(12) STANDARD PATENT (11) Application No. **AU 2009226812 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Semi continuous operational method for producing copolymers

(51) International Patent Classification(s)
C08F 220/04 (2006.01) ***C08F 220/26*** (2006.01)

(21) Application No: **2009226812** (22) Date of Filing: **2009.02.10**

(87) WIPO No: **WO09/115371**

(30) Priority Data

(31) Number	(32) Date	(33) Country
08102758.3	**2008.03.19**	**EP**

(43) Publication Date: **2009.09.24**
(44) Accepted Journal Date: **2013.08.15**

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(56) Related Art
D2 : US 2007/0161724 A1 (MORARU et al) 12 July 2007
D1 : US 2006/0183820 A1 (ASANO et al) 17 August 2006

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
24. September 2009 (24.09.2009)

PCT

(10) Internationale Veröffentlichungsnummer
WO 2009/115371 A1

(51) Internationale Patentklassifikation:
C08F 220/04 (2006.01) ***C08F 220/26*** (2006.01)

(21) Internationales Aktenzeichen: PCT/EP2009/051481

(22) Internationales Anmeldedatum:
10. Februar 2009 (10.02.2009)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
08102758.3 19. März 2008 (19.03.2008) EP

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(81) Bestimmungsstaaten *(soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Bestimmungsstaaten *(soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

— *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*

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(54) Title: SEMI CONTINUOUS OPERATIONAL METHOD FOR PRODUCING COPOLYMERS

(54) Bezeichnung: SEMIKONTINUIERLICH BETRIEBENES VERFAHREN ZUR HERSTELLUNG VON COPOLYMEREN

(57) Abstract: The invention relates to a method for producing a copolymer in a semi-continuous operational mode in a polymerisation device containing a polymerisation reactor that is connected to a dosing device. An acid monomer, and a polyether macromonomer and water are respectively introduced into the dosing device and the polymerisation reactor, said acid monomer being fed into the polymerisation reactor from the dosing device, and prior to and/or during the feeding process of the acid monomer into the polymerisation reactor, a radical polymerisation initiator is introduced into the polymerisation reactor such that an aqueous medium is obtained in the polymerisation reactor, in which the acid monomer and polyether macromonomer are converted by radical polymerisation in order to form the copolymer. The polyether macromonomer introduced into the polymerisation reactor is converted by radical polymerisation to at least 70 Mol -%. An acid structure unit is produced by converting the acid monomer into the copolymer, said acid structure unit lowering the pH-value of the aqueous medium to a lower amount than that of the acid monomer. Dosing of the acid monomer occurs in the polymerisation reactor in such a manner that a polymerisation pH value is set in the aqueous medium and then, as many acid monomers per time unit are introduced into the polymerisation reactor until the conversion of 70 Mol-% of the polyether macromonomer introduced into the polymerisation reactor is reached, such that the difference in the pH-value in the aqueous medium and the initially set polymerisation-pH-value is at most ± 0,3.

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur Herstellung eines Copolymers in semikontinuierlicher Betriebsweise in einer Polymerisationsvorrichtung enthaltend einen mit einer Dosiereinrichtung verbundenen Polymerisationsreaktor, wobei Säuremonomer in der Dosiereinrichtung sowie Polyethermakromonomer und Wasser in dem Polymerisationsreaktor jeweils vorgelegt werden, Säuremonomer aus der Dosiereinrichtung in den Polymerisationsreaktor eindosiert wird, vor und/oder während der Eindosierung des Säuremonomers in den Polymerisationsreaktor radikalischer Polymerisationsinitiator in den Polymerisationsreaktor eingeleitet wird, so dass in dem Polymerisationsreaktor ein wässriges Medium entsteht, in welchem Säuremonomer und Polyethermakromonomer unter Bildung des Copolymers durch radikalische

[Fortsetzung auf der nächsten Seite]

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Polymerisation umgesetzt werden, das in dem Polymerisationsreaktor vorgelegte Polyethermakromonomer zu mindestens 70 Mol-% durch die radikalische Polymerisation umgesetzt wird, durch die Umsetzung des Säuremonomers in dem Copolymer eine Säurestruktureinheit entsteht, welche sich auf den pH-Wert des wässrigen Mediums in einem geringeren Maße senkend auswirkt als das Säuremonomer als solches, wobei die Dosierung des Säuremonomers in den Polymerisationsreaktor in der Weise erfolgt, dass zunächst in dem wässrigen Medium ein Polymerisations-pH-Wert eingestellt wird und anschließend bis zur Umsetzung von 70 Mol-% des in dem Polymerisationsreaktor vorgelegten Polyethermakromonomers soviel Säuremonomer pro Zeiteinheit in den Polymerisationsreaktor eingeleitet wird, dass der pH-Wert in dem wässrigen Medium höchstens ± 0,3 vom zunächst eingestellten Polymerisations-pH-Wert abweicht.

Semi continuous operational method for producing copolymers

Description:

The present invention relates to a process for the preparation of a copolymer, the copolymer and the use of the copolymer.

It is known that admixtures in the form of dispersants are often added to aqueous slurries of pulverulent inorganic or organic substances, such as clays, silicate powder, chalk, carbon black, crushed rock and hydraulic binders, in order to improve their processability, i.e. kneadability, spreadability, sprayability, pumpability or flowability. Such admixtures are capable of breaking up solid agglomerates, dispersing the particles formed and in this way improving the processability. This effect is also utilized in a targeted manner in the preparation of building material mixtures which contain hydraulic binders, such as cement, lime, gypsum or anhydrite.

In order to convert these building material mixtures based on said binders into a ready-to-use, processable form, as a rule substantially more mixing water is required than would be necessary for the subsequent hydration or hardening process. The proportion of cavities formed by the excess, subsequently evaporating water in the concrete body leads to significantly poorer mechanical strengths and stabilities.

In order to reduce this excess proportion of water at a predetermined processing consistency and/or to improve the processability at a predetermined water/binder ratio, admixtures, which are generally referred to as water-reducing agents or super plasticizers, are used. In particular, copolymers which are prepared by free radical copolymerization of acid monomers with polyether macromonomers are used in practice as such compositions.

In practice, the copolymerization is generally effected by the semi-batch procedure. WO 2005/075529 describes a semicontinuous preparation process for said copolymers, in which the polyether macromonomer is initially introduced and the acid monomer is then metered into the initially introduced substance over time. Although the process described is already economical and high-performance superplasticizers are obtained as a product of the process, efforts are still being made further to improve the quality of the product of the process and to do so as far as possible without adversely affecting the cost-efficiency of the process to a substantial extent.

It is therefore an object of the present invention to provide an economical process for the preparation of copolymers which show good performance as dispersants for hydraulic binders, especially as superplasticizers/water-reducing agents.

This object is achieved by a process for the preparation of a copolymer in a semicontinuous mode of operation in a polymerization apparatus containing a polymerization reactor connected to a metering device, in each case acid monomer being initially introduced into the metering device and polyether macromonomer and water into the polymerization reactor, acid monomer being metered from the metering device into the polymerization reactor, free radical polymerization initiator being passed into the polymerization reactor before and/or during the metering of the acid monomer into the polymerization reactor, so that an aqueous medium forms in the polymerization reactor, in which aqueous medium acid monomer and polyether macromonomer are reacted by free radical polymerization with formation of the copolymer, at least 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor being converted by the free radical polymerization, the conversion of the acid monomer giving rise in the copolymer to an acid structural unit which reduces the pH of the aqueous medium to a lesser extent than the acid monomer as such, the metering of the acid monomer into the polymerization reactor being effected in such a way that first a polymerization pH is established in the aqueous medium and then, until the conversion of 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.3 from the initially established polymerization pH.

