(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
24 January 2019 (24.01.2019)

(10) **International Publication Number**
WO 2019/016334 A1

(51) **International Patent Classification:**
C08F 2/32 (2006.01) ***C08F 220/06*** (2006.01)

(21) **International Application Number:**
PCT/EP2018/069683

(22) **International Filing Date:**
19 July 2018 (19.07.2018)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
17182690.2 21 July 2017 (21.07.2017) EP

(71) **Applicant: BASF SE** [DE/DE]; Carl-Bosch-Straße 38, 67056 Ludwigshafen (DE).

(72) **Inventors: WEISS, Thomas**; Carl-Bosch-Strasse 38, 67056 Ludwigshafen (DE). **LEYRER, Reinhold J.**; Wasgauring 4, 67125 Dannstadt-Schauernheim (DE).

(74) **Agent: ELLWANGER, Arndt**; Ellwanger & Baier Patentanwälte Partnerschaftsgesellschaft, Friedrichsplatz 9, 68165 Mannheim (DE).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) **Title:** A PROCESS FOR OBTAINING A POLYMER BASED ON ANIONIC OR NONIONIC MONOMERS WITH AN AT LEAST BIMODAL MOLECULAR WEIGHT DISTRIBUTION

(57) **Abstract:** The present invention relates to a process for obtaining a polymer by polymerization of at least one anionic monomer and/or at least one nonionic monomer, at least one crosslinker and optionally further monomers, such as chain transfer agents. The polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) and at least one second peak (P2), wherein the first peak has a lower average sedimentation coefficient of ≤ 100 Sved and the second peak has a higher average sedimentation coefficient of ≥ 1000 Sved. The polymerization is carried out in two subsequent steps I) and II). In step II), the crosslinker is either completely absent or present in a very limited amount. Step II) is carried out after the polymerization of step I) is finished or vice versa.

WO 2019/016334 A1

A process for obtaining a polymer based on anionic or nonionic monomers with an at least bimodal molecular weight distribution

Description

The present invention relates to a process for obtaining a polymer by polymerization of at least one anionic monomer and/or at least one nonionic monomer, at least one crosslinker and optionally further monomers, such as chain transfer agents. The polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) and at least one second peak (P2), wherein the first peak has a lower average sedimentation coefficient of ≤ 100 Sved and the second peak has a higher average sedimentation coefficient of ≥ 1000 Sved. The polymerization is carried out in two subsequent steps I) and II). In step II), the crosslinker is either completely absent or present in a very limited amount. Step II) is carried out after the polymerization of step I) is finished or vice versa.

US 2008/0312343 discloses inverse latex compositions and on the use thereof as a thickeners and/or emulsifiers, for example for production of cosmetic or pharmaceutical formulations. The inverse latex compositions comprise at least 50 to 80% by weight of at least one linear, branched or crosslinked organic polymer (P), at least 5 to 10% by weight of a water-in-oil-type emulsifier system, 5 to 45% by weight of at least one oil and up to 5% water. The polymer P comprises uncharged monomers and optionally cationic or anionic monomers. The inverse latex composition may optionally comprise up to 5% by weight of an oil-in-water-type emulsifier system. The inverse latex compositions can be prepared by inverse emulsion polymerization.

WO 02/057400 relates to thickened fabric conditioners containing a particular polymeric thickener which is obtained by polymerizing from 5 to 100 mole percent of a cationic vinyl addition monomer, from 0 to 95 mole percent of acrylamide, and from 70 to 300 ppm of a difunctional vinyl addition monomer cross-linking agent. As compared to such compositions comprising a similar product but obtained from a polymerization reaction using between 5 and 45 ppm cross-linking agent, considerable advantages are obtained. Especially, the delivery of fragrance present in the softening composition is more efficiently carried over to the fabrics to be treated.

