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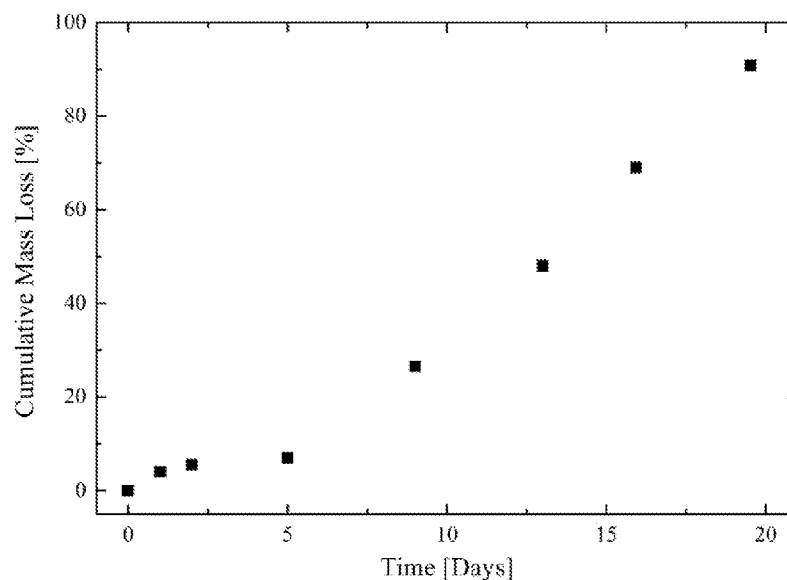


Fig. 1

(57) **Abstract:** The present invention relates to a fluid for controlling the permeability of a subterranean formation comprising an aqueous solution of at least one thermo-responsive polymer with block structure A-B-A', wherein: - A and A', the same as or different from one another, each represent a thermo-responsive oligomer group; - B is an oligomer group comprising n repeat units, the same as or different from one another, wherein: (i) at least one of the repeat units has a solubility of the corresponding monomer, in water at 20°C, equal to or greater than 120 g/l, (ii) n is a whole number within the range 30–1000. The present invention also relates to a method for controlling the permeability of a subterranean formation in which the aforesaid fluid is used.



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FLUID FOR CONTROLLING THE PERMEABILITY OF A  
SUBTERRANEAN FORMATION, AND USE THEREOF

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The present invention relates to a fluid for  
5 controlling the permeability of a subterranean  
formation, and use thereof.

In particular, the present invention relates to  
an aqueous fluid comprising a thermo-responsive  
polymer. Once injected into a subterranean formation,  
10 through an effect of the geothermal heat of the  
subterranean formation the fluid comprising the thermo-  
responsive polymer undergoes *in situ* a phase  
transition, becoming a gel of viscosity such as to  
locally modify the permeability of the formation to  
15 fluids. The present invention may be used  
advantageously in the oil industry, particularly in  
improved oil recovery operations (*IOR*) or enhanced oil  
recovery (*EOR*), to modify the permeability of a  
subterranean formation to displacement fluids, for  
20 example water or gas, that are used in the production  
of oils and hydrocarbon gases.

As is known, in processes of improved recovery of  
hydrocarbon fluids (oil and gas) from a subterranean  
formation, the hydrocarbon fluid initially present in  
25 the pores of the reservoir rock is brought to the  
surface by means of displacement by an immiscible fluid  
(also called a displacement fluid) that takes its  
place. To this end, wells are drilled within the oil  
field for the injection of the displacement fluid,  
30 generally water, that are arranged in such a way as to  
create in the subsoil the most uniform possible  
advancing front to displace the hydrocarbon fluid

towards the production well.

The technique of displacement by injections of water (water flooding) has long been the simplest and most economical method used to sustain production in an oil field and increase the overall recovery factor of the hydrocarbon fluid.

The quantity of hydrocarbon fluid that can be displaced towards the production wells by water injection depends, among other factors, on the degree of heterogeneity of the reservoir rock and the properties of the hydrocarbon fluid (above all the viscosity). In particular, fractures, channels or levels of high permeability (the latter also called thief zones) constitute preferential flow pathways. The natural tendency of fluids to flow through the most permeable portions of the reservoir rock means that, with the passage of time, the water injected into the subsoil continues to flow away along these fractures, channels or levels of high permeability, reaching the producer wells directly without or only minimally infiltrating the zones of the reservoir rock in which the hydrocarbon fluid is still present, thus producing no displacement effect.

In these situations, the production of water can increase until it dominates that of the hydrocarbon fluid, thus rendering the production of the latter barely or not at all advantageous from an economic standpoint.

Furthermore, the co-production of water implicates the adoption of specific treatment plants so as to be able to safely dispose of the water produced, or of systems for its re-injection into the subsoil.

These measures involve high consumption of energy and materials, and increase the overall cost of hydrocarbon extraction.

In the state of the art, the problem of  
5 undesirable production of water and of the inadequate efficiency of the recovery of the hydrocarbons by displacement with water is dealt with by injecting into the subsoil liquid compositions containing chemical compounds that are capable of modifying the  
10 permeability characteristics of the subterranean formation. The compounds most in use for this purpose are generally in the form of polymers, gels or foams. These compounds are here also called "blocking agents". The blocking agents block the pores of the formation  
15 zones with the highest permeability, diverting the flow of the displacement fluid towards the zones that are still rich in hydrocarbon fluid, thus increasing the production capacity of the well.

US 2009/0264321 describes a method for modifying  
20 the permeability of a subterranean formation based on injecting into the subsoil a composition comprising encapsulated expandable polymeric microspheres. Once injected into the subsoil, following an activation event (for example a variation in temperature or pH),  
25 the polymeric microspheres escape from the capsules in which they are enclosed and disperse into the formation, where they swell up by absorbing the displacement fluid with which they are in contact. Swelling of the microspheres within the pores of the  
30 formation prevents the flow of the displacement fluid, which is thus diverted towards other zones of the formation. However, the properties of the aforesaid

encapsulated polymeric microspheres cannot be easily modifiable and therefore optimizable as a function of the specific conditions of the formation. Furthermore, the aforesaid microspheres alter the permeability of the formation irreversibly, so that any errors of injecting the blocking agent are not remediable.

Also known in the state of the art are blocking agents composed of thermo-responsive polymers. Thermo-responsive polymers are polymers that show a drastic and discontinuous change in chemicophysical properties with temperature. The term thermo-responsive is commonly used with reference to the solubility of the polymer in a given solvent. A polymer having a solubility with thermo-responsive characteristics presents a region of immiscibility in the temperature-composition diagram, characterised by at least one phase transition that is reversible in response to a variation in temperature. In general, two different types of phase transition are seen in a solution of a thermo-responsive polymer, each of which is characterised by a specific critical temperature:

- in a first type of transition, the polymers that are soluble in a given solvent become insoluble in the same solvent as its temperature rises; the temperature at which this phase transition occurs is called the lower critical solution temperature(LCST);

- in a second type of transition, the polymers that are insoluble in a given solvent become soluble as the temperature rises; the temperature at which this phase transition occurs is called the upper critical solution temperature(UCST);

Further information on thermo-responsive polymers

and their solubility properties are given, for example, in *Chem. Soc. Rev.*, 2013, 42, 7214, and *Polymers* 2011, 3, 1215-1242.

US 2012/0264655 describes the use of blocking  
5 agents based on thermo-responsive polymers and hydrogels in combination with various treatment fluids for oil extraction operations. The treatment fluids (e.g. drilling fluids, fracturing fluids, etc.) contain a gelling agent formed of a thermo-responsive graft  
10 polymer comprising a water-soluble main chain (e.g. Polyacrylic acid) onto which are grafted a plurality of side chains having thermo-responsive functional groups. The polymeric side chains confer on the polymer a characteristic LCST value, determining the course of  
15 its solubility as a function of temperature.