Acid monomer is to be understood as meaning monomers which are capable of free radical polymerization, have at least one carbon double bond, contain at least one acid function and react as an acid in the aqueous medium. Furthermore, acid monomer is also to be understood as meaning monomers capable of free radical polymerization, having at least one carbon double bond and, owing to the hydrolysis reaction in the aqueous medium, forming at least one acid function and reacting as an acid in the aqueous medium (example: maleic anhydride). In the context of the present invention, polyether macromonomers are compounds capable of free radical polymerization and having at least one carbon double bond and at least two ether oxygen atoms, with the proviso that the polyether macromonomer structural units present in the copolymer have side chains which contain at least two ether oxygen atoms.

It is not necessary initially to introduce all polyether macromonomer reacted by free radical polymerization in the polymerization reactor into the polymerization reactor before the acid monomer is metered in. However, preferably at least 50 mol%, particularly preferably at least 80 mol% and in many cases about 100% of the polyether macromonomer structural units are incorporated into the copolymer by reaction of polyether macromonomer which is initially introduced into the polymerization reactor before the acid monomer is metered in. The (usually) not more than 50 mol%, preferably (usually) not more than 20 mol% of the polyether macromonomer then optionally remaining are as a rule fed continuously to the polymerization reactor while the acid monomer has been metered in. Polyether macromonomer can be fed to the polymerization reactor separately from the acid monomer (cf. Synthesis example 4 below) and/or as a mixture with the acid monomer (by, for example, also initially introducing polyether macromonomer in addition to the acid monomer into the metering device).

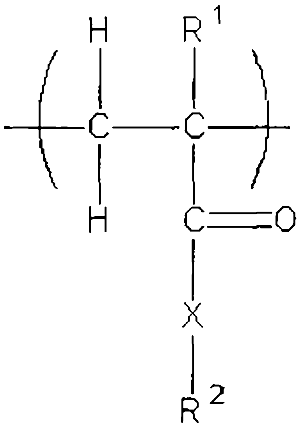
The circumstance that the conversion of the acid monomer into the copolymer results in the formation of an acid structural unit which reduces the pH of the aqueous medium to a lesser extent than the acid monomer as such means that the acid monomer has a higher acid strength than the corresponding acid structural unit in the copolymer (this situation occurs in the case of most acid monomers/acid monomer structural units).

The metering device may have various forms and can be manually and/or automatically controlled. In the case of manual control, for example, a person can read the relevant pH continuously on a pH meter which has been set up and can accordingly continuously meter in the acid monomer from a container. Automatic control can couple the feed rate of the acid monomer (preferably continuously) directly with the corresponding pH measuring signal.

A substantial advantage of the process according to the invention is that, owing to the special metering, it is possible to prepare strictly uniform copolymers – and to do so with respect to molecular weight (low dispersion index of the molecular weight distribution) and with regard to the relative proportion of the monomer structural units in the copolymer (chemical uniformity). This uniformity of the copolymer results in the end in particularly good suitability as a superplasticizer for hydraulic binders. The process according to the invention can also be regarded as being economical (a good effect is achieved with only little metering effort – "high metering efficiency").

In a preferred embodiment of the invention, the reaction of the acid monomer produces a structural unit in the copolymer, which unit is according to one of the general formulae (Ia), (Ib), (Ic) and/or (Id)

(Ia)



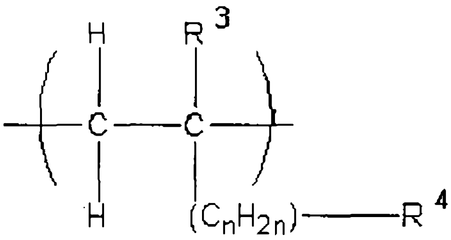
where

R^1 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

X is identical or different and is represented by NH-(C_nH_{2n}) where n = 1, 2, 3 or 4 and/or O-(C_nH_{2n}) where n = 1, 2, 3 or 4 and/or by a unit not present;

R^2 is identical or different and is represented by OH, SO_3H, PO_3H_2, O-PO_3H_2 and/or para-substituted C_6H_4-SO_3H, with the proviso that, if X is a unit not present, R^2 is represented by OH;

(Ib)



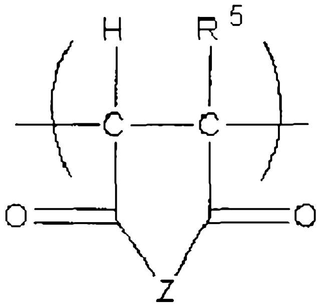
where

R^3 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

n = 0, 1, 2, 3 or 4;

R^4 is identical or different and is represented by SO_3H, PO_3H_2, O-PO_3H_2 and/or C_6H_4-SO_3H present in para-substituted form;

(Ic)

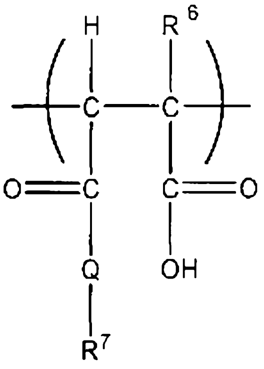


where

R^5 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

Z is identical or different and is represented by O and/or NH;

(Id)



where

R^6 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

Q is identical or different and is represented by NH and/or O;

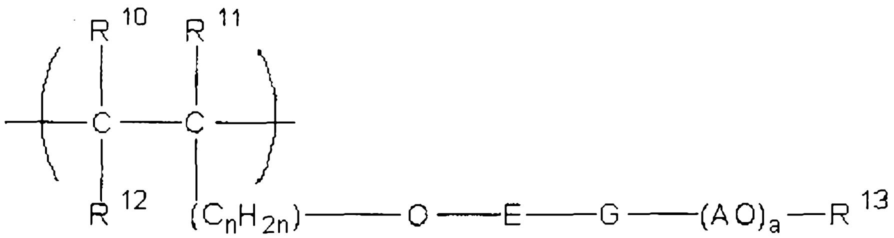
R^7 is identical or different and is represented by H, (C_nH_{2n})-SO_3H where n = 0, 1, 2, 3 or 4, (C_nH_{2n})-OH where n = 0, 1, 2, 3 or 4; (C_nH_{2n})-PO_3H_2 where n = 0, 1, 2, 3 or 4, (C_nH_{2n})-OPO_3H_2 where n = 0, 1, 2, 3 or 4, (C_6H_4)-SO_3H, (C_6H_4)-PO_3H_2, (C_6H_4)-OPO_3H_2 and/or $(C_mH_{2m})_e$-O-$(A'O)_\alpha$ -R^9 where m = 0, 1, 2, 3 or 4, e = 0, 1, 2, 3 or 4, A' = $C_{x'}H_{2x'}$ where x' = 2, 3, 4 or 5 and/or $CH_2C(C_6H_5)H$-, α= an integer from 1 to 350 with R^9 identical or different and represented by a straight-chain or branched C_1 - C_4 alkyl group.

It should be mentioned that acid functions in the copolymer which are presented above may be present at least partly in neutralized form.

Methacrylic acid, acrylic acid, maleic acid, maleic anhydride, a monoester of maleic acid or a mixture of a plurality of these components is used as the acid monomer.

