

NOVEL COPOLYMER AS A WATER-REDUCING AGENT IN A
HYDRAULIC COMPOSITION

5 The present invention relates to novel copolymers and to their use as water-reducing agents in hydraulic compositions, such as concrete and mortar compositions.

Such compositions are intended for all the construction markets.

10 Hydraulic compositions generally comprise various chemical additives intended to improve their properties. Among these, “water-reducing” agents, also known as “dispersants”, “fluidizers”, “plasticizers” or “superplasticizers”, have the function of improving the state of dispersion of the mineral particles in the compositions. These chemical agents lead to a reduction in the water content of hydraulic compositions,
15 which makes it possible to improve the performance qualities of these compositions, and especially their mechanical strength.

A wide variety of dispersants for hydraulic compositions has already been proposed. These agents differ in their chemical composition and the properties induced within the
20 compositions containing them.

Historically, the first compounds proposed as dispersants were lignosulfonates as described in US 3 772 045. Polycondensates of formaldehyde and naphthalene or melamine sulfonates were then implemented, as illustrated in US 3 359 225 and
25 US 4 258 790.

More recently, a novel family of dispersants, consisting of carboxylic polymers of comb type, has been developed. In general, these polymers have a backbone generally of (meth)acrylic nature and side chains ending with hydrophilic groups, for example
30 polyoxyalkyl side groups.

By way of example, WO 97/39037 describes the synthesis of polymers of comb type, which may be used as water-reducing agents in cements, by polymerization using an

acrylic monomer and a polyether macromonomer, such as an oxyethylene and oxypropylene (meth)acrylate.

Mention may also be made of the dispersing copolymers proposed in WO 2006/028252.

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CN 1148329C also proposes, as dispersants for cements, copolymers obtained by polymerization using a monomer of monocarboxylic acid type, such as (meth)acrylic acid; and a monomer of polyalkylene glycol ether type in which the proportion of ethoxylated units is at least 90 mol% of all of the alkoxyl units, preferably a polyethylene glycol ether.

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JP 2006/282414 relates to an agent for developing high strength for cement. It contains, as essential components, (a) glycerol or a glycerol derivative and (b) a copolymer based on polycarboxylic acid having a compound of polyoxyalkylene type on a side chain.

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US 6 211 317 describes emulsion copolymers of unsaturated carboxylic acid derivatives, oxyalkylene alkenyl glycol ethers, unsaturated dicarboximides or amides and vinyl monomers. They are described for their use as additives for hydraulic binders, in particular cement.

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KR 10086040 describes copolymers of unsaturated monomers based on polyalkylene ether supplemented with at least two alkylene glycols and (meth)acrylate monomers. It describes their use as cement additives.

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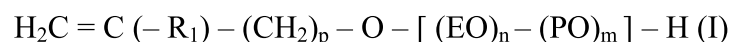
The present invention is directed toward proposing novel dispersants for gaining access to better reduction of the water content of hydraulic compositions, without, however, impairing their fluidity or workability.

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More particularly, according to a first of its aspects, the present invention relates to a copolymer obtained by polymerization using a monomer mixture comprising:

- at least one anionic monomer (a) comprising a polymerizable unsaturated function and a carboxylic group; and

- at least one monomer (b) of formula (I):



in which:

R_1 represents a hydrogen atom or a CH_3 group;

5 p is 1 or 2;

$[(\text{EO})_n - (\text{PO})_m]$ represents a polyalkoxyl chain made of ethoxyl units EO and propoxyl units PO, distributed in blocks, alternately or randomly,

m and n represent integers ranging between 1 and 250, the sum of m and n being greater than or equal to 10, with the proviso that the mole proportion of the ethoxyl units in the polyalkoxyl chain $(n)/(m+n)$ is greater than or equal to 70% and strictly less than 90%.

A copolymer as defined above, comprising at least units derived from the anionic monomers (a) and units derived from the monomers (b) of formula (I), is referred to simply in the rest of the text as “copolymer according to the invention”.

Surprisingly, the inventors have discovered that such a copolymer makes it possible to significantly reduce the amount of water in the hydraulic composition in which it is implemented.

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Thus, advantageously, as illustrated in the experimental tests that follow, the copolymers according to the invention may be implemented as admixtures in hydraulic compositions as “water-reducing” agents, and even as “high-efficiency water-reducing” agents.

25 In the context of the present invention, the term “water-reducing” agent or “plasticizer” means an agent which, in accordance with standard ADMIXTURE NF EN 934-2, allows a water reduction for admixed concrete of at least 5% relative to reference concrete. A “high-efficiency water-reducing agent” or “superplasticizer” is an admixture which allows a water reduction for admixed concrete of at least 12% relative to reference concrete.

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Moreover, this water reduction does not take place to the detriment of the performance qualities of the hydraulic composition, for example of the concrete, especially its fluidity or workability. In other words, the copolymers according to the invention allow, for the

same workability, a reduction in the water content of a given hydraulic composition, such as a concrete.

As detailed in the example that follows, the dispersing properties of the water-reducing agent in the hydraulic composition may be evaluated by measuring the slump, in accordance with standard EN 12350-2. The greater the slump value, the more workable the hydraulic composition. Specifically, it is essential to preserve good initial workability of the hydraulic composition, for example of the concrete, insofar as this property conditions its implementation, for example for filling shuttering.

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Other characteristics, advantages and modes of application of the copolymer according to the invention will emerge more clearly on reading the description and the example that follow, which are given as nonlimiting illustrations.

15 In the rest of the text, the expressions “between ... and ...”, “ranging from ... to ...” and “varying from ... to ...” are equivalent and are intended to mean that the limits are included, unless otherwise mentioned.

Unless otherwise mentioned, the expression “containing/comprising a(n)” should be understood as meaning “containing/comprising at least one”.

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COPOLYMER OF THE INVENTION:

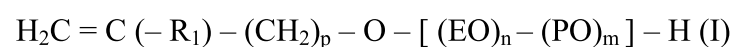
As indicated previously, the copolymer according to the invention is obtained by polymerization using at least:

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- one or more anionic monomers comprising a polymerizable unsaturated function and a carboxylic group, noted as “monomers (a)” in the rest of the text; and

- one or more monomers of formula (I) below, noted as “monomers (b)” in the rest of the text,

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in which:

R_1 represents a hydrogen atom or a CH_3 group;

p is 1 or 2;

[(EO)_n – (PO)_m] represents a polyalkoxyl chain made of ethoxyl units EO and propoxyl units PO, distributed in blocks, alternately or randomly,

m and n represent integers ranging between 1 and 250, the sum of m and n being greater than or equal to 10, with the proviso that the mole proportion of the ethoxyl units in the polyalkoxyl chain (n)/(m+n) is greater than or equal to 70% and strictly less than 90%.