WO 2009/019225 relates to an aqueous dispersion of an alkali-soluble copolymer which is suitable as an associative thickener. The copolymer comprises polymerized-in units of a) at least one ethylenically unsaturated carboxylic acid, b) at least one nonionic ethylenically unsaturated surfactant monomer, c) at least one C_1-C_2-alkyl methacrylate and d) at least one C_2-C_4-alkyl acrylate, where the alkyl chain length averaged over the number of alkyl groups of the alkyl acrylate is 2.1 to 4.0. The associative thickeners can be prepared by emulsion polymerization. The associative thickeners are suitable for use in detergents and cleaners.

Liquid Dispersion Polymer (LDP) compositions are disclosed in WO 2005/097834. These LDP compositions comprise a hydrophilic, water-soluble or swellable polymer with a neutralization content of approximately 25 to approximately 100%, a nonaqueous carrier phase and an oil-in-water surfactant. The hydrophilic, water-soluble or swellable polymer is preferably obtained by polymerization, for example of acrylic acid or methacrylic acid. The LDP dispersions are suitable for producing microparticulate thickeners, as are used, for example, in aqueous or organic compositions, in particular in personal care or pharmaceutical formulations.

EP-A 172 025 relates to a dispersion in a continuous liquid phase of a polymer which is formed by polymerization of an ethylenically unsaturated monomer comprising a hydrophobic group of at least 8 carbon atoms and an ethylenically unsaturated monomer copolymerizable therewith. The dispersion is stable, essentially anhydrous and comprises at least 40% by weight of polymer. During the polymerization, anionic monomers, for example, can be used as copolymerizable, ethylenically unsaturated monomer. The polymerization can be carried out as an inverse emulsion polymerization.

WO 2013/068394 relates to a thickener comprising at least one cationic polymer and at least one activator, wherein the ratio of activator to cationic polymer is > 10:100 [% by weight/% by weight]. The cationic polymer is preparable by polymerization of at least one water-soluble, ethylenically unsaturated monomer and at least one ethylenically unsaturated associative monomer. WO 2013/068394 further relates to a process for preparing the inventive thickener and to surfactant-containing formulations comprising at least one thickener. WO 2013/068394 further provides for the use of the surfactant-containing formulations, for example as a softener or as a liquid washing composition, and to the use of the thickener, for example as a viscosity modifier.

WO 2013/174621 relates to an inverse dispersion comprising i) at least one anionic or nonionic polymer obtainable by the polymerization of a) at least one anionic monomer and optionally at least one nonionic monomer (compound A), b) optionally at least one crosslinker (compound B), c) optionally at least one chain transfer agent (compound C), ii) at least one stabilizing agent, wherein the stabilizing agent has one or more hydrophobic units with more than 30 carbon atoms per hydrophobic unit, iii) at least one oil phase.

WO 2013/068392 relates to a thickener comprising at least one polymer and at least one activator where the ratio of activator to polymer is > 10:100 [% by weight/% by weight]. The polymer is preparable by polymerizing at least one water-soluble, ethylenically unsaturated monomer comprising at least one anionic monomer and/or at least one nonionic monomer, and at least one ethylenically unsaturated associative

monomer. Furthermore, the thickener can be used as a viscosity modifier or in surfactant-containing formulations, for example as a softener or as a liquid detergent.
WO 2013/068388 relates to a thickener preparable by a process in which a polymer is prepared by inverse emulsion polymerization at a constant temperature of at least 40°C. During the inverse emulsion polymerization, the components used are at least one water-soluble, ethylenically unsaturated monomer comprising at least one anionic monomer and/or at least one nonionic monomer, and at least one ethylenically unsaturated associative monomer.

European application EP16152590.2 is drawn to a process for obtaining a cationic polymer by polymerization of at least one cationic monomer, at least one crosslinker and optionally further monomers, such as nonionic monomers, associative monomers and/or chain transfer agents. The cationic polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) and at least one second peak (P2), wherein the first peak has a lower average sedimentation coefficient of ≤ 100 Sved and the second peak has a higher average sedimentation coefficient of ≥ 1 000 Sved. The polymerization is carried out in two subsequent steps I) and II). In step II), the crosslinker is either completely absent or present in a very limited amount. Step II) is carried out after the polymerization of step I) is finished or vice versa.