In a preferred embodiment, the reaction of the polyether macromonomer produces in the copolymer a structural unit which is according to one of the general formulae (IIa), (IIb) and/or (IIc)

(IIa)



where

R^{10}, R^{11} and R^{12} are in each case identical or different and, independently of one another, are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6 alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in the ortho-, meta- or para-substituted form and/or a unit not present;

G is identical or different and is represented by O, NH and/or CO-NH, with the proviso that, if E is a unit not present, G is also present as a unit not present; and

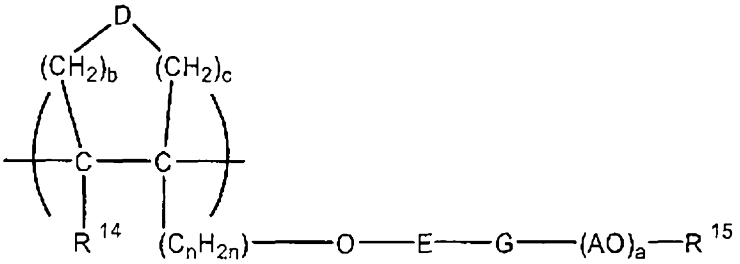
A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 (preferably x = 2) and/or $CH_2CH(C_6H_5)$;

n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

a is identical or different and is represented by an integer from 2 to 350 (preferably 10 - 200);

R^{13} is identical or different and is represented by H, a straight-chain or branched C_1 - C_4 alkyl group, CO-NH_2, and/or $COCH_3$;

(IIb)



where

R^{14} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6 alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in ortho-, meta- or para-substituted form and/or by a unit not present;

G is identical or different and is represented by a unit not present, or O, NH and/or CO-NH, with the proviso that, if E is a unit not present, G is also present as a unit not present;

A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or $CH_2CH(C_6H_5)$;

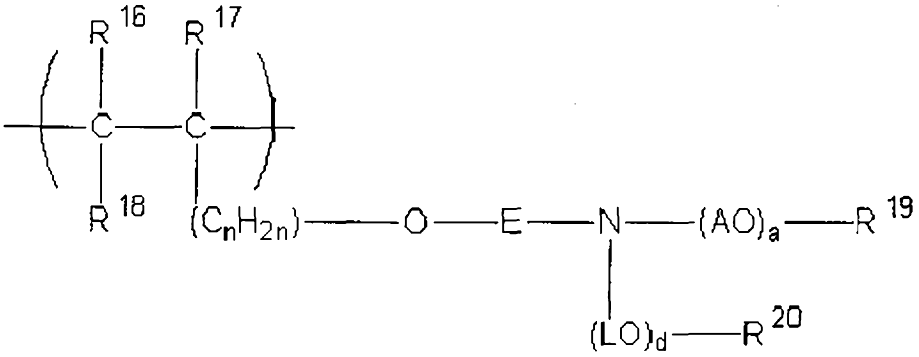
n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

a is identical or different and is represented by an integer from 2 to 350;

D is identical or different and is represented by a unit not present, NH and/or O, with the proviso that, if D is a unit not present: b = 0, 1, 2, 3 or 4 and c = 0, 1, 2, 3 or 4, where b + c = 3 or 4, and
with the proviso that, if D is NH and/or O: b = 0, 1, 2 or 3, c = 0, 1, 2 or 3, where b + c = 2 or 3;

R^{15} is identical or different and is represented by H, a straight-chain or branched C_1 - C_4 alkyl group, CO-NH_2, and/or $COCH_3$;

(IIc)



$$-\left(C(R^{16})(R^{18})-C(R^{17})\left[(C_nH_{2n})-O-E-N\left[(LO)_d-R^{20}\right]-(AO)_a-R^{19}\right]\right)-$$

where

R^{16}, R^{17} and R^{18} are in each case identical or different and, independently of one another, are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6

alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in ortho-, meta- or para-substituted form and/or by a unit not present;

A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or $CH_2CH(C_6H_5)$;

n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

L is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or CH_2-$CH(C_6H_5)$;

a is identical or different and is represented by an integer from 2 to 350;

d is identical or different and is represented by an integer from 1 to 350;

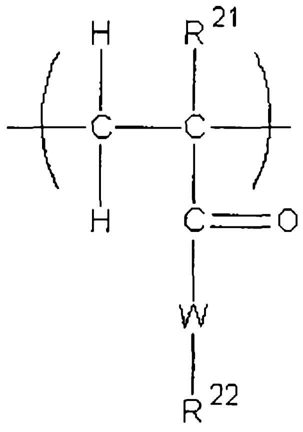
R^{19} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group,

R^{20} is identical or different and is represented by H and/or a straight-chain C_1 - C_4 alkyl group.

A preferably used polyether macromonomer is alkoxylated isoprenol and/or alkoxylated hydroxybutyl vinyl ether and/or alkoxylated (meth)allyl alcohol and/or vinylated methylpolyalkylene glycol having preferably in each case an arithmetic mean number of oxyalkylene groups of 4 to 400.

In addition to the acid monomer and the polyether macromonomer, further monomer types may also be used. These are then reacted as a rule so that in practice a vinylically unsaturated compound is passed into the polymerization reactor as monomeric starting material, which compound is reacted by polymerization and thereby produces in the copolymer a structural unit which is present according to the general formula (IIIa) and/or (IIIb)

(IIIa)



$$-\left(\overset{H}{\underset{H}{C}}-\overset{R^{21}}{\underset{C(=O)-W-R^{22}}{C}}\right)-$$

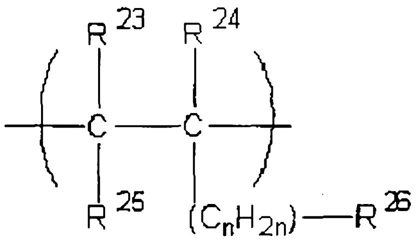
where

R^{21} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group (preferably H or CH_3);

W is identical or different and is represented by O and/or NH;

R^{22} is identical or different and is represented by a branched or straight-chain C_1 - C_5-monohydroxyalkyl group (C_1, C_2, C_3, C_4 or C_5 is in each case typical but C_2 and/or C_3 is preferred);

(IIIb)



where

R^{23}, R^{24} and R^{25} are in each case identical or different and, in each case independently, are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group (preferably H and/or CH_3);

n is identical or different and is represented by 0, 1, 2, 3 and/or 4;

R^{26} is identical or different and is represented by (C_6H_5), OH and/or $-COCH_3$.

Typical monomers which produce the structural units (IIIa) or (IIIb) by polymerization are, for example, 2-hydroxypropyl acrylate, isoprenol or allyl alcohol. In this context, hydroxybutyl vinyl ether could also be mentioned as a further typical monomer.

Usually, altogether at least 45 mol%, but preferably at least 80 mol%, of all structural units of the copolymer are produced by free radical polymerization of acid monomer and polyether macromonomer.

In a preferred embodiment, polyether macromonomer is initially introduced into the polymerization reactor in an amount per mole of acid monomer metered in such that an arithmetic mean molar ratio of acid monomer structural units to polyether macromonomer structural units to polyether macromonomer structural units of 20:1 to

1:1, preferably of 12:1 to 1:1, is established in the copolymer formed.

As a rule, a redox initiator is used as the free radical polymerization initiator. In general, the system $H_2O_2/FeSO_4$ is then chosen as the redox initiator, preferably together with a reducing agent. Sodium sulphite, the disodium salt of 2-hydroxy-2-sulphinatoacetic acid, disodium salt of 2-hydroxy-2-sulphonatoacetic acid, sodium hydroxymethanesulphinate, ascorbic acid, isoascorbic acid or mixtures thereof are suitable as reducing agents. Other systems are also suitable as the redox initiator system, for example those which are based on tert-butyl hydroperoxide, ammonium peroxodisulphate or potassium peroxodisulphate.