The copolymer according to the invention may optionally comprise other polymerizable monomers. The optional monomers optionally included in the composition of the copolymer of the invention may be of varied nature, as detailed in the rest of the text.

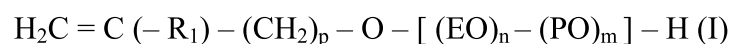
In particular, said anionic monomers (a) and said monomers (b) of formula (I) may represent more than 80 mol%, in particular more than 90 mol%, and more particularly more than 95 mol%, of the total number of moles of constituent monomers of the copolymer.

According to an implementation variant, the copolymer according to the invention is formed solely from units derived from the monomers (a) and (b). In other words, the copolymer according to the invention may be obtained by polymerization using a monomer mixture formed from one or more anionic monomers (a) and from one or more monomers (b) of formula (I).

The distribution of the units derived from the monomers (a) and those derived from the monomers (b) in the copolymer according to the invention may be of block, alternating or random type. According to one embodiment, it is a random or alternating distribution. According to another embodiment, it is a distribution of block type.

The copolymer according to the invention may be obtained by polymerization using a monomer mixture consisting of:

- at least one anionic monomer (a) comprising a polymerizable unsaturated function and a carboxylic group; and
- at least one monomer (b) of formula (I):



in which:

R_1 represents a hydrogen atom or a CH_3 group;

p is 1 or 2;

5 $[(\text{EO})_n - (\text{PO})_m]$ represents a polyalkoxyl chain made from ethoxyl units EO and propoxyl units PO, distributed in blocks, alternately or randomly,

m and n represent integers ranging between 1 and 250, the sum of m and n being greater than or equal to 10, with the proviso that the mole proportion of the ethoxyl units in the polyalkoxyl chain $(n)/(m+n)$ is greater than or equal to 70% and strictly less than 90%.

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The amounts of monomers (a) and (b) implemented then correspond to 100% by weight of the total amount of monomers forming the copolymer according to the invention.

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Anionic monomer (a) bearing a polymerizable unsaturated function and a carboxylic group:

The anionic monomers (a) included in the composition of the copolymer according to the invention may be chosen more particularly from acrylic acid, methacrylic acid, maleic acid, itaconic acid and crotonic acid, and mixtures of these monomers.

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Said monomer(s) (a) may be in acid form, for example, carboxylic acid and/or in salt form, for example carboxylate.

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It is understood that only one or a mixture of several different monomers (a) may be included in the composition of the copolymer according to the invention. For example, it may be a mixture of acrylic acid monomers and methacrylic acid monomers or alternatively a mixture of maleic acid, acrylic acid and methacrylic acid monomers.

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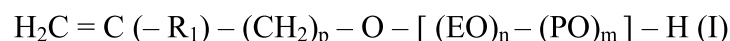
According to a particular embodiment, the copolymer according to the invention is formed from at least acrylic acid and/or methacrylic acid, in particular from at least acrylic acid (AA).

According to an implementation variant, said anionic monomer(s) (a) included in the composition of the copolymer according to the invention are chosen from acrylic acid and methacrylic acid, and a mixture thereof.

- 5 According to a particular embodiment, said anionic monomer(s) (a) may represent from 50 to 99 mol%, in particular from 60 to 95 mol%, especially from 70 to 95 mol% and more particularly from 80 to 90 mol%, of the total number of moles of constituent monomers in the copolymer according to the invention.

10 Monomer (b) of formula (I):

As indicated previously, the monomers (b) included in the composition of the copolymer according to the invention correspond to formula (I) below:



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in which:

R_1 represents a hydrogen atom or a CH_3 group;

p is 1 or 2;

$[(\text{EO})_n - (\text{PO})_m]$ represents a polyalkoxyl chain made of ethoxyl units EO and propoxyl units PO;

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m and n represent integers ranging between 1 and 250, the sum of m and n being greater than or equal to 10, with the proviso that the mole proportion of the ethoxyl units in the polyalkoxyl chain $(n)/(m+n)$ is greater than or equal to 70% and strictly less than 90%.

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The term “polyalkoxyl” chain means a chain of poly(alkylene glycol) type. The term “poly(alkylene glycol)” means a polymer of an alkylene glycol derived from an olefinic oxide.

- 30 The poly(alkylene glycol) chain of the monomer (b) according to the invention is formed from ethoxyl (or “ethylene-oxy”) units, noted “EO”, of formula $-\text{CH}_2-\text{CH}_2-\text{O}-$ and from propoxyl (or “propylene-oxy”) units, noted “PO”, of formula $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$.

The schematic representation “[(EO)_n – (PO)_m]” makes no assumption as to the order of the ethoxyl and propoxyl units in the polyalkoxyl chain. Specifically, the polyalkoxyl chain may have a distribution of the EO and PO units of block, random or alternating type.

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According to a particular embodiment, the EO and PO units are distributed in blocks.

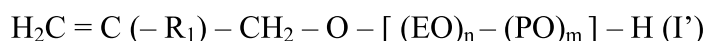
In particular, the polyalkoxyl chain of the monomer (b) may be of diblock type and may be formed from a polyoxyethylene block and from a polyoxypropylene block.

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According to an implementation variant, p in the abovementioned formula (I) is 1.

In other words, according to this embodiment variant, said monomer(s) (b) included in the composition of the copolymer according to the invention correspond to formula (I')

15 below:

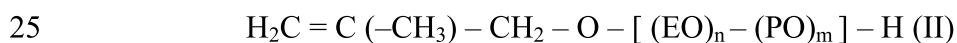


in which R₁, n and m are as defined previously.

According to a particular embodiment, the copolymer according to the invention is formed from at least one monomer (b) of the abovementioned formula (I) or (I'), in which R₁ represents a methyl group.