WO 1995026455 describes a method for controlling the permeability in a subterranean formation, which comprises injecting an aqueous solution of at least one thermo-responsive polymer into a well up to a zone of  
20 the formation having a temperature higher than the temperature of the solution in the well. The thermo-responsive polymer has an LCST temperature intermediate between the temperature of the solution in the well and the temperature of the zone. Through an effect of the  
25 temperature increase caused by the heat transmitted from the zone to the solution, the thermo-responsive polymer becomes insoluble, thus altering the permeability of the formation. According to WO1995026455, the LCST temperature of the thermo-  
30 responsive polymer may be regulated by advantageous selection of the type of monomers and/or co-monomers, their weight ratios, or by adding further compounds

capable of modifying the LCST temperature. The thermo-responsive polymers are prepared by bulk polymerisation or suspension polymerisation. The effects of permeability modification may be rendered reversible,  
5 for example by injecting refrigerant liquids into the formation which, by lowering the temperature of the formation to values below the LCST temperature, cause the inverse transition phase of solubilisation of the polymer.

10 The methods known in the prior art for controlling the permeability of a subterranean formation, that are based on the use of thermo-responsive polymers, have the disadvantage of not allowing adequate controlling of the permeability-  
15 modifying effects induced by the transition phase of the polymer at temperatures above the LCST. In particular, the modifications are often irreversible or necessitate further interventions, such as the injection of refrigerant fluids as described in WO  
20 1995026455.

In consideration of the aforesaid state of the art, the Applicant therefore set the primary objective of providing a fluid for controlling the permeability of a subterranean formation, which at least partially  
25 overcomes the drawbacks of the prior art.

Within the scope of this primary objective, one object of the present invention is to provide an aqueous fluid for controlling the permeability of a subterranean formation comprising a thermo-responsive  
30 polymer, wherein the LCST temperature at which occurs the transition phase from soluble polymer to viscous gel is easily regulable, and therefore adaptable to the



specific conditions of the subterranean formation the permeability of which is to be modified.

A second object of the present invention is to provide a fluid for controlling the permeability of a subterranean formation that is easily injectable into the formation and whose effect of blocking of the pores due to formation of the gel phase is at least partially reversible, preferably without this reversibility being induced by external actions, such as for example the injection of refrigerant fluids.

A third object of the present invention is to provide a fluid for controlling the permeability of a subterranean formation that can be prepared by a simple method at moderate cost.

The Applicant has now found that these and other objects, which will be better illustrated in the description that follows, can be achieved by means of an aqueous fluid comprising a thermo-responsive polymer having a block structure A-B-A', wherein the outer blocks A and A', the same as or different from one another, are oligomer groups with thermo-responsive characteristics, and therefore having a characteristic and defined LCST, whereas the central block B is a hydrophilic oligomer group of relatively high length.

It has in fact been observed that by synthesising a polymer with the aforementioned A-B-A' block structure, in which the thermo-responsive blocks A and A' are distanced one from the other by a hydrophilic oligomer segment of sufficient length, it is possible to prepare aqueous solutions of said polymers which change state, becoming viscous gels, at a well-defined temperature (LCST). The LCST value of the polymer A-B-

A', and therefore the temperature at which the phase transition occurs, may be easily regulated by modifying the composition of the thermo-responsive blocks A and/or A', for example by incorporating hydrophilic and hydrophobic monomers and/or by varying the length of the oligomers A and/or A'.

The aforementioned thermo-responsive A-B-A' polymers are soluble at low temperatures, that is, at a temperature below the LCST, whereas they form a gel phase of relatively high viscosity at high temperatures, that is, at a temperature above the LCST. As a result of this, they can be easily injected into the subterranean formation in the form of aqueous solutions of low viscosity at temperatures below the LCST, whereas they act as blocking agents following phase transition to viscous gel, in the zones in which the temperature of the formation exceeds the LCST.

Without making reference to any particular theory, it is considered that, at temperatures above the LCST, the blocks A of the polymer A-B-A' collapse, forming micellar structures which, being linked to one another via a "bridge" composed of the oligomer block B, give rise to a reticulated structure of relatively high viscosity (physical gel).

Advantageously, the blocks A and A' of the A-B-A' polymers can also include portions that are degradable over time in the temperature conditions of the subterranean formation, for example by effect of a hydrolysis reaction. Degradation of the aforesaid degradable portions leads to a structural modification of the original blocks A and A', with consequent variation of the thermo-responsive behaviour of the

polymer. In particular, following the degradation an increase in the LCST of the polymer occurs; when the LCST of the degraded polymer exceeds the temperature of the subterranean formation, the phase transition of the viscous gel into fluid polymeric solution occurs.

Due to the A-B-A' block structure, the polymers according to the present invention may be prepared so as to have the LCST more suitable for the specific geothermal profile of the subterranean formation, so increasing the efficacy of the displacement fluids (lower production of water) and consequently the productivity of the fluid hydrocarbons (oil or gas).

In accordance with a first aspect, the present invention therefore relates to a fluid for controlling the permeability of a subterranean formation comprising an aqueous solution of at least one thermo-responsive polymer with an A-B-A' block structure, wherein:

- A and A', the same as or different from one another, each represent a thermo-responsive oligomer group;

- B is an oligomer group comprising n repeat units, the same as or different from one another, wherein:

- (i) at least one of the repeat units has a solubility of the corresponding monomer, in water at 20°C, equal to or greater than 120 g/L,

- (ii) n is a whole number within the range 30 - 1000.

In accordance with a second aspect, the present invention relates to a method for controlling the permeability of a subterranean formation comprising:

- a. providing a fluid comprising an aqueous

solution of at least one thermo-responsive polymer with block structure A-B-A', wherein:

- A and A', the same as or different from one another, each represent a thermo-responsive oligomer group;

- B is an oligomer group comprising n repeat units, the same as or different from one another, wherein:

(i) at least one of the repeat units has a solubility of the corresponding monomer, in water at 20°C, equal to or greater than 120 g/l,

(ii) n is a whole number within the range 30 - 1000;

b. positioning said treatment fluid in a subterranean formation.

In accordance with a third aspect, the present invention relates to the use of the aforesaid fluid to modify the permeability of a subterranean formation.

In accordance with a further aspect, the present invention relates to the use of the aforesaid fluid to limit the infiltration of water into a well for extracting an oil or hydrocarbon gas from a subterranean formation.

For the purposes of the present description and of the attached claims, the lower critical solubility temperature (LCST) of a polymer is to be understood as determined by the turbidimetric method described in the examples.

For the purposes of the present description and of the attached claims, the "degree of polymerisation" of a polymer, also denoted as DP (degree of polymerisation), is the mean number of repeat units

present in a polymer, determined by  $^1\text{H}$  NMR spectroscopy with methods known to the person skilled in the art, on a solution of the polymer in  $\text{CDCl}_3$  as the solvent (99.8% D atoms) at a polymer concentration of 15 mg/mL.

5 For the purposes of the present description and of the attached claims, the terms "oligomer" and "polymer" include the terms homopolymer and co-polymer, unless explicitly indicated otherwise or in any event unless otherwise deducible from the text. The oligomers and  
10 the polymers, that is, can be formed from the same repeat unit or from two or more repeat units different from each other. As used herein, the term polymer includes oligomers and polymers.

For the purposes of the present invention, the  
15 mean molecular weight in number  $M_n$  of an oligomer or polymer is understood to be determined by gel permeation chromatography (GPC), using polystyrene as the standard.

For the purposes of the present invention,  
20 "repeat unit" is understood to mean the constitutive unit of a polymer or an oligomer; said constitutive unit may correspond to one monomer or to two or more monomers, from which it derives following polymerisation; said monomer or monomers from which the  
25 repeat unit derives are here also denoted as "corresponding monomer" of the repeat unit.

Further information about the structure of oligomers and polymers can be found, for example, in Alfred Rudin, Phillip Choi, "The Elements of Polymer  
30 Science and Engineering", 3rd edition, Elsevier, 2013.

For the purposes of the present description and of the attached claims, the verb "comprise" and the terms

derived therefrom also include the verb "consist" and "consist essentially in", and the terms derived therefrom.

The limits and the numerical intervals expressed  
5 in the present description and in the attached claims also include the numerical value or numerical values mentioned. Furthermore, all the values and sub-intervals of a limit or numerical interval must be understood as specifically included as if they were  
10 explicitly mentioned.