In one embodiment, initiator components, e.g. H_2O_2, and the polyether macromonomer are passed simultaneously in premixed form (preferably in one stream) into the polymerization reactor.

In principle, however, all compounds decomposing into free radicals under polymerization conditions can be used as initiators, such as, for example, peroxides, hydroperoxides, persulphates, azo compounds and perphosphates. When the free radical formers are combined with suitable reducing agents, known redox systems or redox catalysts are obtained. Suitable reducing agents are, for example, sodium sulphite, the disodium salt of 2-hydroxy-2-sulphonatoacetic acid, the disodium salt of 2-hydroxy-2-sulphinatoacetic acid, sodium hydroxymethanesulphinate, ascorbic acid, iso-ascorbic acid, amines, such as diethanolamine or triethanolamine, hydroxylamine or mixtures thereof. Expediently, water-soluble salts of transition metals, such as iron, cobalt, nickel or silver, are additionally employed with the use of redox systems or catalysts, iron salts (present predominantly in divalent form) preferably being used here.

In general, a component of the redox initiator system and/or reducing agent is passed into the polymerization reactor after the polymerization pH has been established and during the metering in of the acid monomer.

As a rule, the polymerization pH in the aqueous medium is established so that, with regard to the free radical polymerization initiator used, the free radical formation per unit time (free radical yield) is high, preferably approximately maximum. The polymerization initiator used or the polymerization initiator system used thus so to speak usually approximately already predetermines the polymerization pH.

Typically, the aqueous medium is present in the form of an aqueous solution.

Usually, the polymerization reactor is present as a semicontinuous stirred tank.

Frequently, at least 80 mol%, preferably at least 90 mol%, of the polyether macromonomer initially introduced into the polymerization reactor is converted by the free radical polymerization.

As a rule, a conversion of 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.2, preferably not more than ± 0.1 (ideally not at all) from the initially established polymerization pH.

In general, at least 80 mol% of the polyether macromonomer initially introduced into the polymerization reactor is converted by the free radical polymerization and, until conversion of 80 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.3 from the initially established polymerization pH.

Usually, the polymerization pH is 4.0 to 7.0, preferably 4.5 to 6.5 and particularly preferably 4.8 to 6.0 and the temperature of the aqueous medium during the free radical polymerization is 0 to 90°C, preferably 10 to 35°C.

Preferably, the acid monomer is initially introduced together with water into the metering unit and an aqueous solution of the acid monomer is metered from the metering unit into the polymerization reactor, it being possible for a portion of the acid monomer to be converted by the addition of base into the corresponding acid monomer salt before being metered into the polymerization reactor. Such a partial neutralization of the acid monomer effected beforehand can be used in addition to the metering rate as a further control parameter for regulating the pH in the aqueous medium.

As a rule, the polymerization pH in the aqueous medium is established by metering the acid monomer into the polymerization reactor and optionally by adding a base to the polymerization reactor and/or to the metering device so that acid monomer and/or acid monomer salt may be present in the polymerization reactor even before the polymerization pH is established.

In general, a chain regulator, which is preferably present in dissolved form, is passed into the polymerization reactor.

The invention also relates to a copolymer which can be prepared by the process described above. The copolymer according to the invention is usually present as a comb polymer.

The invention furthermore relates to the use of the copolymer according to the invention as a dispersant for hydraulic binders or for latent hydraulic binders.

Below, the invention is to be described in more detail with reference to working examples.

Synthesis examples and comparative examples

Synthesis Example 1

200 g of demineralized water and 225 g (0.075 mol) of vinyloxybutyl polyethylene glycol-3000 (adduct of 65 mol of ethylene oxide with hydroxybutyl monovinyl ether having an average molecular weight of 3000 g/mol) were initially introduced into a glass reactor equipped with a stirrer, pH electrode and a plurality of feed devices and were cooled to a polymerization starting temperature of 15°C (initially introduced mixture).

16.2 g (0.2025 mol) of acrylic acid were homogeneously mixed with 42 g of demineralized water in a separate feed vessel. The solution was adjusted, with cooling, to a temperature of 20°C and a pH of 4.0 with 7.7 g of a 40% strength potassium hydroxide solution. 0.7 g of 3-mercaptopropionic acid was then added as a molecular weight regulator (solution A).

At the same time, a second solution consisting of 1.5 g of Brüggolit FF6 (from Brüggemann GmbH) and 23.5 g of water was prepared (solution B).

23.3 g of solution A and then 1.8 g of a 20% strength aqueous sodium hydroxide solution were added to the initially introduced mixture with stirring and cooling so that a pH of 5.8 resulted.

After this pH had been reached, 0.015 g of iron(II) sulphate heptahydrate, 0.1 g of solution B and 0.94 g of hydrogen peroxide (30% in water) were added in succession to the initially introduced mixture. At the same time, the addition of solution A and solution B to the stirred and initially introduced mixture was started.
The feed rate of solution A was modified here according to the following metering profile so that the pH in the initially introduced mixture over the entire period of addition of 45 minutes was kept constant at a value of 5.8 +/- 0.1:

t (min)	0	1.5	3	6	9	12	15	18	21	24	27	30	33	36	39	45
Solution A (g/h)	29	59	103	123	115	103	88	71	56	44	35	26	21	15	13	0

Solution B was added simultaneously over the same period of 45 minutes at a metering rate of 7 g/h. Thereafter, the metering rate of solution B was increased to 50 g/h and pumped into the initially introduced mixture over a period of 10 minutes with stirring. After complete addition of solutions A and B, peroxide was no longer found in the reaction vessel.

The polymer solution obtained was then adjusted to a pH of 6.5 with about 10 g of a 20% strength sodium hydroxide solution.

The copolymer obtained occurred as slightly yellow solution which had a solids content of 46.5%. The average molecular weight of the copolymer was Mw 63000 g/mol; Mp 48000 g/mol; residual PEG: 11%; polydispersity 1.63.

Comparative example 1-1:

Example 1 was repeated with the difference that only 1.2 g of 20% NaOH was required for establishing the pH of 5.8 in the initially introduced mixture and the metering of solution A was effected at a constant rate of 58 g/h over a period of 45 minutes. First, an increase of the pH to a maximum value of 6.2 after 12 minutes was observed and, in the further course of the addition of solution A, a reduction at the end of the addition to 5.8. The solids content of the copolymer solution obtained was 47%. The average molecular weight was Mw 66000 g/mol or Mp 47000 g/mol with a residual proportion of PEG of 14% and a polydispersity of 1.78.

Comparative example 1-2:

Synthesis example 1 was repeated analogously to Comparative example 1-1 with a linear metering rate of solution A. However, the increase of the pH in the polymerization mixture which was observed in the first 12 minutes of the addition of A was corrected by addition of 25% strength sulphuric acid, and the decrease of the pH observed from 13 minutes was corrected by addition of 20% strength aqueous sodium hydroxide solution, so that the measured pH in the reactor could be kept constant at 5.8 +/- 0.1.