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In particular, according to a particular embodiment, the copolymer according to the invention is formed from at least one monomer (b) of formula (II) below:

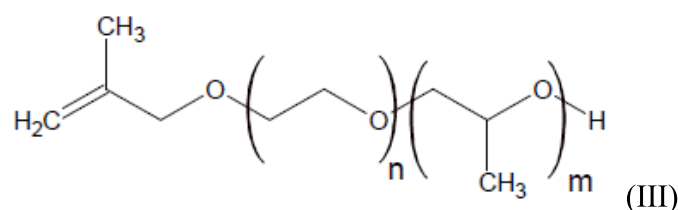


in which n and m are as defined previously.

As indicated previously, the schematic representation “[(EO)_n – (PO)_m]” makes no assumption as to the order of the ethoxyl and propoxyl units in the polyalkoxyl chain. The polyalkoxyl chain may have a distribution of the EO and PO units of block, random or alternating type, in particular of block type.

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According to one particular embodiment, the copolymer according to the invention is obtained from at least one monomer (b) of formula (III) below:

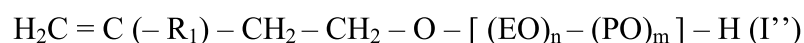


m and n being as defined previously.

In the abovementioned formula (III), the polyalkoxyl chain is formed from a first
5 polyoxyethylene block and from a second polyoxypropylene block.

According to another implementation variant, p in the abovementioned formula (I) is 2.

In other words, according to this implementation variant, said monomer(s) (b) included
10 in the composition of the copolymer according to the invention correspond to formula (I'') below:

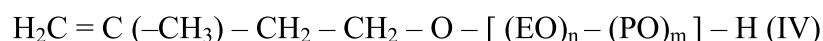


in which R_1 , n and m are as defined previously.

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According to a particular embodiment, the copolymer according to the invention is formed from at least one monomer (b) of the abovementioned formula (I''), in which R_1 represents a methyl group.

20 According to a particular embodiment, the copolymer according to the invention is formed from at least one monomer (b) of formula (IV) below:



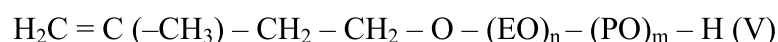
in which n and m are as defined previously.

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As indicated previously, the schematic representation “[(EO)_n – (PO)_m]” makes no assumption as to the order of the ethoxyl and propoxyl units in the polyalkoxyl chain. The polyalkoxyl chain may have a distribution of the EO and PO units of block, random or alternating type, in particular of block type.

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According to a particular embodiment, the copolymer according to the invention is obtained from at least one monomer (b) of formula (V) below:



5 m and n being as defined previously.

In the abovementioned formula (V), the polyalkoxyl chain is formed from a first polyoxyethylene block and from a second polyoxypropylene block.

10 As for the anionic monomers (a), it is understood that only one or a mixture of several different monomers (b) may be included in the composition of the copolymer according to the invention.

Thus, according to a particular embodiment, the copolymer according to the invention is
15 obtained from at least one mixture of at least one monomer (b₁) of formula (I) in which R₁ represents a hydrogen atom and from at least one monomer (b₂) of formula (I) in which R₁ represents a methyl group.

In particular, the copolymer according to the invention may be obtained from at least
20 one mixture of at least one monomer (b₁') of the abovementioned formula (I'), in which R₁ represents a hydrogen atom and from at least one monomer (b₂') of the abovementioned formula (I'), in which R₁ represents a methyl group (in other words, a monomer (b₂') of the abovementioned formula (II)).

25 In the context of this particular embodiment, said monomer(s) (b₁') and said monomer(s) (b₂') included in the composition of the copolymer according to the invention may be implemented in a monomer(s) (b₁')/monomer(s) (b₂') mole ratio ranging from 10 to 0.01, in particular from 1 to 0.1.

30 According to yet another particular embodiment, the copolymer according to the invention may be obtained from at least one mixture of at least one monomer (b₁') of the abovementioned formula (I') and from at least one monomer (b₂'') of the abovementioned formula (I''). In particular, the copolymer according to the invention may be obtained from at least one mixture of at least one monomer (b₁') of the

abovementioned formula (I') in which R_1 represents a methyl group (in other words, a monomer (b_1') of the abovementioned formula (II)) and from at least one monomer (b_2'') of the abovementioned formula (I'') in which R_1 represents a methyl group (in other words, a monomer (b_2'') of the abovementioned formula (IV)).

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According to an essential characteristic of said monomer(s) (b) included in the composition of the copolymer according to the invention, the mole proportion of the ethoxyl units EO in the polyalkoxyl chain (i.e. $(n)/(m+n)$ in the abovementioned formula (I), (I'), (II) or (III)) is greater than or equal to 70% and strictly less than 90%.

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In particular, the mole proportion of the ethoxyl units EO in the polyalkoxyl chain may be between 70% and 88%, in particular greater than or equal to 72%, and more particularly greater than or equal to 75%.

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According to a particular embodiment, the mole proportion of the ethoxyl units EO in the polyalkoxyl chain may be less than or equal to 85%, in particular less than or equal to 80%.

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The mole ratio between the ethoxyl units and the propoxyl units in the polyalkoxyl chain may be more particularly between 2.5 and 8, in particular between 2.8 and 7.5 and especially between 3 and 6.

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As indicated previously, the total number of ethoxyl and propoxyl units in the polyalkoxyl chain (in other words the sum of m and n) of the monomer (b) is greater than or equal to 10.

According to a particular embodiment, it may be between 10 and 150, in particular between 18 and 110 and more particularly between 20 and 70.

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The polyalkoxyl chain of the monomer (b) according to the invention may thus have a number-average molar mass of between 450 and 7500 g/mol, in particular between 900 and 5500 g/mol and more particularly between 1000 and 3500 g/mol.

It is understood that the different variants and particular embodiments given above may be combined, as far as is possible, to define other variants or particular embodiments.

5 The monomers (b) according to the invention may be prepared via techniques known to those skilled in the art, by increasing the desired polyalkoxyl chain by polymerization using ethylene oxide and propylene oxide monomers on an allylic or methallylic alcohol.

10 According to a particular embodiment, said monomer(s) (b) may represent from 1 to 50 mol%, in particular from 5 to 40 mol%, especially from 5 to 30 mol% and more particularly from 10 to 20 mol%, of the total number of moles of constituent monomers in the copolymer according to the invention.

15 Said monomer(s) (b) may be implemented in various forms, especially in solid form, in particular in powder or flake form, or in liquid form (liquid formed from the monomers (b)), or aqueous solution of the monomers (b)).

