group consisting of optionally substituted C_1 to C_{22} alkyl thio optionally substituted aryl- $(C_1$ to C_6 alkyl)thio and optionally substituted heteroaryl- $(C_1$ to C_6 alkyl)thio wherein the groups are optionally substituted by a substituent selected from carboxy, C_1 to C_6 alkoxy-carbonyl, halo, sulfonate, phosphate, amino, $(C_1$ to C_6 alkyl)amino, di $(C_1$ to C_6 alkyl)amino and oxo; and wherein R^1 may be the group of formula II



wherein R^3 and R^4 are independently selected from the group consisting of C_1 to C_6 alkyl; cycloaliphatic of 4 to 6 ring members optionally substituted with 1 to 3 C_1 to C_4 alkyl; heterocyclic of 4 to 6 ring members comprising carbon and 1 to 3 heteroatoms selected from nitrogen and oxygen optionally substituted with 1 to 3 groups selected from halo and C_1 to C_4 alkyl; aryl optionally substituted with 1 to 3 C_1 to C_4 alkyl; heteroaryl of 5 or 6 ring members comprising carbon and 1 to 3 heteroatoms selected from nitrogen optionally substituted with 1 to 3 substituents selected from halo and C_1 to C_4 alkyl; and the group wherein R^3 and R^4 link to form a heterocyclic or heteroaromatic ring of 5 or 6 ring members comprising one or more carbon and 1 to 3 nitrogen atoms and optionally substituted with 1 to 3 groups selected from halo and C_1 to C_4 alkyl;

R^2 is selected from the group consisting of C_1 to C_{12} alkyl optionally substituted with from 1 to 3 substituents selected from the group consisting of carboxyl, cyano; cycloaliphatic of 4 to 6 ring members optionally substituted by 1 to 3 C_1 to C_4 alkyl; heterocyclic of 4 to 6 constituent ring members comprising 1 to 3 heteroatoms selected from nitrogen and oxygen; aryl optionally substituted with 1 to 3 C_1 to C_4 alkyl; heteroaryl optionally substituted with 1 to 3 C_1 to C_4 alkyl and the group of formula III:



wherein R^1 is as herein defined; and

Poly is a polymer comprising one or more monomers selected from the group consisting of N-vinyl lactams of 5 to 9 constituent ring atoms optionally substituted with 1 to 3 C_1 to C_6 alkyl; isopropenyl-2-oxazoline; N-(C_1 to C_6 alkyl) acrylamides; N,N-di(C_1 to C_6 alkyl) acrylamides, N-(C_1 to C_6 alkyl)methacrylamide; N,N-di(C_1 to C_6 alkyl)methacrylamides; vinyl-N-(C_1 to C_6 alkyl)alkyl acetamides; N-(C_1 to C_6 alkyl)alkylaminoalkylacrylate; N,N-di(C_1 to C_6 alkyl)aminoalkylacrylate; N-(C_1 to C_6 alkyl)aminoalkylmethacrylate; N,N-di(C_1 to C_6 alkyl)aminoalkylmethacrylate; hydroxyethylmethacrylate; hydroxyethylacrylate; vinyl acetate; and acrylamide (C_1 to C_6 alkyl) sulfonic acids.

7. A process according to any one of claims 1 to 6, wherein in the trithiocarbonate or dithiocarbamate residues, which are present as the group $R^1-C(S)S$ in formula I, is selected from the group consisting of :

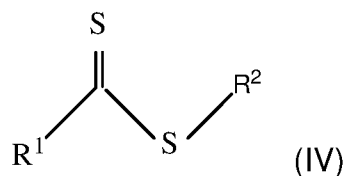
(i) (optionally substituted C_2 to C_{22} alkyl)thiocarbonothioylthio such as including (unsubstituted C_2 to C_{22} alkyl)thiocarbonothioylthio such as (dodecylthio)carbonothioylthio-, (carboxy- C_2 to C_{22} alkyl)thiocarbonothioylthio such as and ((2-carboxyethyl)thio)carbonothioylthio- and (substituted C_2 to C_{22} alkyl) carbonothioylthio- comprising one or more substituents selected from amino ($-NH_2$), C_1 to C_6 alkylamino and di-(C_1 to C_6 alkyl)amino, oxo ($=O$), carboxy and (C_1 to C_6 alkoxy)-carbonyl such as ((1-carboxyethyl)thio)carbonothioylthio- and (3-amino-3-oxopropylthio)carbonothioylthio- ;