Synthesis example 2:

The procedure was as in Synthesis example 1, but the 3-mercaptopropionic acid was added separately and the following monomer combination was used:

Initially introduced mixture:

Vinyloxybutylpolyethylene glycol-1100:	85.8 g (0.078 mol)
Vinyloxybutylpolyethylene glycol-5800:	127.6 g (0.022 mol)
in demineralized water:	210.0 g

Solution A:

Maleic anhydride:	7.8 g (0.08 mol)
Acrylic acid:	2.9 g (0.04 mol)
Hydroxypropyl acrylate:	10.4 g (0.08 mol)
Hydroxyethyl acrylate:	4.6 g (0.04 mol)

Potassium hydroxide solution (40% in water): 12.5 g
in demineralized water 76.5 g

40.5 g of solution A, 0.3 g of solution B and 0.5 g of 3-mercaptopropionic acid were added to the initially introduced mixture with stirring and cooling so that a pH of 5.8 resulted.

1.9 g of 3-mercaptopropionic acid were then added to the remaining solution. The following metering profile was used over the period of addition of 30 minutes, it having been possible to maintain a constant pH of 5.6 +/-0.2 in the polymerization mixture:

t (min)	0	2	4	8	10	12	14	16	18	22	26	30
Solution A (g/h)	225	250	261	250	225	184	151	121	93	58	36	0

Solution B was pumped into the initially introduced mixture over said period of 30 minutes simultaneously at a constant metering rate of 15 g/h and then at a metering rate of 50 g/h over a further period of 10 minutes with stirring. After complete addition of solutions A and B, peroxide was no longer detectable in the reaction vessel.

The copolymer obtained occurred in slightly yellowish solution which had a solids content of 44%. The average molecular weight of the copolymer was Mw 31000 g/mol or 28000 g/mol. 3.8 % residual monomer (PEG) were found. The polydispersity of the copolymer was 1.53.

Comparative example 2-1:

Example 2 was repeated but the metering of solution A was carried out at a constant rate of 108 g/h over a period of 45 minutes. Here, first an increase of the pH to a maximum value of 5.9 after 4 minutes and, in the further course of the addition of solution A, a reduction to 5.4 up to the end of the addition were observed.

Solids content of the copolymer solution obtained: 44%
Average molecular weight: Mw 33000 g/mol; Mp 30000 g/mol;
Residual PEG: 4.4%;
Polydispersity: 1.57

Comparative example 2-2:

Synthesis example 2 was repeated analogously to Comparative example 2-1 with a linear metering rate of solution A. However, the increase of pH in the polymerization mixture which was observed in the first 4 minutes of the addition of A was corrected by addition of 25% strength sulphuric acid, and the decrease of the pH observed from 4.5

minutes onwards was corrected by addition of 20% strength sodium hydroxide solution, so that the measured pH in the reactor could be kept constant at 5.8.

Synthesis example 3:

The procedure was as described in Synthesis example 1 but the following monomer combination was used:

Initially introduced mixture:
Isoprenoloxybutylpolyethylene glycol-500: 37.5 g (0.075 mol)
Isoprenoloxybutylpolyethylene glycol-1100: 82.5 g (0.075 mol)
in demineralized water: 87.0 g

Solution A
Acrylic acid: 16.2 g (0.225 mol)
Hydroxypropyl acrylate: 5.9 g (0.045 mol)
Potassium hydroxide solution (40% in water): 12.5 g
in demineralized water 49.5 g

Solution B
Brüggolit E01: 1.5 g
in demineralized water 23.5 g

29.0 g of solution A, 0.5 g of solution B and 1.05 g of 3-mercaptopropionic acid were added to the initially introduced mixture with stirring and cooling so that a pH of 5.1 resulted.

0.9 g of 3-mercaptopropionic acid was then added to the remaining solution A. The following metering profile was used over the period of 45 minutes, it having been possible to maintain a constant pH of 5.1-5.2 in the polymerization mixture:

t (min)	0	1.5	3	6	9	12	15	18	21	24	27	30	33	36	39	45
Solution A (g/h)	37	74	130	155	144	130	111	89	70	55	44	33	27	19	16	0

The copolymer obtained occurred as a slightly yellowish solution which had a solids content of 43%. Average molecular weight: Mw 25000 g/mol; Mp 20000 g/mol; residual PEG: 6.5%; polydispersity: 1.64.

The polymer solution obtained was then adjusted to a pH of 6.5 with about 28 g of a 20% strength aqueous sodium hydroxide solution.

Comparative example 3-1:

Example 3 was repeated but the metering solution A was effected at a constant rate of 62 g/h over a period of 45 minutes. Here, first an increase of the pH to a maximum value of 5.1 after 5.4 minutes and, in the further course of the addition of solution A, a reduction to 5.0% up to the end of the addition were observed.
Solids content of the copolymer solution obtained: 43%
Average molecular weight: 27,000 g/mol.

Comparative example 3-2:

Synthesis example 3 was repeated analogously to Comparative example 3-1 with a linear metering rate of solution A.
However, the increase of the pH in the polymerization mixture which was observed in the first 7 minutes of the addition of A was corrected by addition of 25% strength sulphuric acid, and the subsequently observed decrease of the pH was corrected by addition of 20% strength sodium hydroxide solution, so that the measured pH in the reactor could be kept constant at 5.1.

Synthesis example 4

100 g of demineralized water and 112.5 g (0.0375 mol) of vinyloxybutyl polyethylene glycol-3000 (adduct of 65 mol of ethylene oxide with hydroxybutyl monovinyl ether having an average molecular weight of 3000 g/mol) were initially introduced into a glass reactor equipped with a stirrer, pH electrode and a plurality of feed devices and were cooled to a polymerization starting temperature of 15°C (initially introduced mixture).

16.2 g (0.2025 mol) of acrylic acid were homogeneously mixed with 42 g of demineralized water in a separate feed vessel. The solution was adjusted, with cooling, to a temperature of 20°C and a pH of 4.0 with 7.7 g of a 40% strength potassium hydroxide solution. 0.7 g of 3-mercaptopropionic acid was then added as a molecular weight regulator (solution A1). In a second separate feed vessel, 100 g of demineralized water and 112.5 g (0.0375 mol) of vinyloxybutylpolyethylene glycol-3000 (adduct of 65 mol of ethylene oxide with hydroxybutyl monovinyl ether having an average molecular weight of 3000 g/mol) were mixed (solution A2).

At the same time, a second solution consisting of 1.5 g of Brüggolit FF6 (from Brüggemann GmbH) and 23.5 g of water was prepared (solution B).

23.3 g of solution A1 and then 1.8 g of a 20% strength aqueous sodium hydroxide solution were added to the initially introduced mixture with stirring and cooling so that a pH of 5.8 resulted.

After this pH had been reached, 0.015 g of iron(II) sulphate heptahydrate, 0.1 g of solution B and 0.94 g of hydrogen peroxide (30% in water) were added in succession to the initially introduced mixture. At the same time, the addition of solutions A1, A2 and B to the stirred and initially introduced mixture was started.

The feed rate of solution A1 was modified here according to the following metering profile so that the pH in the initially introduced mixture over the entire period of addition of 45 minutes was kept constant at a value of 5.8 +/- 0.1:

t (min)	0	1.5	3	6	9	12	15	18	21	24	27	30	33	36	39	45
Solution A1 (g/h)	29	59	103	123	115	103	88	71	56	44	35	26	21	15	13	0

Solution A 2 was metered simultaneously according to the following metering profile from the separate initially introduced mixture:

t (min)	0	1.5	3	6	9	12	15	18	21	24	27	30	33	36	39	45
Solution A2 (g/h)	144	288	504	603	561	504	432	345	273	213	171	128	103	72	63	0

Solution B was added simultaneously over the same period of 45 minutes at a metering rate of 7 g/h. Thereafter, the metering rate of solution B was increased to 50 g/h and pumped into the initially introduced mixture over a period of 10 minutes with stirring. After complete addition of solutions A1, A2 and B, peroxide was no longer found in the reaction vessel.