In particular, the monomers (b) are water-soluble.

20 Preferably, said monomer(s) (b) are implemented in liquid form, in particular as an aqueous solution, this form being particularly suitable for the synthesis of the copolymer according to the invention.

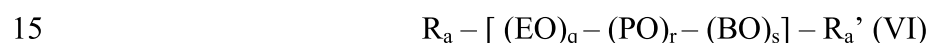
25 The mole ratio between said anionic monomer(s) (a) and said monomer(s) (b) included in the composition of the copolymer according to the invention may more particularly be between 1 and 99, in particular between 2.3 and 19 and more particularly between 4 and 9.

Optional monomers:

30 As indicated previously, the copolymer according to the invention may be obtained by polymerization using a monomer mixture comprising, besides said monomer(s) (a) and said monomer(s) (b), one or more additional monomers, different from the monomers (a) and (b), noted “monomers (c)” in the rest of the text.

The additional monomers (c) may be chosen more particularly from:

- 2-acrylamino-2-methylpropane sulfonic acid (AMPS);
- vinylsulfonates, in particular sodium styrene sulfonate;
- 5 - amines;
- esters containing a hydroxyl group, for example hydroxyethyl methacrylate (HEMA); hydroxyethyl acrylate; hydroxypropyl methacrylate and hydroxypropyl acrylate;
- alkylene glycol acrylate or methacrylate phosphates, in particular ethylene glycol
- 10 methacrylate phosphate or ethylene glycol acrylate phosphate;
- acrylamide or methacrylamide;
- phosphonic monomers, such as alkyl vinylphosphonates and alkyl phosphonates;
- the macromonomers of formula (VI) below:



in which:

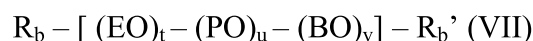
$[(EO)_q - (PO)_r - (BO)_s]$ represents a polyalkoxyl chain made of alkoxyl units, distributed in blocks, alternately or randomly, chosen from ethoxyl units EO, propoxyl units PO and butoxyl units BO;

20 q , r and s represent, independently of each other, 0 or an integer ranging between 1 and 250, the sum of m , n and p being between 10 and 250;

R_a represents a radical chosen from the group consisting of acrylic esters, methacrylic esters and a mixture of these esters; and

25 R_a' represents hydrogen or an alkyl group containing from 1 to 4 carbon atoms;

- the hydrophobic monomers of formula (VII) below:



in which:

30 $[(EO)_t - (PO)_u - (BO)_v]$ represents a polyalkoxyl chain made of alkoxyl units, distributed in blocks, alternately or randomly, chosen from ethoxyl units EO, propoxyl units PO and butoxyl units BO;

t, u and v represent, independently of each other, 0 or an integer ranging between 1 and 250, the sum of m, n and p being between 10 and 250;

R_b represents a radical chosen from the group consisting of acrylic esters, methacrylic esters and a mixture of these esters; and

5 R_b' represents an alkyl group containing from 8 to 40 carbon atoms, crosslinking monomers.

According to a particular embodiment, in the abovementioned formula (VI), s is equal to 0; and q and r represent an integer ranging between 1 and 250, for example between 10
10 and 150 or between 10 and 100.

According to a particular embodiment, in the abovementioned formula (VII), v is equal to 0; and t and u represent an integer ranging between 1 and 250, for example between 10 and 150 or between 10 and 100.

15 Said additional monomer(s) (c) may also be chosen from crosslinking monomers.

The copolymer according to the invention may, for example, comprise a single crosslinking monomer.

20 According to another embodiment, it comprises two different crosslinking monomers.

The crosslinking monomer may have a hydrophilic, hydrophobic or amphiphilic nature.

25 Examples of these compounds include di(meth)acrylate compounds such as polyalkylene glycol di(meth)acrylate, especially polypropylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,6-butylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate,
30 1,9-nonanediol di(meth)acrylate, but also 2,2'-bis(4-(acryloxypropyloxyphenyl)propane, 2,2'-bis(4-(acryoxydiethoxyphenyl)propane and zinc acrylate; tri(meth)acrylate compounds such as trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, pentaerythritol tri(meth)acrylate and tetramethylolmethane tri(meth)acrylate; tetra(meth)acrylate compounds such as ditrimethylolpropane

tetra(meth)acrylate, tetramethylolmethane tetra(meth)acrylate and pentaerythritol tetra(meth)acrylate; hexa(meth)acrylate compounds such as dipentaerythritol hexa(meth)acrylate; penta(meth)acrylate compounds such as dipentaerythritol penta(meth)acrylate; allyl compounds such as allyl (meth)acrylate, diallyl phthalate, diallyl itaconate, diallyl fumarate and diallyl maleate; polyallyl sucrose ethers containing from 2 to 8 groups per molecule, polyallyl pentaerythritol ethers such as pentaerythritol diallyl ether, pentaerythritol triallyl ether and pentaerythritol tetraallyl ether; polyallyl trimethylolpropane ethers such as diallyl trimethylolpropane ether and triallyl trimethylolpropane ether. Other polyunsaturated compounds include divinyl glycol, divinylbenzene, divinylcyclohexyl and methylenebisacrylamide.

According to another aspect, the crosslinking monomers may be prepared via an esterification reaction of a polyol with an unsaturated anhydride such as maleic anhydride, itaconic anhydride or (meth)acrylic anhydride, or via an addition reaction with an isocyanate such as 3-isopropenyldimethylbenzene isocyanate.

Use may also be made of the following compounds to obtain crosslinking monomers: polyhaloalkanols such as 1,3-dichloroisopropanol and 1,3-dibromoisopropanol; haloepoxyalkanes such as epichlorohydrin, epibromohydrin, 2-methylepichlorohydrin and epiiodohydrin; polyglycidyl ethers such as 1,4-butanediol diglycidyl ether, glycerine 1,3-diglycidyl ether, ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, polypropylene glycol diglycidyl ether, bisphenol A-epichlorohydrin epoxy resin, and mixtures thereof.

According to a particular embodiment, the crosslinking monomer is chosen from (meth)acrylates bearing at least two polymerizable ethylenically unsaturated double bonds (prepared, for example, by esterification of (meth)acrylic acid with a linear or branched polyol containing from 2 to 12 carbon atoms and at least two hydroxyl groups), polyalkenyl polyether containing at least two polymerizable ethylenically unsaturated double bonds (prepared, for example, by etherification of alkenyl halide with a linear or branched polyol containing from 2 to 12 carbon atoms and at least two hydroxyl groups) and mixtures of these crosslinking monomers.