For a better understanding of the features of the present invention, in the description reference will be made to the following drawings:

- Fig. 1 (degradation test): graph of the  
15 percentage loss of mass of Polymer 1 (with respect to the initial weight of the sample) as a function of the observation time;

- Fig. 2 (degradation test): graph of the pH  
20 value of the liquid phase as a function of the observation time.

The block A or A' of the polymer A-B-A' may be formed of an oligomer comprising a single type of repeat units or two or more repeat units different from each other. The blocks A and A' may be the same as or  
25 different from one another.

The oligomer group A and/or A' preferably has a lower critical solubility temperature (LCST) within the range 30°C - 100°C, more preferably within the range 40°C - 80°C.

30 To have thermo-responsive characteristics, the oligomer that forms the block A and/or A' preferably comprises at least one hydrophilic portion and at least

one hydrophobic portion.

The hydrophilic portion is preferably formed of polyoxyethylene chains, polylactide chains, C<sub>2</sub>-C<sub>10</sub> alkyl chains, linear or branched, containing amide groups.

5        The hydrophobic portion is preferably obtained from monomers comprising at least one ester or amide group, such as, for example, the compounds (meth)acrylate and (meth)acrylamide.

In a preferred embodiment, the thermo-responsive  
10       block A and/or A' is a graft polymer comprising a poly(meth)acrylic or poly(meth)acrylamide linear main chain and a plurality of side chains, connected to said main chain, selected from: poly(ethylene glycol) -[-CH<sub>2</sub>-CH<sub>2</sub>-O]<sub>m</sub>-H, poly(ethylene glycol) methyl ether -[-CH<sub>2</sub>-CH<sub>2</sub>-O]<sub>m</sub>-CH<sub>3</sub>, HEMA-polylactide --CO-O-CH<sub>2</sub>-CH<sub>2</sub>-O-[-CO-(CH<sub>3</sub>)CH-O]<sub>m</sub>-H, alkylamide, linear or branched, and combinations thereof, where m is an integer number  
15       within the range 2 - 10.

In an embodiment, the A block and/or A' block is  
20       an oligomer containing a plurality of polymer side chains.

In an embodiment, the B block is a linear oligomer that contains no polymer side chains.

In a preferred embodiment, the thermo-responsive  
25       blocks A and/or A' are preferably oligomer groups formed of one or more repeat units deriving from monomers selected from: (meth)acrylic acid, oligo(ethylene glycol) methyl ether methacrylate (OEGMA), [2-(methacryloyloxy)ethyl]- trimethylammonium  
30       chloride (MADQUAT), HEMA-polylactide, potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, polymerisable esters

comprising polyoxyethylene chains  $-[\text{CH}_2\text{-CH}_2\text{-O}]_x\text{-H}$  where  $x$  is an integer number within the range 10 - 1000, N-isopropylacrylamide, N,N-dimethylaminoethyl methacrylate, dimethylacrylamide.

5            Preferably, the OEGMA compound used to form the block A and/or A' has a mean molecular weight  $M_n$  within the range 100 - 10,000 Dalton, more preferably within the range 100 - 5,000 Dalton.

             In a preferred embodiment, the thermo-responsive  
10    block A and/or A' is preferably a co-polymer of two or more OEGMAs having a different molecular weight from one another, for example OEGMAs that differ from one another in the length of the side chains.

             In a preferred embodiment, the thermo-responsive  
15    block A and/or A' is preferably a co-polymer comprising OEGMA as a first co-polymer and at least one second hydrophobic co-monomer selected from:  $\text{C}_1\text{-C}_4$  alkyl-(meth)acrylate (e.g. MMA or BA), (dimethylamino)ethyl methacrylate (DMAEMA) and combinations thereof.

20            In one embodiment of the present invention, the hydrophobic co-monomer selected is a vinyl oligoester that is biodegradable using hydrolysis reactions, such as for example HEMA-poly lactide.

             By appropriately selecting the type of hydrophilic  
25    and hydrophobic units, their molecular weight and the relative molar ratio, it is possible to regulate the LCST value of the A or A' unit and therefore also the behaviour of the final polymer A-B-A' in response to variations of temperature.

30            Preferably the degree of polymerisation DP of the polymer that forms the blocks A and A', that is, the total number of repeat units present in the blocks A



and A', is within the range 2 - 1000, preferably 3 - 500, more preferably 5 - 450, even more preferably 6 - 400.

The block B of the polymer A-B-A' is an oligomer  
5 formed of a single type of repeat units or (homopolymer) or of two or more different types of repeat units (copolymer).

Preferably, the oligomer group that forms the block B comprises one or more repeat units  
10 corresponding to monomers selected from: (meth)acrylic acid, polymerisable esters comprising polyoxyethylene chains  $[-CH_2-CH_2-O]_r-H$  where r is an integer number within the range 10 - 500, more preferably 20 - 300, oligo(ethylene glycol)methyl ether methacrylate  
15 (OEGMA), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, (meth)acrylamide 2-hydroxypropyl methacrylamide, glycerol monomethacrylate, 2-hydroxyethyl methacrylate,  
20 methacryloyloxyethyl phosphorylcholine, carboxybetaine, sulfobetaine and combinations thereof.

In an alternative embodiment, the oligomer group that forms the block B is a poly(ethylene glycol) chain (PEG,  $HO-[CH_2CH_2-O]_n-H$ ), where n is a whole number  
25 comprised between 30 and 300, preferably functionalised at both ends with the CTA of RAFT polymerisation to obtain a macromolecule of the type CTA-PEG-CTA which enables the symmetrical structure A-B-A to be obtained in a single polymerisation stage.

30 Preferably the overall degree of polymerisation DP of the block B, that is, the total number of repeat units, the same as or different from one another,

present in the block B, is within the range 10 - 1000, preferably 20 - 500, more preferably 50 - 500.

In one embodiment, the block B possesses no thermal response characteristic.

5 In another embodiment, the block B does possess thermal response characteristics, but these do not substantially alter the thermal response properties of the polymer A-B-A'. For example, the block B may be a thermo-responsive polymer having an LCST temperature  
10 higher than the LCST temperature of the blocks A and A'. Therefore this polymer has no influence on the thermal response behaviour of the polymer A-B-A', in that the phase transition to viscous gel occurs at the LCST of the blocks A and A', which is lower than that  
15 of the block B.

In an embodiment, in the block copolymer A-B-A':

- the B block comprises poly(ethylene glycol) (PEG) in the main chain having a mean molecular weight  $M_n$  within the range 500 - 10,000 Dalton, more  
20 preferably within the range 1,000 - 5,000 Dalton;

- the A block and/or A' block are oligomer groups comprising, as corresponding monomer, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), preferably having a mean molecular weight  $M_n$  within the range 100  
25 - 1,000.

In another embodiment, in the block copolymer A-B-A':

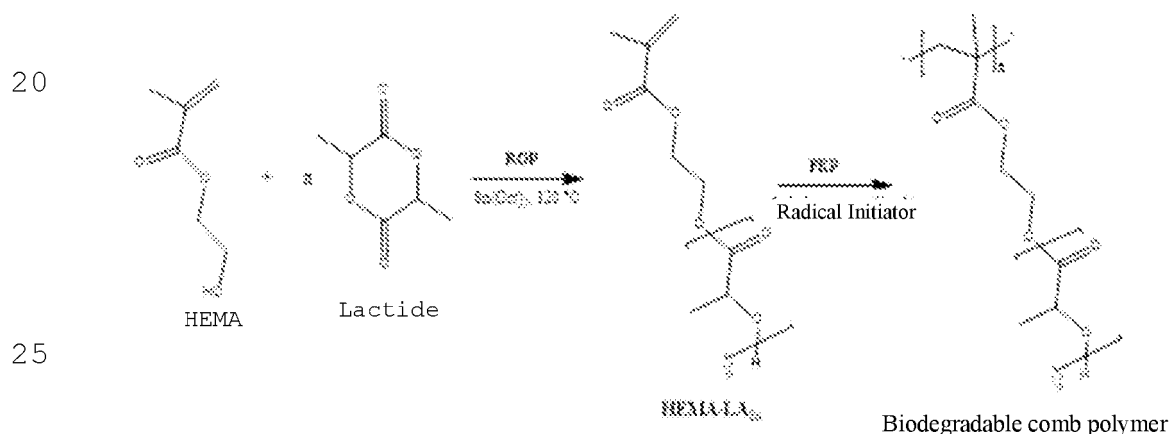
- the B block is an oligomer group comprising, as corresponding monomer, [2-(methacryloyloxy)ethyl]-  
30 trimethylammonium chloride (MADQUAT),

- the A block and/or A' block are oligomer groups comprising, as corresponding monomer, OEGMA having a

mean molecular weight  $M_n$  within the range 100 – 1,000.