(ii) (Optionally substituted-heteroaryl)carbamoylethioylthio, including unsubstituted heteroaryl)carbamoylethioylthio such as methyl(4-pyridyl)carbamoylethioylthio;

(iii) Nitrogen containing heteroarylcarbodithioate (dithiocarbamates) optionally substituted with 1 to 3 substituents such as halo and/or C_1 to C_6 alkyl such as 3,5-dimethyl-1H-pyrazole-carbodithioate and 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate; and

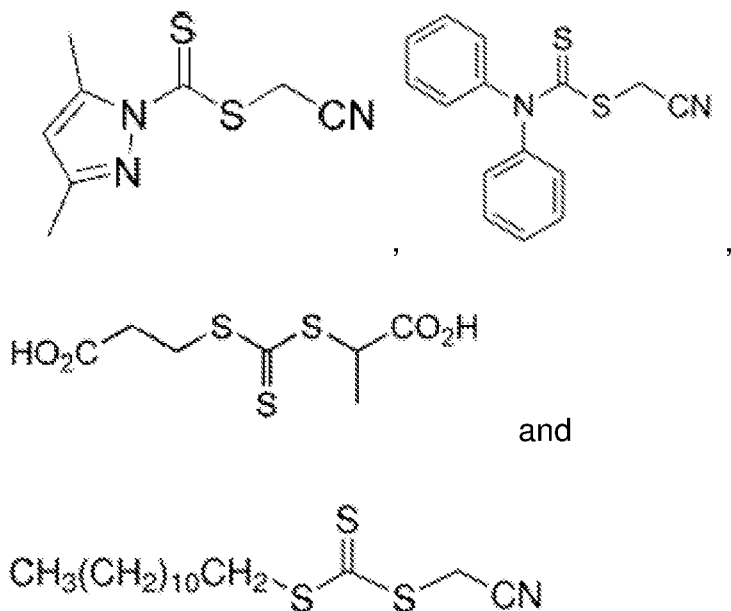
(iv) (optionally substituted aryl)thio carbonothioylthio-, Including (optionally substituted phenyl) thiocarbonothioylthio- such as (benzylthio)carbonothioylthio-.

8. A process according to claim 5 or claim 6 wherein the at least one trithiocarbonate or dithiocarbamate residue, which is present as the group R¹-C(S)S in formula I, is selected from the group consisting of 3,5-dimethylpyrazol-1-yl, diphenylamino, hydroxycarbonylethylthio and laurylthio.
9. A process according to any one of claims 1 to 5 wherein the trithiocarbonate or dithiocarbamate is a residue of a RAFT agent of formula III



wherein R¹ and R² are defined according to any one of claims 3 to 5

10. A process according to any one of claims 1 to 5 wherein the trithiocarbonate or dithiocarbamate is a residue of a RAFT agent of formula selected from the group consisting of:



11. A process according to any one of claim 1 to 10 wherein the polymer is a copolymer of two or more monomers selected from the group consisting of N-vinyl lactams, N-alkylacrylamides, vinyl-N-alkylacetamides, 2-isopropenyloxazoline.

12. A process according to any one of claim 1 to 11 wherein the polymer has a molecular weight of at least 500.
13. A process according to any one of claim 1 to 11 wherein the polymer has a molecular weight of from 500 to 100,000.
14. A process according to any one of claims 1 to 13 wherein the polymer is a linear polymer comprising a terminal covalently bonded trithiocarbonate or dithiocarbamate group.
15. A process according to any one of claims 1 to 10 wherein the polymer is a star, branched, or hyperbranched polymer comprising a multiplicity of polymeric branching arms wherein a multiplicity of the branching arms comprise terminal trithiocarbonate or dithiocarbamate groups.
16. A process according to claim 15 wherein the polymer further comprises monomer residues selected from crosslinking agents and RAFT agent inimers.
17. A process according to any one of claims 1 to 12 wherein the polymer comprises one or more polymer segments selected from the group consisting of polyacryloylpyrrolidine, polydiethylacrylamide, polyisopropylacrylamine, N-methylvinylacetamide, polyisobutylacrylamide, polyisopropylmethacrylamide, vinylcaprolactam and polyethyloxazoline.
18. A process according to any one of claims 1 to 17 wherein the hydrate inhibitor is added to the hydrocarbon fluid in an amount in the range of from 0.01 to 5% by weight based on the weight of water in the hydrocarbon fluid.
19. A process according to any one of claims 1 to 18 wherein the hydrate inhibitor is added to the hydrocarbon fluid with an additional thermodynamic hydrate inhibitor selected from the group consisting of methanol, ethanol, isopropanol, monoethyleneglycol and mixtures thereof.
20. A process according to claim 19 wherein the weight ratio of the hydrate inhibitor to further hydrate inhibitor is in the range of from 0.001 to 2%.