According to one embodiment of the present invention, the copolymer comprises two crosslinking monomers:

- 5 - said first crosslinking monomer being a (meth)acrylate containing at least two polymerizable ethylenically unsaturated double bonds (prepared, for example, by esterification of (meth)acrylic acid with a linear or branched polyol containing from 2 to 12 carbon atoms and at least two hydroxyl groups), and
- 10 - said second crosslinking monomer being a polyalkenyl polyether containing at least two polymerizable ethylenically unsaturated double bonds (prepared, for example, by etherification of alkenyl halide with a linear or branched polyol containing from 2 to 12 carbon atoms and at least two hydroxyl groups).

According to another embodiment, the copolymer comprises two crosslinking monomers of different nature, for example trimethylolpropane tri(meth)acrylate (TMPTA or 15 TMPTMA) and trimethylolpropane diallyl ether (TMPDAE).

It is understood that the content of additional monomer(s) implemented, for example of crosslinking monomer(s), is adjusted so as not to alter the desired properties of the copolymer.

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In general, said additional monomer(s) (c) may represent less than 20 mol%, in particular less than 15 mol%, especially less than 10 mol% and more particularly less than 5 mol% of the total number of moles of constituent monomers in the copolymer according to the invention.

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The various particular modes described for each of the monomers included in the composition of the copolymer according to the invention may be combined.

According to a particular embodiment, the copolymer according to the invention may 30 thus be obtained by polymerization using a monomer mixture comprising, or even being formed from:

- one or more anionic monomers (a) chosen from acrylic acid, methacrylic acid and mixtures thereof, in particular acrylic acid; and

- one or more monomers (b) of the abovementioned formula (I'), in particular of the abovementioned formula (II), in which the ethoxyl and propoxyl units are more particularly distributed in blocks.

5 According to a particular embodiment, the copolymer according to the invention comprises at least units derived from acrylic acid and units derived from a monomer of formula (II), in particular of formula (III), as described previously.

10 According to a first particular embodiment, the copolymer according to the invention is obtained by polymerization of at least:

- 50 to 99 mol% of at least one anionic monomer (a), in particular as defined previously; and
- 1 to 50 mol% of at least one monomer (b) of formula (I), in particular as defined previously,

15 the molar percentages of each monomer being expressed relative to the total number of moles of constituent monomers of the copolymer.

According to a second particular embodiment, the copolymer according to the invention is obtained by polymerization of at least:

- 20
- 70 to 95 mol% of at least one anionic monomer (a), in particular as defined previously; and
 - 5 to 30 mol% of at least one monomer (b) of formula (I), in particular as defined previously;

the molar percentages of each monomer being expressed relative to the total number of moles of constituent monomers of the copolymer.

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According to a third particular embodiment, the copolymer according to the invention is obtained by polymerization of at least:

- 30
- 80 to 90 mol% of at least one anionic monomer (a), in particular as defined previously; and
 - 10 to 20 mol% of at least one monomer (b) of formula (I), in particular as defined previously;

the molar percentages of each monomer being expressed relative to the total number of moles of constituent monomers of the copolymer.

According to these three particular embodiments, the sum of the molar percentages of the monomers (a) and of the monomers (b) is equal to 100%. In other words, the copolymer is, according to these three embodiments of the invention, formed solely from units derived from the monomers (a) and (b) in the indicated molar proportions.

The copolymer according to the invention may have a weight-average molecular mass M_w of between 15 000 and 250 000 g/mol, in particular between 20 000 and 200 000 g/mol and more particularly between 25 000 and 175 000 g/mol.

10

The weight-average molecular mass or M_w may be determined by size exclusion chromatography (SEC), as described more precisely in the example that follows.

The copolymer according to the invention may be prepared in the form of salts, which may or may not be stoichiometric, and may or may not be mixed, and made with alkali metals, alkaline-earth metals, amines or quaternary ammoniums.

15

According to a particular embodiment, the copolymer according to the invention is in acid form.

20

According to another embodiment, the copolymer according to the invention is in neutralized form.

According to yet another embodiment, the copolymer according to the invention is in partially or totally neutralized form.

25

According to a particular embodiment, the copolymer is neutralized with an ion chosen from the group consisting of the potassium ion, the sodium ion, the lithium ion, the calcium ion, the magnesium ion, the ammonium ion, the diethanolammonium ion, and a mixture of these ions.

30

The copolymer according to the invention may be prepared via conventional polymerization techniques using the monomers (a), (b) and optionally (c).

According to an implementation variant, the copolymer according to the invention may be obtained by radical polymerization, especially by controlled radical polymerization.

AREAS OF APPLICATION:

- 5 As mentioned previously, the copolymers according to the invention are particularly efficient as water-reducing agents in hydraulic compositions.

According to another of its aspects, the invention thus relates to the use of a copolymer as defined previously as a water-reducing agent in a hydraulic composition.

10

The invention also relates to a water-reducing agent for hydraulic compositions comprising, or even consisting of, one or more copolymers as defined previously.

15

Preferably, the water-reducing agent consists of a copolymer or a mixture of copolymers according to the invention.

20

The water-reducing agent may be implemented in various forms, in particular in liquid form. It may especially be in the form of an aqueous solution of one or more copolymers according to the invention, the solids content of which may more particularly be between 25 and 65%, for example between 30 and 60%.

According to yet another of its aspects, the invention relates to a hydraulic composition comprising at least one copolymer according to the invention.

- 25 The hydraulic compositions may be of diverse nature. They may be intended for the manufacture of a grout, a putty, an adhesive, a concrete or a mortar. They may comprise impurities, for example clays. These compositions may especially comprise latices, fibers, organic aggregates, inorganic aggregates, fillers and/or CaCO_3 .

- 30 The hydraulic compositions, for example the concrete and mortar compositions, for which the water-reducing agent according to the invention may be useful may comprise as hydraulic binder various types of cements, for instance the cements CEM I, CEM II, CEM III, CEM IV and CEM V as described in standard EN 197-1. Among these, the cements CEM I do not comprise any additive. It is, nevertheless, possible to add to these

cements slags, fly ash, or calcium fillers, or siliceous fillers. The concrete compositions may be concretes of different strength classes, such as C20/25 to C100/115.