The polymer solution obtained was then adjusted to a pH of 6.5 with about 11 g of a 20% strength sodium hydroxide solution.

The copolymer obtained occurred as slightly yellow solution which had a solids content of 46.3%. The average molecular weight of the copolymer was Mw 60000 g/mol; Mp 46000 g/mol; residual PEG: 12%; polydispersity 1.64.

Determination of the pH:

The pH of the aqueous medium (which is usually not present as an ideal solution - because organic components are usually also present in relatively high concentration in the aqueous medium in addition to water) is generally expediently measured using a glass electrode. In the experimental examples described above, the pH of the aqueous medium was based in each case on the measured quantity which is obtained by introducing a pH combination electrode of the type H 6381 from Schott AG (glass electrode) under the respective temperature and concentration conditions specified by the experiment described into the reaction mixture and outputting its generated signal by means of a multiparameter measuring instrument of the type ProfilLine Multi 197i from WTW as a number. The calibration of the abovementioned pH combination electrode is effected using commercially available pH buffer solutions (pH 4.00 and pH 7.00) as a function of the temperature.

Analysis of the copolymers from the synthesis and comparative examples:

The polymers from the synthesis examples and the comparative examples were analyzed by means of size exclusion chromatography with respect to average molar mass and conversion (column combination: OH-Pak SB-G, OH-Pak SB 804 HQ and OH-Pak SB 802.5 HQ from Shodex, Japan; eluent: aqueous solution of HCO_2NH_4 (0.05 mol/l) 80% by volume and acetonitrile 20% by volume; injection volume 100 µl; flow rate 0.5 ml/min). The calibration for the determination of the average molar mass was effected using linear poly(ethylene oxide) and polyethylene glycol standards. As a measure of the conversion, the peak of the copolymer is standardized to a relative height of 1 and the height of the peak of the unconverted macromonomer/PEG-containing oligomer is used as a measure of the content of residual monomer.

Use examples of the copolymers from the synthesis examples and comparative examples:

The polymers from the synthesis examples and the comparative examples were investigated with regard to their properties as concrete superplasticizers in a suitable test system. For this purpose, all polymers were adjusted to a uniform solids content and uniform pH of 6.5 ± 0.2 with NaOH in water (30% by weight) and small amounts of a conventional antifoam were added for controlling the air pore content.

Use Example 1:

First, 7.00 kg of a Portland cement (Karlstadt CEM I 42.5 R), 2 kg of a K-S flour Füller's calcite MS 12 and furthermore 5.45 kg of quartz sand (0/0.5 and 0/1.0), 16.98 kg of sand 0/4, 5.65 kg of gravel 4/8 and 18.60 kg of gravel 8/16 were combined and were dried and blended for 10 seconds. Thereafter, 0.5 kg of initially introduced water were added and mixing was effected for a further 120 seconds. Thereafter, 3.61 kg of remaining water were added and mixing was effected for a further 60 seconds. Thereafter, in each case $7.70 \cdot 10^{-3}$ kg (calculated on the basis of 100%) of polymer (based on the polymer solids content) was added and mixing was effected for a further 60 seconds (corresponds to a water/cement ratio of 0.59 and a polymer dose of 0.11% of solids, based on the amount of cement weighed in). The consistency according to DIN EN 12350-5 was then determined directly after the preparation and after 10, 30 and 60 minutes. The following values were determined:

Polymer from	Slump (cm) after x min.				Consistency (cm) after x min.			
	0	10	30	60	0	10	30	60
Synthesis example 1	24	24	23	22	66	66	62.5	58.5
Synthesis example 4	23	23	23	22	64	63	61.5	59.5
Comp. example 1-1	20	22	21	16	57	60.5	56.5	47.5
Comp. example 1-2	22	21	19	18	59	55	53	48.5

Use Example 2:

The procedure was as described in Use Example 1, but the mixture was adapted as follows:

Cement Allmendingen CEM I 42.5 R	7.00 kg
K-S flour Füller's calcite MS 12	2.00 kg
Quartz sand (0/0.5 and 0/1.0)	5.57 kg
Sand 0/4	17.06 kg
Gravel 4/8	4.29 kg
Gravel 8/16	18.60 kg
Initially introduced water	0.5 kg
Remaining water	3.46 kg
Polymer (100%)	0.0133 kg

This gave a water/cement ratio of 0.57 and a superplasticizer dose of 0.19% (polymer solids, based on cement):

Polymer	Slump (cm) after x min.				Consistency (cm) after x min.			
	0	10	30	60	0	10	30	60
Synthesis example 2	22	22	21	21	60.5	60.5	57.5	56.5
Comp. example 2-1	19.5	20.5	20	18	55	56.5	55.5	50
Comp. example 2-2	22	21	20	19	59.5	57.5	55	54.5

Use Example 3:

The procedure was as described in Use Example 1 but the mixture was adapted as follows:

Portland cement Karlstadt CEM I 42.5 R	7.00 kg
K-S flour Füller's calcite MS 12	2.00 kg
Quartz sand (0/0.5 and 0/1.0)	5.47 kg
Sand 0/4	17.05 kg
Gravel 4/8	5.67 kg
Gravel 8/16	18.68 kg
Initially introduced water	0.5 kg

Remaining water	3.53 kg
Polymer (100 %)	0.0126 kg

This gives a water/cement value of 0.58 and a superplasticizer dose of 0.18% (solids, based on cement weight):

Polymer	Slump (cm) after x min.				Consistency (cm) after x min.			
	0	10	30	60	0	10	30	60
Synthesis example 3	23	22.5	21	20	63.5	62	59.5	57.5
Comp. example 3-1	15	20.5	18	17.5	46.5	58	51	49.5
Comp. example 3-2	22	21	19	18	59	57	50.5	48.5

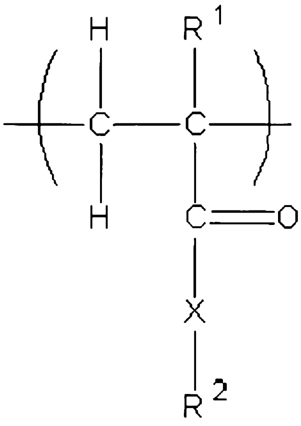
The polymers prepared according to the invention show better plasticizing effects (water reduction) in the same dose directly after preparation of the concrete in comparison with the reference products. Furthermore, they have neither subsequent plasticization undesired for the user nor a marked loss of processability, i.e. the performance characteristics essential for the concrete manufacturer as the user of the products are substantially improved in the case of the polymers according to the invention.

CLAIMS:

1. Process for the preparation of a copolymer in a semicontinuous mode of operation in a polymerization apparatus containing a polymerization reactor connected to a metering device, in each case acid monomer being initially introduced into the metering device and polyether macromonomer and water into the polymerization reactor, acid monomer being metered from the metering device into the polymerization reactor, free radical polymerization initiator being passed into the polymerization reactor before and/or during the metering of the acid monomer into the polymerization reactor, so that an aqueous medium forms in the polymerization reactor, in which aqueous medium acid monomer and polyether macromonomer are reacted by free radical polymerization with formation of the copolymer, at least 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor being converted by the free radical polymerization, the conversion of the acid monomer giving rise in the copolymer to an acid structural unit which reduces the pH of the aqueous medium to a lesser extent than the acid monomer as such, the metering of the acid monomer into the polymerization reactor being effected in such a way that first a polymerization pH is established in the aqueous medium and then, until the conversion of 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.3 from the initially established polymerization pH.