21. A process according to any one of claims 1 to 20 which provides corrosion inhibition wherein the hydrocarbon fluid is in contact with a metal, particularly ferrous metal, and the hydrate inhibitor comprising the RAFT agent is present in an amount sufficient to inhibit corrosion of the metal.

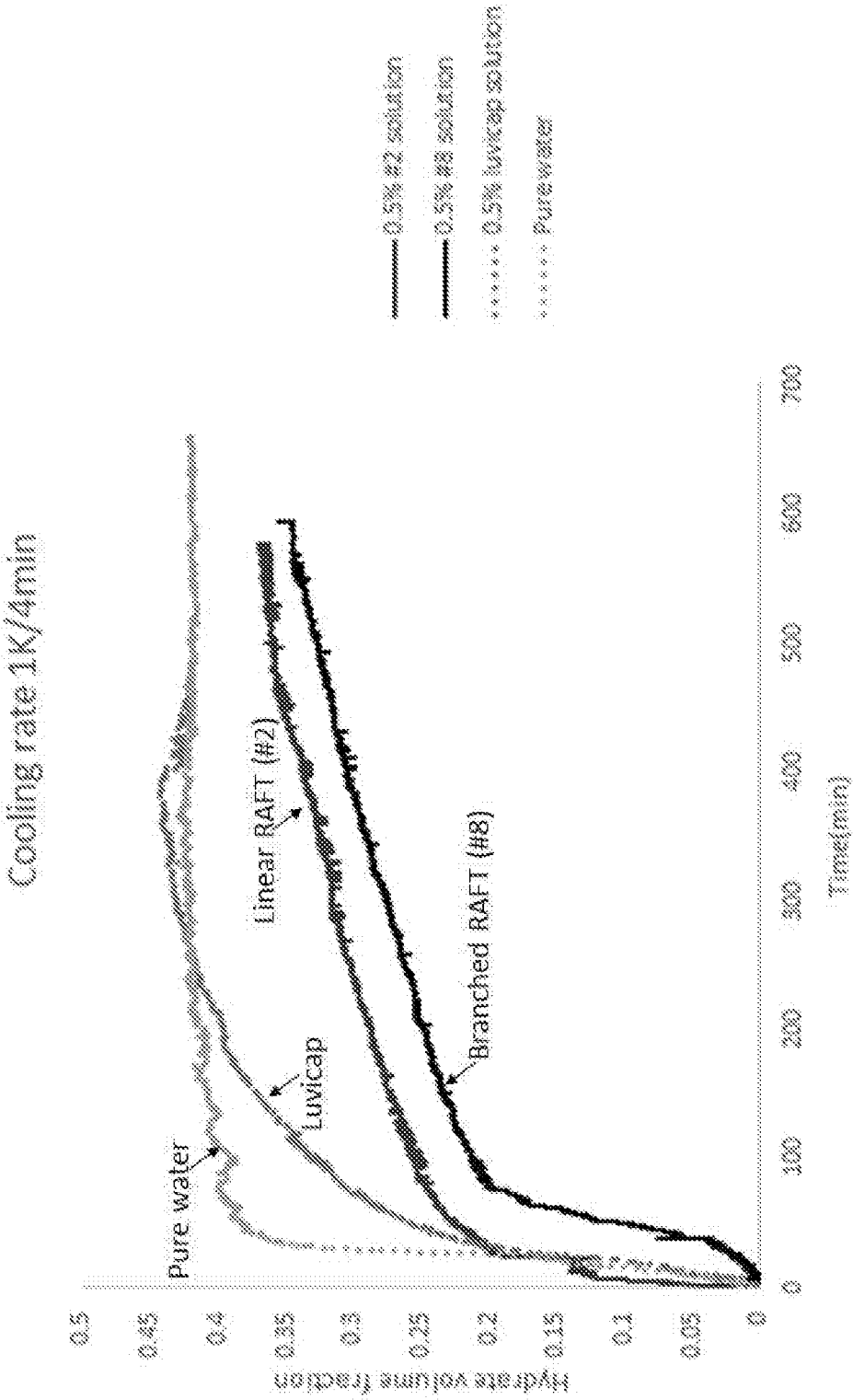


Figure 1

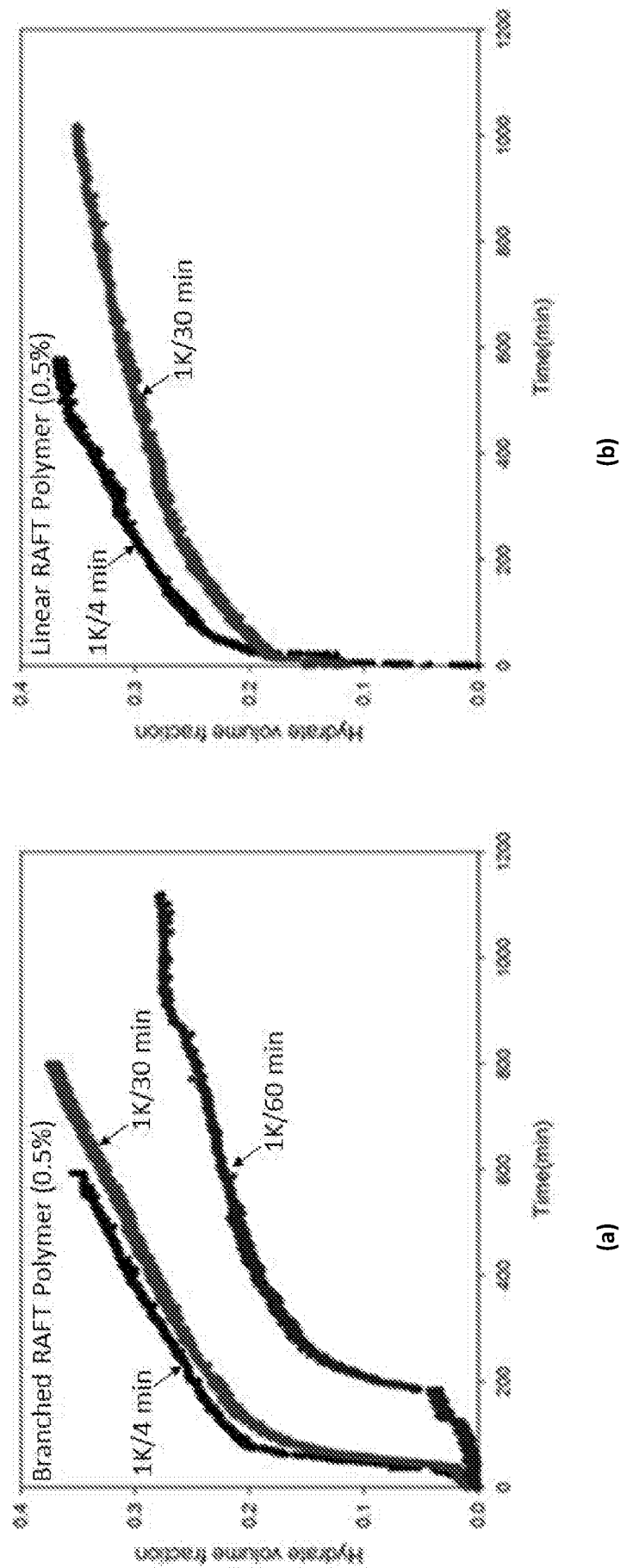
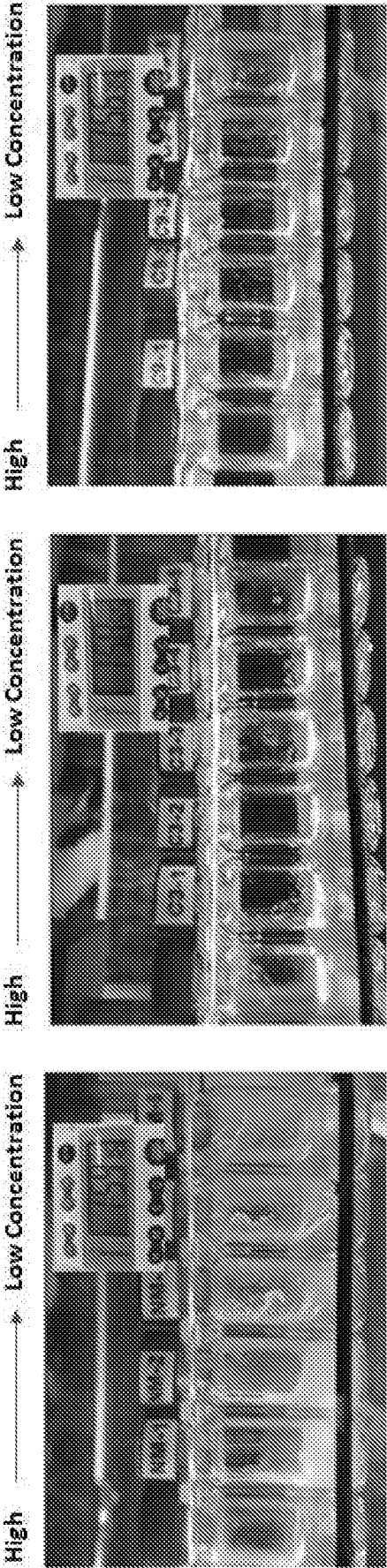