5 The hydraulic composition may be more particularly an aqueous formulation comprising, besides said copolymer(s) according to the invention, water and at least one hydraulic binder. It may also optionally comprise one or more additional additives.

10 The hydraulic binder may comprise at least one cement, for example a Portland cement. Examples that may also be mentioned include hydraulic binders of aluminous cement type and sulfo-alumino calcic cement.

The hydraulic composition may be, for example, a ready-mix concrete.

15 The hydraulic composition according to the invention may comprise, for example, from 8 to 75% by weight, for example from 10 to 50% or from 10 to 40% by weight of hydraulic binder, relative to the total weight of the hydraulic composition.

20 The water-reducing agent according to the invention may, for example, be incorporated at the time of mixing of the concrete.

The water-reducing agent according to the invention may be implemented in a proportion of from 0.05 to 3% by weight of copolymer(s), in particular from 0.25 to 2.5% by weight, relative to the total weight of the composition.

25 It falls to a person skilled in the art to adjust the amount of water-reducing agent according to the invention with regard to the targeted hydraulic composition. The dosing of the water-reducing agent depends mainly on the amount of hydraulic binder in the hydraulic composition.

30 According to a particular embodiment, the hydraulic composition according to the invention comprises, relative to the total weight of the composition:

- from 2 to 15% by weight of water;
- from 10 to 30% by weight of hydraulic binder comprising a cement; and

- from 0.05 to 3% by weight of one or more copolymers according to the invention.

According to this embodiment, the hydraulic composition according to the invention
5 may also comprise, in addition, from 10 to 60% by weight of sand.

According to a particular embodiment, the hydraulic composition according to the invention may comprise, relative to the total weight of the composition:

- from 2 to 15% by weight of water;
- 10 - from 10 to 30% by weight of hydraulic binder comprising a cement;
- from 0.05 to 3% by weight of one or more copolymers according to the invention;
- from 10 to 60% by weight of sand; and
- from 10 to 60% by weight of one or more gravels.

15

Needless to say, the invention is not in any way limited to these particular embodiments.

A hydraulic composition according to the invention may comprise various ingredients conventionally implemented in the field of hydraulic compositions, chosen in particular
20 from sand, gravels, aggregates, fine or ultrafine fillers, for example calcium carbonate or silica, antifoams, thickeners, stabilizers, biocidal or antibacterial agents, and setting accelerators or retarders.

The present invention also relates to the use of a water-reducing agent according to the
25 invention for preparing a hydraulic composition in particular comprising water and a hydraulic binder itself comprising a cement.

The invention will now be described by means of the example that follows, which is given as a nonlimiting illustration of the invention.

30

EXAMPLE:

1. Preparation of the hydraulic compositions:

1.1. Preparation of the copolymers:

Measurement of the molecular mass of the copolymers:

The molecular mass of the copolymers is determined by size exclusion chromatography (SEC).

5

Such a technique implements a WATERSTM brand liquid chromatography machine equipped with two detectors. One of these detectors combines static dynamic light scattering at an angle of 90° with viscometry measured with a VISCOTEKTM MALVERNTM viscometer detector. The other of these detectors is a WATERSTM brand
10 refractometric concentration detector.

15

This liquid chromatography machine is equipped with size exclusion columns suitably chosen by a person skilled in the art so as to separate the various molecular weights of the polymers studied. The liquid elution phase is an aqueous phase containing 1% KNO₃.

20

In a detailed manner, in a first step, 0.9% by dry weight of the polymerization solution is diluted in the SEC eluent, which is a 1% KNO₃ solution. The resulting solution is then filtered through a 0.2 µm filter. 100 µL are then injected into the chromatography machine (eluent: 1% KNO₃ solution).

25

The liquid chromatography machine contains an isocratic pump (WATERSTM 515) whose flow rate is set at 0.8 ml/min. The chromatography machine also comprises an oven, which itself comprises in series the following column system: a WATERSTM ULTRAHYDROGEL GUARD COLUMN precolumn 6 cm long and with an inside diameter of 40 mm, a WATERSTM ULTRAHYDROGEL linear column 30 cm long and with an inside diameter of 7.8 mm, and two WATERSTM 120 Å ULTRAHYDROGEL columns 30 cm long and with an inside diameter of 7.8 mm.

30

The detection system, for its part, is composed firstly of a WATERSTM RI 410 refractometric detector and secondly of a MALVERNTM 270 DUAL DETECTOR viscometer and 90° angle light scattering dual detector. The oven is brought to a temperature of 55°C, and the refractometer is brought to a temperature of 45°C.

The chromatography machine is calibrated with a single 19k PEO standard of MALVERNTM PolyCALTM type.

• Copolymer A (not in accordance with the invention):

5 Copolymer A is obtained by polymerization using a monomer mixture formed from:

- 85.9 mol% of acrylic acid; and
- 4.1 mol% of methallyl polyethylene glycol (Mw = 2400 g/mol).

Protocol for synthesizing copolymer A:

10 The chemical products used are:

- 0.33 g of iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$),
- 6.0 g of DMDO (1,8-dimercapto-3,6-dioxaoctane, CAS No.: 14970-87-7),
- 891.8 g of 60% methallyl polyethylene glycol (Mw = 2400 g/mol),
- 97.5 g of acrylic acid,
- 15 - 16.8 g of 35% aqueous hydrogen peroxide solution,
- 16.9 g of 40% sodium bisulfite.

The iron sulfate, 20% of the DMDO and 90% of the 60% methallyl polyethylene glycol are introduced into the reactor containing 150 g of water. The reactor is heated to
20 55-60°C. Acrylic acid, a solution containing the remainder of the DMDO and of the 60% methallyl polyethylene glycol, the aqueous hydrogen peroxide solution and a sodium bisulfite solution are injected in parallel into the reactor over 1 hour 40 minutes. The injection tubes are rinsed with 120 g of water and the reactor is maintained at a temperature of 58-62°C for 1 hour 30 minutes.

25

The product is cooled and then neutralized by adding 109.4 g of 50% NaOH.

Copolymer A obtained has a molecular mass, measured as described previously, of
30 160 300 g/mol.