In a further preferred embodiment, the oligomer that forms the block A and/or A' comprises one or more degradable repeat units, that is, containing weak bonds  
 5 capable of progressively breaking over time in the conditions of the region of the subterranean formation in which the polymer A-B-A' is present in the form of a gel. Examples of these degradable units are the monomers used in the state of the art for the synthesis  
 10 of biodegradable polymers.

For example, in a preferred embodiment, one biodegradable unit utilisable for the purposes of the present invention is the macromonomer HEMA-poly(lactide), obtainable for example by ring opening  
 15 polymerisation (ROP) of the lactide cyclic ester with hydroxyethyl methacrylate (HEMA). This polymerisation reaction is illustrated schematically in the figure below:



with n preferably comprised between 1 and 10 and x preferably comprised between 10 and 500.

30 The polymerisation of the HEMA-lactide macromonomer in the block A and/or A' leads to the introduction into these blocks of side chains composed

of oligoesters, that are degradable by effect of hydrolysis of the ester bonds. The time necessary for the degradation is determined principally by the length of the chain of oligoesters and can be regulated by appropriate selection of the HEMA/lactide ratio during the synthesis of the macromonomer.

Preferably, the HEMA/lactide molar ratio is within the range 1 - 10.

When the polymer A-B-A' is present in the subterranean formation in the form of a gel, following degradation of the oligoester chains, a progressive increase in the hydrophilic properties of the polymer A-B-A' and, consequently, of its LCST is observed. When the LCST of the polymer exceeds the temperature of the formation in which the gel is found, the latter undergoes a change in state, transitioning from gel to soluble polymer and forming a fluid aqueous phase, which can then once again move through the formation.

Moreover, it will be noted that, in the case of the HEMA-lactide, the product of degradation of the oligoester chains is composed principally of molecules of lactic acid, a biocompatible substance.

In a preferred embodiment, block B comprises at least one cation functionality. This cation functionality may be introduced by preparing the polymer B from monomers comprising cation functionalities. The following are examples of these monomers: [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2-aminoethyl methacrylate hydrochloride.

When block B comprises cation functionalities, the gel that is formed from the soluble polymer A-B-A'

is capable of interacting more effectively with the surface of the pores of the subterranean formation, establishing electrostatic interactions with the carbonate rocks of the formation, which render the blocking action of the gel more effective.

The triblock A-B-A' polymers according to the present invention may be prepared with the polymerisation techniques known in the state of the art, such as free-radical polymerization (FRP) and controlled radical polymerization (CRP). CRP techniques comprise, for example: atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) and reversible addition-fragmentation transfer polymerization (RAFT).

In particular, for the preparation of thermo-responsive block polymers according to the present invention, CRP techniques of controlled polymerisation are preferred, which yield polymer chains of homogeneous length and therefore having a similar thermal response behaviour. The homogeneity of the length of the polymer chains guarantees the obtaining of A-B-A' polymers having a well-defined and predeterminable LCST. Among the CRP techniques, the one especially preferred is the RAFT polymerisation technique. As is known, RAFT polymerisation is a process of degenerative transfer polymerisation, in which a chain-transfer agent is added to the starting monomers with the aim of transferring, during polymerisation, the radical function from one polymer chain to another extremely rapidly, thus enabling uniform growth of the polymer chains. Transfer of the radical function occurs by interaction between the

terminal portion of the chain-transfer agent (CTA) and the active radical chain, which brings the latter to a dormant state while rendering the chain previously bound to the CTA agent active again.

5           On account of the above-mentioned mechanism, RAFT polymerisation is especially suitable for the preparation of block copolymers and represents the ideal solution in the production of thermo-responsive materials having well-defined and predeterminable  
10 LCSTs.

          With RAFT polymerisation it is also possible to prepare polymers having polymer chains of well-defined length, as well as being mutually homogeneous. The length of a polymer chain is here expressed by the marker "DP",  
15 previously defined.

          In RAFT polymerisation, the DP of the polymer can be regulated simply, selecting the ratio of the initial monomer concentration to that of the CTA in the polymerisation mixture.

20           In general, the A-B-A' polymers according to the present invention may be prepared by RAFT polymerisation in successive steps, as described by way of example hereinafter.

          In a first step, the synthesis of block A is  
25 performed, by polymerising for example OEGMA300 (that is, oligo(ethylene glycol) methyl ether methacrylate,  $M_n = 300$ ) to obtain poly[OEGMA300<sub>500</sub>], where the marker DP = 500 indicates the degree of polymerisation, that is, the average number of OEGMA300 repeat units present  
30 in the block A oligomer. To this end, the OEGMA300 monomer is set to react with a CTA, for example 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid, and a

polymerisation initiator, for example 4,4'-azobis(cyanovaleric) acid (ACVA), in a polar solvent (e.g. ethanol), at a temperature of approximately 50-80°C, at atmospheric pressure, for 24-48 hours. The  
5 relative quantities of reagents may be calculated in such a way as to determine the desired DP.

Following evaporation of the solvent and recovery of the unreacted monomer (for example, by extraction with diethyl ether), the oligomer that forms block A  
10 can be recovered in the form of a viscous liquid.

The oligomer that forms block A has polymer chains terminating on both sides by the specific functionalities of the CTA used in the first step. This therefore represents a macro-CTA that may be set to  
15 react with the monomer of segment B, in a second step of RAFT polymerisation. In this second step, the monomer of block B acts essentially as a block A chain extender. Block B, for example, may be formed by using OEGMA2000 (that is, oligo(ethylene glycol) methyl ether  
20 methacrylate,  $M_n = 2,000$ ) as the monomer, to obtain poly[OEGMA2000<sub>500</sub>], with DP = 500. The RAFT polymerisation of the second step may be performed under conditions similar to those of the first step. At the end of the second step, a diblock polymer A-B of  
25 the type poly[OEGMA300<sub>500</sub> - OEGMA2000<sub>500</sub>] is therefore obtained. This polymer too, because it contains chains terminated on both sides by the CTA functionalities, may be used as a macro-CTA in a third step of RAFT polymerisation to add the block A' to the diblock  
30 polymer A-B and obtain the triblock polymer A-B-A'. To this end, the polymer poly[OEGMA300<sub>500</sub> - OEGMA2000<sub>500</sub>] is set to react, for example, with the same monomer used

to form the segment A in the first step in the presence of the initiator ACVA in conditions analogous to those of the first step, thus obtaining the A-B-A symmetrical polymer poly[OEGMA300<sub>500</sub> - OEGMA2000<sub>500</sub> - OEGMA300<sub>500</sub>].  
5 However, if a monomer A' different from A is used, an asymmetrical polymer A-B-A' is obtained.

The symmetrical polymers A-B-A, that is where A is equal to A', may be prepared by RAFT polymerisation also via a two-step process. In the first step, the  
10 repeat unit (or repeat units) that forms the oligomer B (which may have been synthesised via RAFT or another polymerisation technique) is reacted with a CTA compound, the latter being present in the reaction mixture in a quantity such as to obtain the oligomer B  
15 terminating on both sides by the specific functionalities of the CTA used (macro-CTA), for example in a molar ratio with respect to the oligomer B greater than or equal to 2, preferably comprised between 2.1 and 4. In the second step, the repeat unit  
20 (or repeat units) that is to form the oligomer A is made to polymerise in the presence of the macro-CTA produced in the first step to obtain the final symmetrical polymer A-B-A.