Figure 2



(a)

(b)

(c)

Figure 3

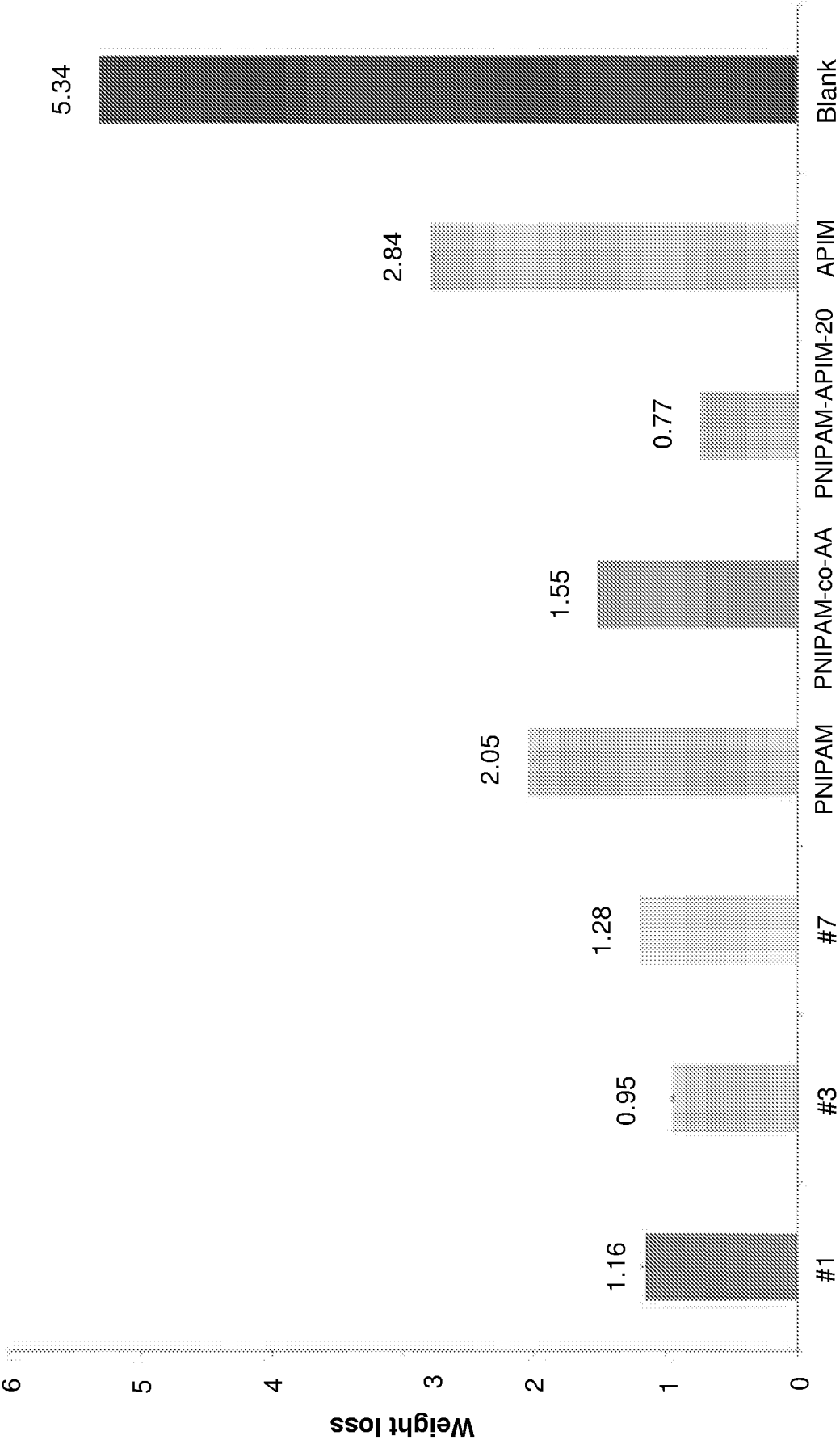


Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2017/050029

A. CLASSIFICATION OF SUBJECT MATTER

C09K 8/52 (2006.01) C10L 3/10 (2006.01) E21B 37/06 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: EPODOC, WPIAP, TXTE public cluster, CAS Registry, CAplus, CNFULL, INFULL, JPFULL, KRFULL, Google Scholar. IPC/CPC marks: C09K8/52, C10L3/10, E21B37/06, C08F2438/03, C08K5/3[8,9]. CAS Registry fields: /rn, /cn, /cns. CAplus fields: /Person, /Company, /Controlled term. Key words: trithiocarbonate, dithiocarbamate, RAFT, gas hydrate, gas clathrate, kinetic inhibitor, end cap, terminus, inimer, DDMAT, macro RAFT. Applicant/Inventor search in CAplus.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 30 March 2017		Date of mailing of the international search report 30 March 2017	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Andrew Davis AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262104067	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2017/050029
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MADY, M. F. <i>et al.</i> , 'The first kinetic hydrate inhibition investigation on fluorinated polymers: Poly(fluoroalkylacrylamide)s', Chemical Engineering Science, 2014, vol. 119, pages 230-235 see § 2.4, 2.5, 2.5.1, 3.1, Tables 2 and 3, Figure 3	1-8, 10-21
A	REE, L. H. S. <i>et al.</i> , 'First investigation of modified poly(2-vinyl-4,4-dimethylazlactone)s as kinetic hydrate inhibitors', Chemical Engineering Science, 2016, vol. 152, pages 248-254. Available online 15 June 2016. see § 2.1, 2.5, Table 2	21