2. Process according to Claim 1, wherein the reaction of the acid monomer produces in the copolymer a structural unit which is according to one of the general formulae (Ia), (Ib), (Ic) and/or (Id)

(Ia)



$$-\!\left(\mathrm{CH_2}-\mathrm{C}(\mathrm{R}^1)(\mathrm{C(=O)}-\mathrm{X}-\mathrm{R}^2)\right)\!-$$

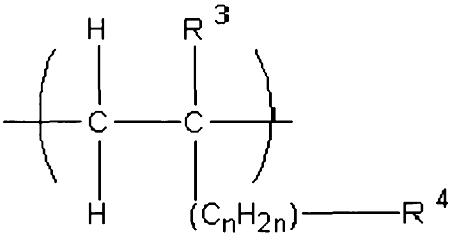
where

R^1 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

X is identical or different and is represented by NH-(C_nH_{2n}) where n = 1, 2, 3 or 4 and/or O-(C_nH_{2n}) where n = 1, 2, 3 or 4 and/or by a unit not present;

R^2 is identical or different and is represented by OH, SO_3H, PO_3H_2, O-PO_3H_2 and/or para-substituted C_6H_4-SO_3H, with the proviso that, if X is a unit not present, R^2 is represented by OH;

(Ib)



$$\left[-CH_2-C(R^3)\left((C_nH_{2n})-R^4\right)- \right]$$

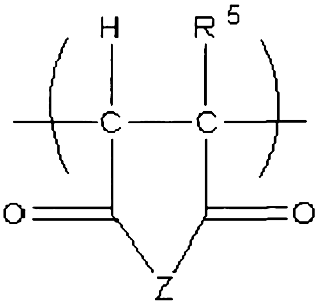
where

R^3 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

n = 0, 1, 2, 3 or 4;

R^4 is identical or different and is represented by SO_3H, PO_3H_2, O-PO_3H_2 and/or C_6H_4-SO_3H present in para-substituted form;

(Ic)

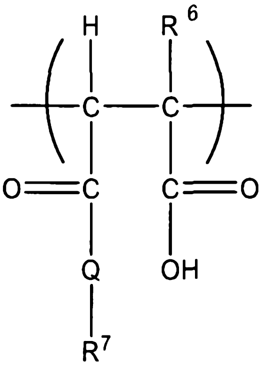


where

R^5 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

Z is identical or different and is represented by O and/or NH;

(Id)



where

R^6 is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

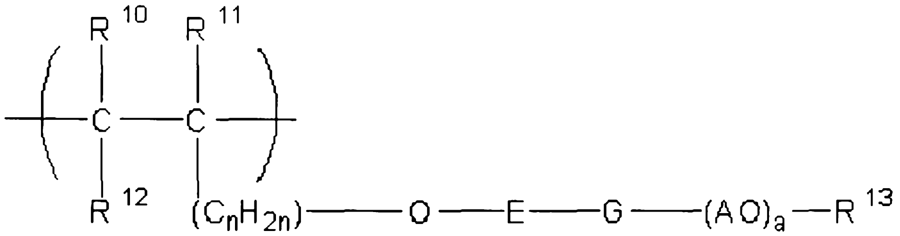
Q is identical or different and is represented by NH and/or O;

R^7 is identical or different and is represented by H, $(C_nH_{2n})\text{-}SO_3H$ where n = 0, 1, 2, 3 or 4, $(C_nH_{2n})\text{-}OH$ where n = 0, 1, 2, 3 or 4; $(C_nH_{2n})\text{-}PO_3H_2$ where n = 0, 1, 2, 3 or 4, $(C_nH_{2n})\text{-}OPO_3H_2$ where n = 0, 1, 2, 3 or 4, $(C_6H_4)\text{-}SO_3H$, $(C_6H_4)\text{-}PO_3H_2$, $(C_6H_4)\text{-}OPO_3H_2$ and/or $(C_mH_{2m})_e\text{-}O\text{-}(A`O)_\alpha\text{-}R^9$ where m = 0, 1, 2, 3 or 4, e = 0, 1, 2, 3 or 4, A` = $C_{x'}H_{2x'}$ where x′ = 2, 3, 4 or 5 and/or $CH_2C(C_6H_5)H\text{-}$, α = an integer from 1 to 350 with R^9 identical or different and represented by a straight-chain or branched C_1 - C_4 alkyl group.

3. Process according to Claim 1 or 2, wherein methacrylic acid, acrylic acid, maleic acid, maleic anhydride, a monoester of maleic acid or a mixture of a plurality of these components is used as the acid monomer.

4. Process according to any one of Claims 1 to 3, wherein the reaction of the polyether macromonomer produces in the copolymer a structural unit which is according to one of the general formulae (IIa), (IIb) and/or (IIc)

(IIa)



$$-\left(\begin{array}{c}R^{10}\\|\\C\\|\\R^{12}\end{array}-\begin{array}{c}R^{11}\\|\\C\\|\\(C_nH_{2n})\end{array}\right)- \quad (C_nH_{2n})-O-E-G-(AO)_a-R^{13}$$

where

R^{10}, R^{11} and R^{12} are in each case identical or different and, independently of one another, are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6 alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in ortho-, meta- or para-substituted form and/or a unit not present;

G is identical or different and is represented by O, NH and/or CO-NH, with the proviso that, if E is a unit not present, G is also present as a unit not present;

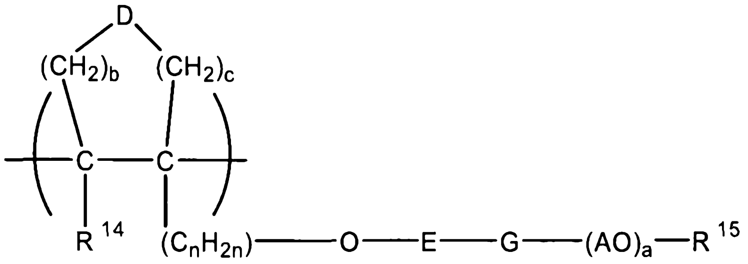
A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 (preferably x = 2) and/or $CH_2CH(C_6H_5)$;

n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

a is identical or different and is represented by an integer from 2 to 350 (preferably 10 - 200);

R^{13} is identical or different and is represented by H, a straight-chain or branched C_1 - C_4 alkyl group, CO-NH$_2$, and/or COCH$_3$;

(IIb)



where

R^{14} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6 alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in ortho-, meta- or para-substituted form and/or by a unit not present;

G is identical or different and is represented by a unit not present, O, NH and/or CO-NH, with the proviso that, if E is a unit not present, G is also present as a unit not present;

A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or $CH_2CH(C_6H_5)$;

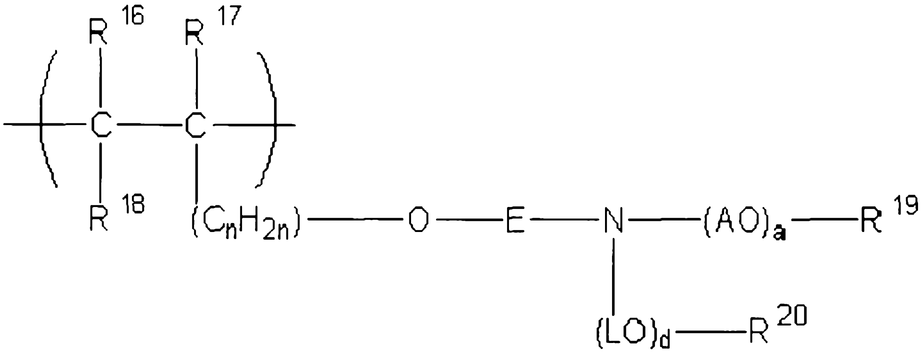
n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

a is identical or different and is represented by an integer from 2 to 350;