According to an alternative synthesis route, the  
25 symmetrical polymers A-B-A may be prepared by synthesising, in a first step, the oligomer blocks A by RAFT polymerisation in the presence of a bifunctional CTA (to obtain A-CTA-A). In a second step, the oligomer A-CTA-A is reacted with the repeat unit that forms the  
30 block B, so as to extend the chain of the oligomer A-CTA-A starting from the central unit until the polymer A-B-A is obtained.



For the purposes of the present invention, the thermo-responsive A-B-A polymers are introduced into the subterranean formation, the permeability of which to fluids in the form of aqueous fluid is to be modified. Preferably, the treatment fluid comprises the A-B-A' polymers in the form of aqueous solution. The concentration of the polymer in the aqueous solution is preferably within the range 0.5-40% by weight, more preferably within the range from 1 to 20% by weight, with respect to the weight of the aqueous solution.

The aqueous fluid comprising the A-B-A' polymer may be used for controlling the permeability of a subterranean formation during oil extraction activity.

For the purposes of the present invention, subterranean formation is intended to mean a zone beneath the land surface, including the surfaces of the seabed. For example, a subterranean formation may be any zone of a formation containing a rock storing a hydrocarbon fluid (oil or gas) and any zone of a well in fluid communication with said formation.

The method for controlling the permeability to fluids of a subterranean formation according to the present invention may be applied both before starting extraction of the hydrocarbon fluid from the subterranean formation and when the extraction well is already in production.

The method according to the present invention may be advantageously applied to the extraction wells termed "mature", that is, to wells that have now reached the limit of their production capacity and are characterised by the extraction of significant quantities of water in association with the oil or

hydrocarbon gas.

The positioning of the fluid for controlling permeability in a subterranean formation may be carried out with the equipment and according to the techniques  
5 known in the oil extraction industry.

The positioning may, for example, be done by injecting the control fluid both via the well for extracting the hydrocarbon fluid and through the other wells generally present in an oil field, such as the  
10 wells for injecting steam, water or other displacement fluids into the subsoil (known as injection wells).

On the basis of the criteria and using the preparation methods disclosed above, the person skilled in the art can select the control fluid comprising the  
15 polymer A-B-A' in such a way that said polymer has an LCST higher than the injection temperature of the fluid and lower than the temperature of the deposits within the zone in which the permeability control is to be carried out.

20 The method according to the present invention may be used within the scope of secondary and tertiary activities for recovery of a hydrocarbon oil, both in water-blocking interventions (water shut-off treatment) and in treatments conforming the subterranean formation  
25 (conformation treatment).

The quantities of aqueous fluid comprising the thermo-responsive polymers to be injected into the subterranean formation can vary widely as a function of its specific geological conformation. The quantities  
30 may be easily determined by the person skilled in the art on the basis of the geological characteristics of the formation and of simple routine experiments.

The following example embodiments are provided merely in order to illustrate the present invention and are not to be understood in a sense limiting the scope of protection defined by the attached claims.

## 5      EXAMPLES

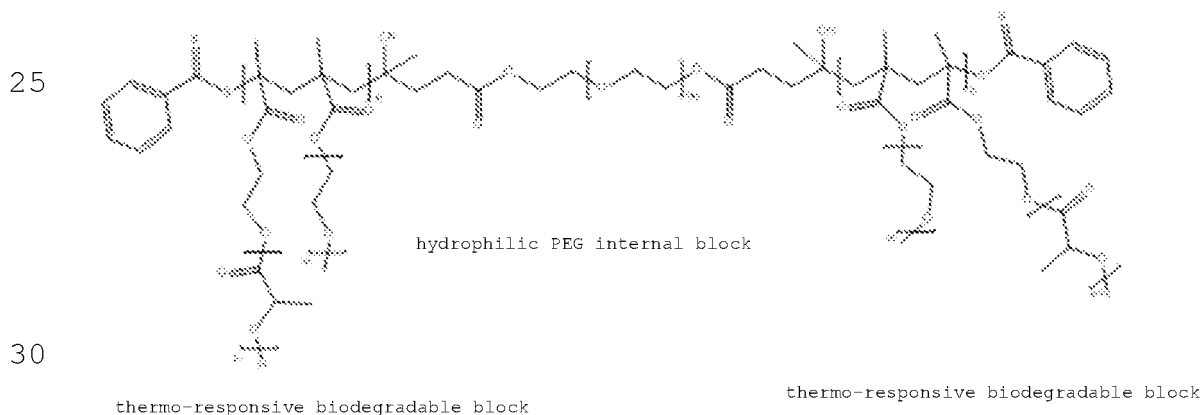
### 1. Determination of the LCST

For the purposes of the present invention, the lower critical solubility temperature (LCST) of a polymer is intended to be determined by the  
 10 turbidimetry method, by measuring the optical transmittance of an aqueous solution 0.2% by weight of the polymer under investigation, at ambient pressure. The transmittance measurements are conducted on the sample maintained at different temperatures. By  
 15 plotting the percentage transmittance recorded against the corresponding temperature of the sample, a sigmoidal curve is obtained. The temperature at the inflection point of the curve is considered the LCST of the polymer.

## 20      2. Preparation of the thermo-responsive polymers

### 2.1 Polymer 1

A thermo-responsive polymer having the following A-B-A block structure was prepared as follows.



### Step 1 - Preparation of the macro-CTA "CTA-B-CTA"

A hydrophilic and bifunctional macro-CTA was synthesised by Steglich esterification between an equivalent of poly(ethylene glycol) (PEG) HO-[CH<sub>2</sub>-CH<sub>2</sub>]<sub>n</sub>-OH (Mn = 4000 g·mol<sup>-1</sup>) and two equivalents of 4-phenyl(carbonothioylthio) pentanoic acid (CPA). To this end, 50 g PEG and 7.7 g CPA were solubilised in 300 mL dichloromethane (DCM). The solution obtained was loaded into a round-bottomed flask immersed in an ice and water bath. Separately, 5.7 g dicyclohexylcarbodiimide (DCC) and 0.27 g 4-dimethylamino pyridine (DMAP) were solubilised in 25 mL DCM. The solution obtained was added dropwise to the one containing PEG and CPA, maintained under magnetic stirring, within an hour. The mixture thus obtained was left to equilibrate at ambient temperature, and then reacted for 18 hours. After concentrating under vacuum to reduce the volume to about half, the product was recovered by precipitation of the reaction mixture in diethyl ether and left to dry in an oven under vacuum at 35°C.

The resulting macro-CTA is a hydrophilic polymer that exhibits no thermal response behaviour.

#### Step 2 - Preparation of the A-B-A polymer

The macro-CTA obtained in step 1 was used in the RAFT polymerisation of OEGMA300 and of HEMA-lactide to obtain the A-B-A block structure (Polymer 1). To this end, 2.59 g OEGMA300, 2.41 g HEMA-lactide, 0.065 g of the macro-CTA in step 1 and 1 mg azobiscyanovaleric acid (ACVA) were dissolved in 25 mL ethanol. The solution was bubbled with nitrogen for 30 minutes, keeping it in an ice and water bath. The RAFT polymerisation was then conducted at 65°C for 24 hours. The polymer was subsequently recovered by precipitation

from the reaction mixture in diethyl ether, followed by drying in an oven under vacuum at 35°C.

The DP of the external A blocks was found to be 500.

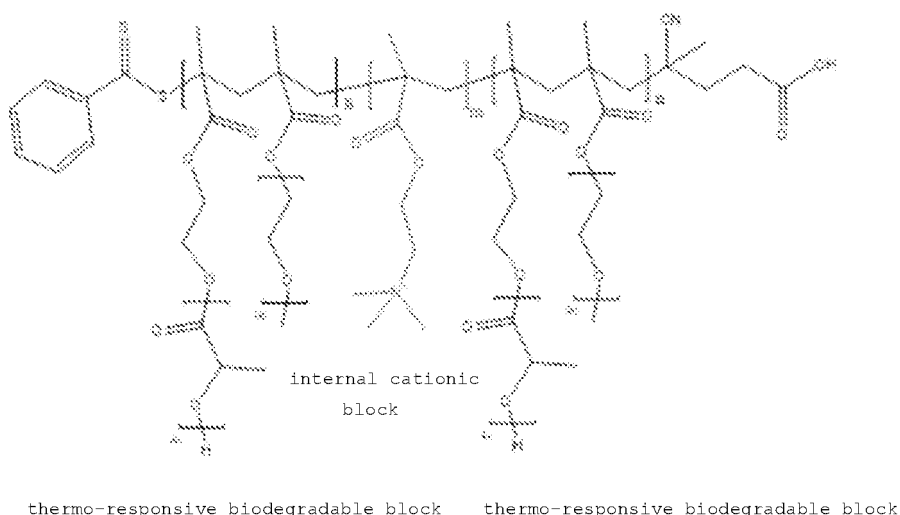
5 The LCST temperature of the Polymer 1 was found to be 45°C.