A	ZHU, Y. <i>et al.</i> 'Thermoresponsive (Co)polymers through Postpolymerization Modification of Poly(2-vinyl-4,4-dimethylazlactone)', Macromolecules, 2013, vol. 46, pages 6475-6484 see Scheme 1	21
A	REYES, F. T. <i>et al.</i> , 'Non-Amide Kinetic Hydrate Inhibitors: Performance of a Series of Polymers of Isopropenyloxazoline on Structure II Gas Hydrates', Energy Fuels, 2013, vol. 27, iss. 6, pages 3154-3160 see Experimental Section	1-8, 10-21
A	US 2015/0322746 A1 (BAKER HUGHES INCORPORATED) 12 November 2015 see [0049]	1-8, 10-21

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☒ Claims Nos.: 9
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
See Supplemental Box
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

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

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

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

Remark on Protest

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

Supplemental Box**Continuation of Box II**

Claim 9 is not clear when it is appended to claim 3 or claim 4 because neither claim 3 nor claim 4 includes an antecedent for the chemical structure variables R^1 and R^2 .

Claim 9 is also not clear because the included chemical structure is denoted with (IV) but the claim specifies a RAFT agent of formula III.

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2017/050029	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2015/0322746 A1 12 November 2015 US 2015322746 A1 12 Nov 2015 US 2013098623 A1 25 Apr 2013 US 9145465 B2 29 Sep 2015 US 2015322330 A1 12 Nov 2015 WO 2013059058 A1 25 Apr 2013			
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			