D is identical or different and is represented by a unit not present, NH and/or O, with the proviso that, if D is a unit not present: b = 0, 1, 2, 3 or 4 and c = 0, 1, 2, 3 or 4, where b + c = 3 or 4, and with the proviso that if D is NH and/or O: b = 0, 1, 2 or 3, c = 0, 1, 2 or 3, where b + c = 2 or 3;

R^{15} is identical or different and is represented by H, a straight-chain or branched C_1 - C_4 alkyl group, CO-NH_2, and/or $COCH_3$;

(IIc)



where

R^{16}, R^{17} and R^{18} are in each case identical or different and, independently of one another are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

E is identical or different and is represented by a straight-chain or branched C_1 - C_6 alkylene group, a cyclohexyl group, CH_2-C_6H_{10}, C_6H_4 present in ortho-, meta- or para-substituted form and/or by a unit not present;

A is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or $CH_2CH(C_6H_5)$;

n is identical or different and is represented by 0, 1, 2, 3, 4 and/or 5;

L is identical or different and is represented by C_xH_{2x} where x = 2, 3, 4 and/or 5 and/or CH_2-$CH(C_6H_5)$;

a is identical or different and is represented by an integer from 2 to 350;

d is identical or different and is represented by an integer from 1 to 350;

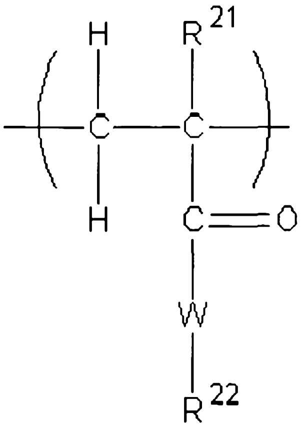
R^{19} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group,

R^{20} is identical or different and is represented by H and/or a straight-chain C_1 - C_4 alkyl group.

5. Process according to any one of Claims 1 to 4, wherein isoprenol and/or alkoxylated hydroxybutyl vinyl ether and/or alkoxylated (meth)allyl alcohol and/or vinylated methyl polyalkylene glycol having preferably in each case an arithmetic mean number of oxyalkylene groups of 4 to 340 is used as the polyether macromonomer.

6. Process according to any one of Claims 1 to 5, wherein a vinylically unsaturated compound is introduced into the polymerization reactor as a monomeric starting material, which compound is reacted by polymerization and thereby produces in the copolymer a structural unit which is present according to the general formula (IIIa) and/or (IIIb)

(IIIa)



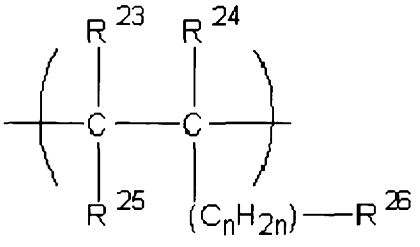
where

R^{21} is identical or different and is represented by H and/or a straight-chain or branched C_1 - C_4 group;

W is identical or different and is represented by O and/or NH;

R^{22} is identical or different and is represented by a straight-chain or branched C_1 - C_5-monohydroxyalkyl group;

(IIIb)



where

R^{23}, R^{24} and R^{25} are in each case identical or different and, in each case independently, are represented by H and/or a straight-chain or branched C_1 - C_4 alkyl group;

n is identical or different and is represented by 0, 1, 2, 3 and/or 4;

R^{26} is identical or different and is represented by (C_6H_5), OH and/or $-COCH_3$.

7. Process according to any one of Claims 1 to 6, wherein a redox initiator system is used as the free radical polymerization initiator.

8. Process according to Claim 7, wherein the combination $H_2O_2/FeSO_4$ which is used together with a reducing agent, is chosen as the redox initiator system.

9. Process according to Claim 8, wherein the disodium salt of 2-hydroxy-2-sulphinatoacetic acid, the disodium salt of 2-hydroxy-2-sulphonatoacetic acid, sodium hydroxymethanesulphinate, ascorbic acid, isoascorbic acid and mixtures thereof are used as the reducing agent.

10. Process according to either of Claims 8 and 9, wherein a component of the redox initiator system and/or reducing agent are passed into the polymerization reactor after the polymerization pH has been established and while the acid monomer is metered in.

11. Process according to any one of Claims 1 to 10, wherein the polymerization pH in the aqueous medium is established so that, based on the free radical polymerization initiator used, the free radical formation per unit time is approximately maximum.

12. Process according to any one of Claims 1 to 11, wherein the aqueous medium is present in the form of an aqueous solution.

13. Process according to any one of Claims 1 to 12, wherein the polymerization reactor is present as a semicontinuous stirred tank.

14. Process according to any one of Claims 1 to 13, wherein at least 80 mol%, preferably at least 90 mol%, of the polyether macromonomer initially introduced into the polymerization reactor is converted by the free radical polymerization.

15. Process according to any one of Claims 1 to 14, wherein, up to a conversion of 70 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.2, preferably not more than ± 0.1, from the initially established polymerization pH.

16. Process according to any one of Claims 1 to 14, wherein at least 80 mol% of the polyether macromonomer initially introduced into the polymerization reactor is converted by the free radical polymerization, and in that, until conversion of 80 mol% of the polyether macromonomer initially introduced into the polymerization reactor, acid monomer is passed into the polymerization reactor in an amount per unit time such that the pH in the aqueous medium deviates by not more than ± 0.3 from the initially established polymerization pH.

17. Process according to any one of Claims 1 to 16, wherein the polymerization pH is 4.0 to 7.0, preferably 4.5 to 6.5 and particularly preferably 4.8 to 6.0 and the temperature of the aqueous medium during the free radical polymerization is 0 to 90°C, preferably 10 to 35°C.

18. Process according to any one of Claims 1 to 17, wherein the acid monomer is initially introduced together with water into the metering unit and an aqueous solution of the acid monomer is metered from the metering device into the polymerization reactor, it being possible for a portion of the acid monomer to be converted into the corresponding acid monomer salt by addition of base before being metered into the polymerization reactor.

19. Process according to any one of Claims 1 to 18, wherein the polymerization pH in the aqueous medium is established by metering the acid monomer into the polymerization reactor and adding a base to the polymerization reactor and/or to the metering device, so that acid monomer and/or acid monomer salt is already present in the polymerization reactor before the polymerization pH is established.

20. Process according to any one of Claims 1 to 19, wherein polyether macromonomer is initially introduced into the polymerization reactor in an amount per mole of acid monomer metered in such that an arithmetic mean molar ratio of acid monomer structural units to polyether macromonomer structural units of 20:1 to 1:1, preferably of 12:1 to 1:1, is established in the copolymer formed.

21. Process according to any one of Claims 1 to 20, wherein altogether at least 45 mol%, but preferably at least 80 mol%, of all structural units of the copolymer are produced by free radical polymerization of acid monomer and polyether macromonomer.

22. Process according to any one of Claims 1 to 21, wherein a chain regulator, which is preferably in dissolved form, is passed into the polymerization reactor.

23. Copolymer which is prepared by the process according to any one of Claims 1 to 22.

24. Use of a copolymer according to Claim 23 as a dispersant for hydraulic binders or for latent hydraulic binders.

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