## 2.2 Polymer 2

A thermo-responsive polymer having the following A-B-A block structure was prepared as follows.

10

15



20

### Step 1 - Preparation of the "CTA-A" macro-CTA

The first thermo-responsive A block was synthesised by dissolving 13 g OEGMA300, 12 g HEMA-lactide, 40 mg CPA and 10 mg ACVA in 130 mL ethanol.

25 The solution was bubbled with nitrogen for 30 minutes and then reacted at 65°C for 24 hours. The polymer was precipitated in diethyl ether and its DP was evaluated as 500. By GPC analysis it was determined that the mean molecular weight of the product was approximately

30 188000 g·mol<sup>-1</sup>, with polydispersity of 1.19.

### Step 2 - Preparation of the "CTA-B-A" macro-CTA

The macro-CTA 1 obtained in step 1 was used in a

second RAFT stage to bind the hydrophilic B block. Specifically, 10 g of macro CTA, 2.4 g MADQUAT and 5 mg ACVA were solubilised in 50 mL of a 50:50 v/v water:ethanol mixture. The solution was bubbled with nitrogen for 30 minutes while keeping it in an ice and water bath, and then left to react at 65°C for 24 hours. The A-B block polymer (macro-CTA 2) was then precipitated in diethyl ether and recovered by filtration under vacuum. The DP calculated for the B block B was found to be 200.

#### Step 3 - Preparation of the A-B-A polymer

Finally, in the third RAFT stage, the A-B-A triblock copolymer was obtained by extending the macro-CTA 2 obtained in the previous step 2 with OEGMA300 and HEMA-lactide. To this end, 10 g of macro-CTA 2, 4.2 g OEGMA300, 3.88 g HEMA-lactide and 3 mg ACVA were dissolved in 80 mL of a 50:50 v/v water:ethanol mixture. The reactive mixture was bubbled with nitrogen for 30 minutes, keeping it in an ice and water bath, and then reacted at 65°C for 24 hours. The A-B-A block polymer was then precipitated in diethyl ether and recovered by filtration under vacuum. The DP of the third block (A) was found to be 500.

The LCST temperature of the Polymer 2 is 45°C.

#### 3. Thermo-responsive solubility

The phase transition of the thermo-responsive polymers 1 and 2 from aqueous polymer solution to viscous gel was verified experimentally, conditioning a test tube containing a sample of aqueous solution of the polymer (30% by weight of polymer with respect to the weight of the solution) at a temperature of 55°C for 30 minutes.

In both cases, at the end of the conditioning, the formation of a viscous gel at the bottom of the test tube was observed. By conditioning the test tube containing the gel again at ambient temperature (25°C),  
5 the inverse transition from gel to aqueous polymer solution was observed.

#### 4.1 Permeability modification tests on packed sand

The effectiveness of an aqueous fluid containing the Polymer 1 according to the present invention in  
10 controlling the permeability of a sample of packed sand was verified experimentally in the following way.

A solution of Polymer 1 (1% by weight) in saltwater was prepared using a synthetic saltwater having the composition given in Table 1 below (density  
15 at 70°C = 0.9465 kg/L; viscosity at 70°C = 0.4058 cP).

20

Table 1 - saltwater composition

Compound	Concentration (g/L)
NaCl	22
MgCl <sub>2</sub> (6H <sub>2</sub> O)	9.7
Na <sub>2</sub> SO <sub>4</sub> (anhydrous)	37
CaCl <sub>2</sub> (anhydrous)	1
KCl	0.65

NaHCO <sub>3</sub>	0.2
H <sub>3</sub> BO <sub>4</sub>	0.023
Total	37.273

On a sample (cylindrical core) of packed sand (passed through a 20-mesh and a 40-mesh sieve) 14.50 cm in length and 5.10 cm in diameter, measurements of permeability to fluids were made using the solution of the Polymer 1 and the saltwater of Table 1 (without thermo-responsive polymer), as the reference fluid.

The cylindrical core, housed in a sample holder, was placed inside a temperature-controlled oven. The measurement system included, in addition to the aforesaid oven, a system of pumps for injecting the fluids into the core at preset flow rate values, and devices for measuring the flow rates of the fluids. A containment overpressure (nitrogen) of 50 bar was applied to the core (on top of the internal pressure) to avoid the effects linked to the compressibility of the sand during injection of the fluids. During fluxing of the fluids in the sample, the load losses between inflow and outflow of the fluid from the sample were measured by means of electronic transducers.

Initially, the permeability of the sample was measured by flushing the reference fluid consisting of the saltwater. The treatment fluid consisting of the solution containing Polymer 1 was then injected, up to saturation of the core. The core was then maintained at a temperature of 70°C for the time necessary for the phase transition to occur, from soluble polymer to gel capable of opposing resistance to the flow of the



injected fluid. In a final step, saltwater was again injected into the core to determine the variation in its permeability following the treatment with the solution of Polymer 1.

5       The permeability of the sample was determined by measuring the load losses in response to variation in the flow rate of the injected fluid.

      The resistance factor  $F_r$  gives an indication of the relative mobility of the aqueous solution of  
10 Polymer 1 within the sample with respect to the mobility of the saltwater alone in the same sample.

      The residual resistance factor  $F_{rr}$  instead provides a measure of the reduction in relative mobility of the reference fluid in the sample following  
15 treatment of the sample with the treatment fluid, with respect to the mobility of the same reference fluid prior to the treatment of the sample with the treatment fluid. Higher values of the parameters  $F_r$  and  $F_{rr}$  indicate a higher resistance of the sample to passage  
20 of a fluid.

      During fluxing of the solution of Polymer 1 in the core at ambient temperature, the value of  $F_r$  was found to be equal to approximately 1.15. This value, being low, indicates that the solution of Polymer 1 is easily  
25 injectable into the sample.

      The saturated sample of solution of Polymer 1 was maintained at a temperature of 70°C for 48 hours and then flushed with saltwater to verify the extent of modification of permeability. The value of  $F_{rr}$   
30 determined for the saltwater flushing was 22.7. The treatment with Polymer 1 thus determined a reduction in the permeability of the saltwater by a factor of

approximately 23.

#### 4.2 Tests of modification of the permeability on sandstone - Chashach

The test described in the preceding point 4.1 was  
5 repeated on a cylindrical core of sandstone of Clashach type, length 14.50 cm and diameter 5.10 cm, using the solution of Polymer 1 and the reference saltwater described above.

During fluxing of the solution of Polymer 1 in the  
10 core at ambient temperature, the value of  $F_r$  was found to be approximately 10.6. This value indicates a resistance to the injection of acceptable magnitude.

The value of  $F_{rr}$  determined for the fluxing of saltwater was 142.8. This value of  $F_{rr}$  confirms the  
15 efficacy of the treatment for controlling the permeability of the sample with the polymers according to the present invention.

#### 5. TEST OF DETERIORATION

To verify the reversibility of the sol-gel  
20 transition following hydrolysis of the ester bonds, Polymer 2 inside a container was conditioned at a temperature of 55°C for 30 minutes, so as to enable formation of the gel. A head of saltwater was then added on top of the gel layer. Change in the biphasic  
25 system, maintained at 55°C, was monitored by measuring the loss of mass by thermogravimetry and the pH of the head of water.

Figs. 1 and 2 give the experimental values for loss of mass and pH of the biphasic system observed as  
30 a function of time.