• Copolymer B (in accordance with the invention):

Copolymer B is obtained by polymerization using a monomer mixture formed from:

- 83.4 mol% of acrylic acid; and

- 16.6 mol% of monomers (b) of formula (I') in which R_1 represents CH_3 and the polyalkoxyl chain, with a mean molar mass of 1990 g/mol, is formed to 75 mol% from ethoxyl units and 25 mol% of propoxyl units, the ethoxyl and propoxyl units being distributed in blocks.

5

Protocol for synthesizing copolymer B:

The chemical products used are:

- 0.31 g of iron sulfate ($FeSO_4 \cdot 7H_2O$),
- 2.0 g of DMDO,
- 10 - 297.3 g of monomers (b),
- 32.5 g of acrylic acid,
- 8.4 g of 35% aqueous hydrogen peroxide solution,
- 8.5 g of 40% sodium bisulfite.

- 15 The iron sulfate, 20% of the DMDO and 90% of the 60% methallyl polyoxyalkylene glycol are introduced into the reactor containing 50 g of water. The reactor is heated to 55-60°C. The acrylic acid, a solution containing the remainder of the DMDO and of 60% methallyl polyoxyalkylene glycol, the aqueous hydrogen peroxide solution and a sodium bisulfite solution are injected in parallel into the reactor over 1 hour 40 minutes.
- 20 The injection tubes are rinsed with 120 g of water and the reactor is maintained at a temperature of 58-62°C for 1 hour 30 minutes.

The product is cooled and then neutralized by adding 109.4 g of 50% NaOH.

- 25 Copolymer B obtained has a molecular mass, measured as described previously, of 172 500 g/mol.

• Copolymer C (in accordance with the invention):

Copolymer C is obtained by polymerization using a mixture formed from:

- 30 - 87.2 mol% of acrylic acid; and
- 12.7 mol% of monomers (b) of formula (I') in which R_1 represents CH_3 and the polyalkoxyl chain, with a mean molar mass of 2700 g/mol, is formed to 88 mol% of ethoxyl units and to 12 mol% of propoxyl units, the ethoxyl and propoxyl units being distributed in blocks.

Protocol for synthesizing copolymer C:

Copolymer C is prepared according to a procedure similar to that described previously for copolymer B.

- 5 Copolymer C obtained has a molecular mass, measured as described previously, of 156 900 g/mol.

1.2. Preparation of the hydraulic compositions:

- 10 In each of the tests, a concrete (350 kg/m^3) is prepared according to standard EN 480-1 by mixing, with stirring, standardized sand (0/4), cement (CEM I 52.5N Holcim), 4/11 and 11/22 gravels, water and an antifoam.

No admixture is added to composition 1 (reference).

- 15 The concrete formulations 2 to 4 are admixed, respectively, with the solutions of copolymers A, B and C prepared as described previously.

- 20 For the preparation of the concrete formulations 2 to 4 incorporating, respectively, copolymers A, B and C, the water/cement weight ratio is adjusted so as to conserve an initial workability similar to that of the reference concrete.

The proportions of each of the constituents of the hydraulic compositions thus prepared are indicated in table 1 below.

- 25 2. Evaluation of the hydraulic compositions:

The compositions are evaluated for their initial fluidity properties (workability at T0), air capture and water reduction properties according to the following protocols.

Measurement of the workability at T0:

- 30 Measurement of the initial fluidity (or workability at T0) is performed at room temperature, using a bottomless cone, of frustoconical shape, made of galvanized steel, known as an Abrams cone, according to standard EN 12350-2. This cone has the following characteristics: upper diameter: $100 \pm 2 \text{ mm}$, lower diameter: $200 \pm 2 \text{ mm}$, height: $300 \pm 2 \text{ mm}$.

The cone is placed on a plate moistened with a sponge.

The cone is then filled with a given amount of each of the preparations. The filling lasts
5 for 2 minutes. The content of the cone is packed using a metal rod.

At the end of filling, the cone is raised vertically, which leads to the slump of its content onto the plate.

10 The concretes may be classified as a function of their workability according to standard EN 206-1.

Measurement of the water reduction:

This is measured according to standard ADMIXTURE NF EN 934-2.

15

The results obtained for the various hydraulic compositions are given in table 1 below.

Test	Composition 1 (negative reference)	Composition 2 (not in accordance)	Composition 3 (in accordance)	Composition 4 (in accordance)
Sand (kg)	34.4	34.4	34.4	34.4
Gravel 4/11 (kg)	15.2	15.2	15.2	15.2
Gravel 11/22 (kg)	24.2	24.2	24.2	24.2
Cement (kg)	14	14	14	14
Admixture (g)	-	Copolymer A (80.9)	Copolymer B (87.9)	Copolymer C (81.1)
Solids content of the admixture	-	39.8 %	36.6 %	39.7 %
Dry % admixture/cement	-	0.23	0.23	0.23

Antifoam (%/admixture)	-	0.5	0.5	0.5
Water (g)	9742	8320	6250	7032
Water/cement weight ratio	0.70	0.59	0.45	0.50
Workability T0	220	220	200	210
Water reduction	0	15 %	36 %	28 %

TABLE 1

The hydraulic compositions all have a homogeneous appearance, without segregation of the constituents.

5

The implementation of copolymers B and C according to the invention makes it possible to reduce the amount of water by 36% and 28%, respectively, in the hydraulic composition, while at the same time maintaining initial fluidity (workability) similar to that of the negative reference.

10

The copolymers according to the invention may be characterized as “high-efficiency water-reducing agents” in accordance with standard ADMIXTURE NF EN 934-2 according to which the term “high-efficiency water-reducing agent” or “superplasticizer” defines an admixture which allows a water reduction for admixed concrete of at least 12% relative to reference concrete.

15

It is thus demonstrated that the copolymers according to the invention (copolymers B and C) make it possible to significantly reduce the amount of water in the hydraulic composition (36% and 28%, respectively) when compared with the implementation of copolymer A not in accordance with the invention (15%), without affecting the workability of said hydraulic composition.