Fig. 1 shows that, after an induction period of around 7 days in duration, in which only a slight

decline (less than 10%) in the mass of the gel was recorded, the mass of the gel began to fall off linearly over time, until, after 20 days, it resulted in the solubilisation of the gel in the head of water, and therefore in its total disappearance. In parallel, as shown by Fig. 2, the pH of the liquid phase declined over time. The reduction in the pH can be attributed to the release of acid species, in particular lactic acid, which accompanies degradation of the polymer.

## CLAIMS

1. Fluid for controlling the permeability of a subterranean formation comprising an aqueous solution of at least one thermo-responsive polymer of block  
5 structure A-B-A', wherein:

- A and A', the same as or different from one another, each represent a thermo-responsive oligomer group;

- B is an oligomer group comprising n repeat  
10 units, the same as or different from one another, wherein:

(i) at least one of the repeat units has a solubility of the corresponding monomer, in water at 20°C, equal to or greater than 120 g/l,

15 (ii) n is a whole number within the range 30 - 1000.

2. Fluid according to claim 1, wherein said A block and/or A' block is an oligomer containing a plurality of polymer side chains.

20 3. Fluid according to anyone of the preceding claims, wherein said B block is a linear oligomer that contains no polymer side chains.

4. Fluid according to claim 1, wherein said A block and/or said A' block has a lower critical  
25 solubility temperature (LCST) within the range 30°C - 100°C.

5. Fluid according to claim 1, wherein said A block and/or said A' block are a graft oligomer group comprising a poly(meth)acrylic or poly(meth)acrylamide  
30 linear main chain and a plurality of side chains, connected to said main chain, selected from: poly(ethylene glycol)  $[-CH_2-CH_2-O]_m-H$ , poly(ethylene

glycol) methyl ether  $[-CH_2-CH_2-O]_m-CH_3$ , HEMA-poly lactide  $--CO-O-CH_2-CH_2-O-[-CO-(CH_3)CH-O]_m-H$ , alkylamide, linear or branched, and combinations thereof, where m is a whole number within the range 2 - 10.

6. Fluid according to claim 1, wherein said A block and/or said A' block are oligomer groups formed by one or more corresponding monomeric units selected from: (meth)acrylic acid, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), HEMA-poly lactide, potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, polymerisable esters comprising polyoxyethylene chains  $[-CH_2-CH_2-O]_x-$  where x is an integer number within the range 10 - 1000, N-isopropylacrylamide, N,N-dimethylaminoethyl methacrylate, dimethylacrylamide.

7. Fluid according to claim 1, wherein said A block and/or said A' block are oligomer groups formed by two or more OEGMA compounds having molecular weight different from one another.

8. Fluid according to claim 1, wherein said A block and/or said A' block have a degree of polymerisation DP within the range 2 - 1,000, preferably 3 - 500, more preferably 5 - 450, even more preferably 6 - 400.

9. Fluid according to claim 6, wherein said OEGMA compound has a mean molecular weight  $M_n$  within the range 100 - 10,000 Dalton, more preferably within the range 100 - 5,000 Dalton.

10. Fluid according to claim 1, wherein said A block and/or said A' block is a co-polymer comprising

OEGMA as a first co-monomer and at least one hydrophobic second co-monomer selected from: C<sub>1</sub>-C<sub>4</sub> alkyl -(meth)acrylate, (dimethylamino)ethyl methacrylate (DMAEMA) and combinations thereof.

5 11. Fluid according to claim 1, wherein the oligomer group of said B block is an oligomer group comprising one or more repeat units selected from: (meth)acrylic acid, polymerisable esters comprising polyoxyethylene chains  $-[-CH_2-CH_2-O]_r-H$  where r is an  
10 integer number within the range 10 - 500, more preferably 20 - 300, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride,  
15 potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, (meth)acrylamide 2-hydroxypropyl methacrylamide, glycerol monomethacrylate, 2-hydroxyethyl methacrylate, methacryloyloxyethyl phosphorylcholine, carboxybetaine,  
20 sulfobetaine and combinations thereof.

12. Fluid according to claim 1, wherein:

- said B block comprises poly(ethylene glycol) (PEG) in the main chain having a mean molecular weight M<sub>n</sub> within the range 500 - 10,000 Dalton, more  
25 preferably within the range 1,000 - 5,000 Dalton;

- said A block and/or A' block are oligomer groups comprising, as corresponding monomer, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), preferably having a mean molecular weight M<sub>n</sub> within the range 100  
30 - 1,000.

13. Fluid according to claim 1, wherein:

- said B block is an oligomer group comprising, as

corresponding monomer, [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT),

- said A block and/or A' block are oligomer groups comprising, as corresponding monomer, OEGMA having a  
5 mean molecular weight  $M_n$  within the range 100 - 1,000.

14. Fluid according to claim 1, wherein said B block comprises at least one cationic pendant group.

15. Fluid according to the preceding claim, wherein said B block comprising at least one cationic  
10 pendant group comprises one or more monomers selected from: [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), [2-(acryloyloxy)ethyl]trimethylammonium chloride, (dimethylamino)ethyl methacrylate DMAEMA and 2-  
15 aminoethyl methacrylate hydrochloride.

16. Fluid according to claim 1, wherein said oligomer group of the A block and/or said A' block comprises one or more degradable repeat units.

17. Fluid according to the preceding claim,  
20 wherein said degradable repeat unit is HEMA-poly(lactide).

18. Method for controlling the permeability of a subterranean formation comprising:

a. providing a fluid comprising an aqueous  
25 solution of at least one thermo-responsive polymer with block structure A-B-A', wherein:

- A and A', the same as or different from one another, each represent a thermo-responsive oligomer group;

30 - B is an oligomer group comprising n repeat units, the same as or different from one another, wherein:

(i) at least one of the repeat units has a solubility of the corresponding monomer, in water at 20°C, equal to or greater than 120 g/l,

5       (ii) n is a whole number within the range 30  
- 1000;

b. positioning said treatment fluid in a subterranean formation.

19. Method according to the preceding claim, wherein said polymer A-B-A' is present in said aqueous  
10 solution in a concentration within the range 0.5-40% by weight, more preferably within the range 1-20% by weight, with respect to the weight of the aqueous solution.

20. Method according to claim 18 or 19, wherein  
15 said step b comprises injecting said fluid via at least one extraction well and/or at least one injection well.

21. Use of a fluid according to any one of claims 1-17 to modify the permeability of a subterranean formation.

20       22. Use of a fluid according to any one of claims 1-17 to limit the infiltration of water in a well for extracting a hydrocarbon oil or gas from a subterranean formation.



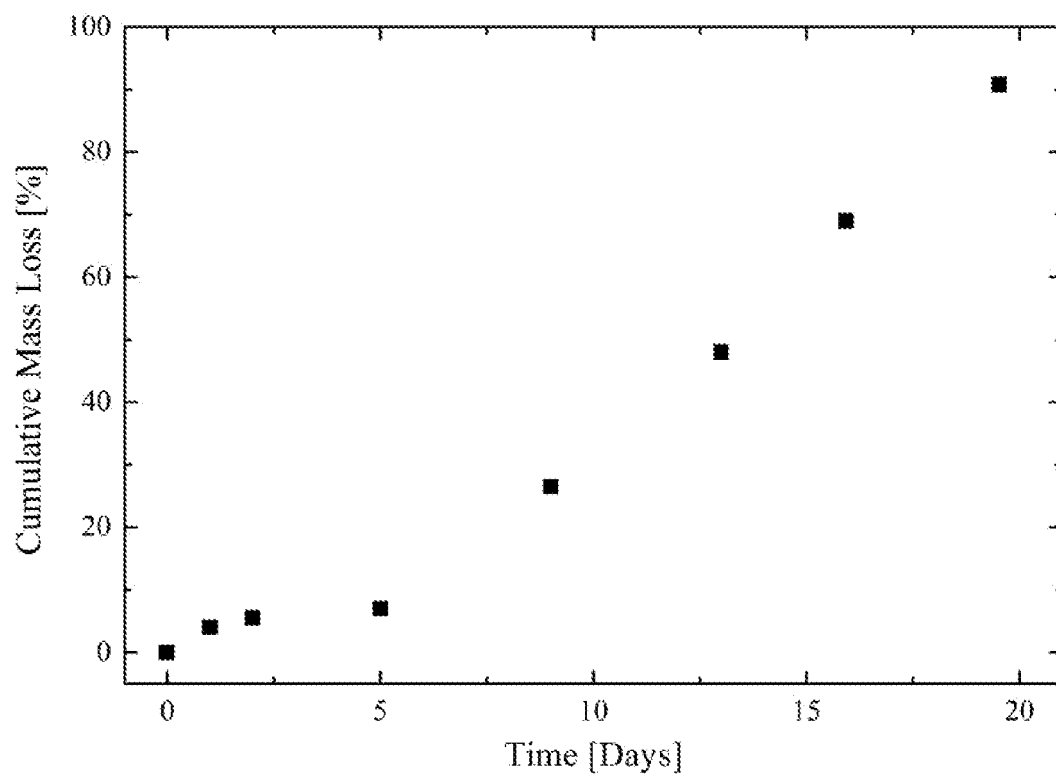


Fig. 1

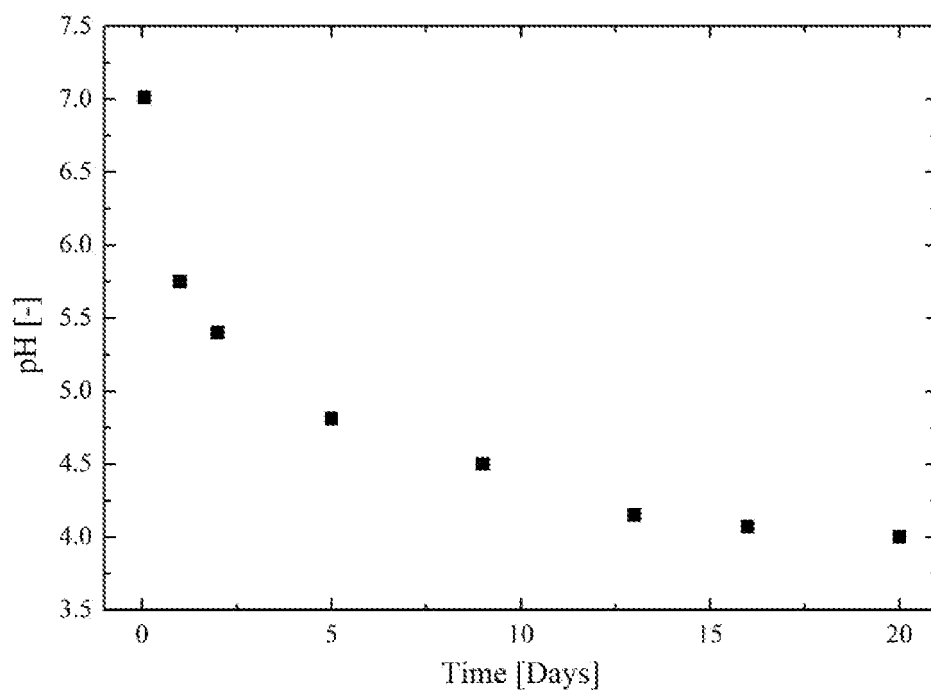


Fig. 2

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2019/056974

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C08G81/02 C08L33/02 C08F220/06 C09K17/22 C09K8/588 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C08G C09J C08L C08F C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X  A	US 3 994 852 A (ADAMS SALLY LEE ET AL) 30 November 1976 (1976-11-30) claim 10 column 2, line 19 - line 45 -----	1-4,6,8, 15-22 5,7,9-14
X	DESHPANDE M C ET AL: "Influence of polymer architecture on the structure of complexes formed by PEG-tertiary amine methacrylate copolymers and phosphorothioate oligonucleotide", JOURNAL OF CONTROLLED RELEASE, ELSEVIER, AMSTERDAM, NL, vol. 81, no. 1-2, 17 May 2002 (2002-05-17) , pages 185-199, XP004351116, ISSN: 0168-3659, DOI: 10.1016/S0168-3659(02)00052-4 figure 1; table 1 -----	1-17
A		18-22
<div style="display: flex; justify-content: space-between; align-items: center;"> <div> <input type="checkbox"/> Further documents are listed in the continuation of Box C.         </div> <div> <input checked="" type="checkbox"/> See patent family annex.         </div> </div>		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">18 November 2019</div>	Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">26/11/2019</div>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <div style="text-align: center; font-weight: bold;">Domínguez Gutiérrez</div>	

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2019/056974

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

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

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-22(partially)  
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 FURTHER INFORMATION sheet PCT/ISA/210
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 an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

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

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

Continuation of Box II.2

Claims Nos.: 1-22(partially)

See separate sheet for complete reasoning.

Regarding claim 1. Claim 1 thus to a copolymer of a completely undefined chemical nature, and lacks support. Claim 1 is drafted in a way that countless commercially-available compounds belonging to multiple technical fields, and have thus use in many different applications, would anticipate its current subject-matter.

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of claim 1 may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT).

For these reasons in addition to all those set in the separate sheet, the search was performed taking into consideration the non-compliance in determining the extent of the search of claim 1.

The search of claim 1 was restricted to:

Claim 1, wherein  
said A block and said A' block are a graft oligomer group comprising a poly(meth)acrylic or poly(meth)acrylamide linear main chain and a plurality of side chains, connected to said main chain, selected from: poly(ethylene glycol)  $[-CH_2-CH_2-O]_m$ -H, poly(ethylene glycol) methyl ether  $[-CH_2-CH_2-O]_m-CH_3$ , HEMA-poly(lactide)  $-CO-O-CH_2-CH_2-O-[-CO-(CH_2)_3-CH_2-O]_m-H$ , alkylamide, linear or branched, and combinations thereof, where m is a whole number within the range 2 - 10, wherein the oligomer

group of said B block is an oligomer group comprising one or more repeat units selected from: (meth)acrylic acid, polymerisable esters comprising polyoxyethylene chains  $[-CH_2-CH_2-O]_r-H$  where r is an integer number within the range 10 - 500, more preferably 20 - 300, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride, potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, (meth)acrylamide 2-hydroxypropyl methacrylamide, glycerol monomethacrylate, 2-hydroxyethyl methacrylate, methacryloyloxyethyl phosphorylcholine, carboxybetaine, sulfobetaine and combinations thereof.

Clearly stating the chemical nature of all blocks using the first-available claims that define each, which also correspond to the only technical features supported by the description that have been acknowledged to provide the desired technical effect, and thus solve the technical problem posed by the present application.

The search of all

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

claims referring to claim 1 is thus also restricted accordingly.

Regarding claim 18.

The reasoning for claim 1 applies here mutatis mutandis.

The search of claim 18 was restricted to:

Claim 18, wherein

said A block and said A' block are a graft oligomer group comprising a poly(meth)acrylic or poly(meth)acrylamide linear main chain and a plurality of side chains, connected to said main chain, selected from: poly(ethylene glycol)  $[-CH_2-CH_2-O]_m-H$ , poly(ethylene glycol) methyl ether  $[-CH_2-CH_2-O]_m-CH_3$ , HEMA-poly(lactide)  $--CO-O-CH_2-CH_2-O-[-CO-(CH_3)CH-O]_m-H$ , alkylamide, linear or branched, and combinations thereof, where m is a whole number within the range 2 - 10, wherein

the oligomer group of said B block is an oligomer group comprising one or more repeat units selected from: (meth)acrylic acid, polymerisable esters comprising polyoxyethylene chains  $[-CH_2-CH_2-O]_r-H$  where r is an integer number within the range 10 - 500, more preferably 20 - 300, oligo(ethylene glycol)methyl ether methacrylate (OEGMA), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (MADQUAT), [2-(methacryloyloxy)ethyl]-trimethylammonium chloride, potassium 3-sulfopropyl methacrylate, 2-acrylamido-2-methylpropanesulfonic acid, (meth)acrylamide 2-hydroxypropyl methacrylamide, glycerol monomethacrylate, 2-hydroxyethyl methacrylate, methacryloyloxyethyl phosphorylcholine, carboxybetaine, sulfobetaine and combinations thereof.

The search of claims referring to claim 18 is thus also restricted accordingly.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/IB2019/056974

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3994852	A	30-11-1976	NONE
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