20

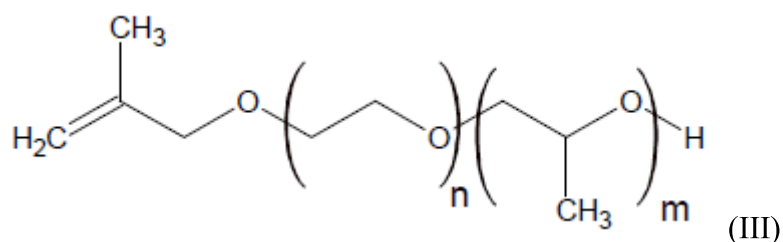
CLAIMS

1. A copolymer obtained by polymerization using a monomer mixture comprising:
 - at least 50 to 99 mol% of at least one anionic monomer (a) comprising a polymerizable unsaturated function and a carboxylic group; and
 - 5 - at least 1 to 50 mol% of at least one monomer (b) of formula (I):

$$\text{H}_2\text{C} = \text{C} (-\text{R}_1) - (\text{CH}_2)_p - \text{O} - [(\text{EO})_n - (\text{PO})_m] - \text{H} \text{ (I)}$$
 in which:
 R_1 represents a hydrogen atom or a CH_3 group;
 p is 1 or 2;
 - 10 $[(\text{EO})_n - (\text{PO})_m]$ represents a polyalkoxyl chain made of ethoxyl units EO and propoxyl units PO, distributed in blocks, alternately or randomly;
 m and n represent integers ranging between 1 and 250, the sum of m and n being greater than or equal to 10, with the proviso that the mole proportion of the ethoxyl units in the polyalkoxyl chain $(n)/(m+n)$ is greater than or
 - 15 equal to 70% and strictly less than 90%,
 wherein
 -the monomer (b) is water soluble, and
 -the sum of the molar percentages of each of the monomers is equal to 100%.
- 20 2. The copolymer as claimed in the preceding claim, in which said monomer(s) (b) are of formula (I') below:

$$\text{H}_2\text{C} = \text{C} (-\text{R}_1) - \text{CH}_2 - \text{O} - [(\text{EO})_n - (\text{PO})_m] - \text{H} \text{ (I')}$$
 in which R_1 , n and m are as defined in claim 1.
- 25 3. The copolymer as claimed in claim 1 or 2, characterized in that it is formed from at least one monomer (b) of formula (II) below:

$$\text{H}_2\text{C} = \text{C} (-\text{CH}_3) - \text{CH}_2 - \text{O} - [(\text{EO})_n - (\text{PO})_m] - \text{H} \text{ (II)}$$
 in which n and m are as defined in claim 1.
- 30 4. The copolymer as claimed in any one of the preceding claims, characterized in that it is formed from at least one monomer (b) of formula (III) below:

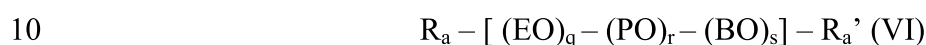


m and n being as defined in claim 1.

5. The copolymer as claimed in any one of the preceding claims, in which the mole proportion of the ethoxyl units in the polyalkoxyl chain of said monomer(s) (b) is between 70% and 88%, in particular is greater than or equal to 75%, and especially less than or equal to 85%, in particular less than or equal to 80%.
6. The copolymer as claimed in any one of the preceding claims, in which the total number of ethoxyl and propoxyl units (m+n) of the polyalkoxyl chain of the monomer (b) is between 10 and 150, in particular between 18 and 110 and more particularly between 20 and 70.
7. The copolymer as claimed in any one of the preceding claims, in which said monomer(s) (b) represent from 5 to 40 mol%, in particular from 5 to 30 mol% and more particularly from 10 to 20 mol%, of the total number of constituent moles of said copolymer.
8. The copolymer as claimed in any one of the preceding claims, in which said anionic monomer(s) (a) are chosen from the group consisting of acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, and mixtures of these monomers, and in particular are chosen from acrylic acid, methacrylic acid, and a mixture thereof.
9. The copolymer as claimed in any one of the preceding claims, in which said monomer(s) (a) represent from 60 to 95 mol%, in particular from 70 to 95 mol% and more particularly from 80 to 90 mol%, of the total number of moles of constituent monomers of said copolymer.

10. The copolymer as claimed in any one of the preceding claims, obtained by polymerization using a monomer mixture comprising, in addition of said anionic monomer(s) (a) and said monomer(s) (b) of formula (I), one or more monomers (c) chosen from:

- 5 - 2-acrylamino-2-methylpropane sulfonic acid (AMPS);
- vinylsulfonates, in particular sodium styrene sulfonate;
- amines;
- phosphonic monomers, such as alkyl vinylphosphonates and alkyl phosphonates;
- the macromonomers of formula (VI) below:



in which:

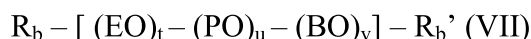
$[(EO)_q - (PO)_r - (BO)_s]$ represents a polyalkoxyl chain made of alkoxyl units, distributed in blocks, alternately or randomly, chosen from ethoxyl units EO, propoxyl units PO and butoxyl units BO;

15 q , r and s represent, independently of each other, 0 or an integer ranging between 1 and 250, the sum of m , n and p being between 10 and 250;

R_a represents a radical chosen from the group consisting of acrylic esters, methacrylic esters and a mixture of these esters; and

R_a' represents hydrogen or an alkyl group containing from 1 to 4 carbon
20 atoms;

- the hydrophobic monomers of formula (VII) below:



in which:

25 $[(EO)_t - (PO)_u - (BO)_v]$ represents a polyalkoxyl chain made of alkoxyl units, distributed in blocks, alternately or randomly, chosen from ethoxyl units EO, propoxyl units PO and butoxyl units BO;

t , u and v represent, independently of each other, 0 or an integer ranging between 1 and 250, the sum of m , n and p being between 10 and 250;

30 R_b represents a radical chosen from the group consisting of acrylic esters, methacrylic esters and a mixture of these esters; and

R_b' represents an alkyl group containing from 8 to 40 carbon atoms; and

- crosslinking monomers,

wherein the monomer (c) represent less than 20% , in particular less than 15%, especially less than 10% and more particularly less than 5%mol of the total number of moles of constituent monomers in the copolymer.

- 5 11. A hydraulic composition comprising at least one copolymer as defined according to any one of claims 1 to 10.
12. The composition as claimed in claim 11, comprising from 0.05 to 3% by weight of one or more copolymers as defined according to any one of claims 1 to 10, in
10 particular from 0.25 to 2.5% by weight, relative to the total weight of said composition.
13. The use of a copolymer as defined according to any one of claims 1 to 10, as a water-reducing agent in a hydraulic composition.
- 15 14. A water-reducing agent for hydraulic compositions comprising at least one copolymer as defined according to any one of claims 1 to 10.