European application EP16152583.7 discloses a cationic polymer obtainable by polymerization of at least one cationic monomer, at least one crosslinker and optionally further monomers, such as nonionic monomers, associative monomers and/or chain transfer agents. The cationic polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) and at least one second peak (P2), wherein the first peak has a rather low average sedimentation coefficient of ≤ 10 Sved and the second peak has a rather high average sedimentation coefficient of ≥ 10,000 Sved. The water-soluble polymer components of the cationic polymer are ≥ 25% by weight related to the total amount of cationic polymer.

There is a steady demand in the market for new and/or cheaper and/or more effective home and personal care formulations and/or the respective polymers contained therein as well as the provision of novel processes for preparing such polymers.

The problem underlying the present invention consists in the provision of a process for preparing novel polymers and/or inverse dispersions, containing at least one of such polymers.

The object is achieved by a process for obtaining a polymer by polymerization of

a) at least one anionic monomer and/or at least one nonionic monomer (monomer component a),

b) at least one crosslinker (monomer component b),

c) optionally at least one chain transfer agent (monomer component c),

wherein the polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) with an average sedimentation coefficient of ≤ 100 Sved and with at least one second peak (P2) with an average sedimentation coefficient of ≥ 1000 Sved, and

wherein the polymerization is carried out in two subsequent steps I) and II) with:

I) polymerization of monomer component a) and monomer component b),

II) polymerization of monomer component a), optionally monomer component c) and in the complete absence or in the presence of < 10 ppm (related to the total amount of polymer) of monomer component b),

wherein step II) is carried out after the polymerization of step I) is finished or step I) is carried out after the polymerization of step II) is finished.

An advantage of the inventive process is that polymers significantly differing in their molecular weight and additionally having an at least bimodal molecular weight distribution can be produced in a single process. Preferably, only one polymerization vessel needs to be employed since the two polymerization steps I) and II) are carried out subsequently. This advantage becomes more evident in case the inventive process is carried out in a preferred embodiment as an emulsion polymerization, more preferably as an inverse emulsion polymerization. This is due to the fact that no coagulum or only a rather small amount of coagulum is produced by the inventive process since the two polymerization steps are carried out subsequently.

This advantage becomes even more evident in connection with those embodiments, wherein an inverse dispersion is prepared/employed containing such polymers obtained by the inventive process or the polymer is prepared within an inverse dispersion, respectively. It has to be noted that dispersions are always shear-sensitive. Due to their shear-sensitivity, (inverse) dispersions tend to easily form coagulum. If, for example, polymers having a wide range of molecular weight have to be produced by a skilled person according to the methods of the prior art, the individual polymer components differing in respect of their molecular weight are usually produced independently from each other and mixed afterwards. However, the handling of such differing polymer mixtures, differing in respect of their molecular weight, is rather difficult, especially if the respective polymers are contained within an inverse dispersion, due to the formation of rather high amounts of coagulum when mixing the individual polymers or inverse dispersions, respectively.

The polymers obtained by the process according to the present invention possess advantageous properties when they are employed, for example, within inverse dispersions, thickeners, deposition aids and/or (aqueous) home and personal care formulations. The polymers contribute to an improved stability and effectiveness of the respective product, such as an aqueous formulation containing the respective polymer, the respective inverse dispersion or the respective deposition aids. Likewise, the polymers according to the present invention can be successfully employed as depositioning aids in liquid laundry formulations, especially in fabric softeners, i.e. to improve the depositioning of softening or freshness active ingredients such as quaternized compounds, silicone or fragrance on the textile fibres.

Another advantage of the polymers obtained by the process according to the present invention is that they contain both polymer components with a lower molecular weight (having an average sedimentation coefficient of ≤ 100 Sved) and polymer components with a higher molecular weight (having an average sedimentation coefficient of ≥ 1000 Sved). The polymers obtained by the process according to the present invention contain both types of said polymer components in a significant amount. The amount of water-soluble polymer components may vary in a very wide range, for example, at least 25 % by weight of the respective polymer components are water-soluble, i.e. the polymer components with a rather low molecular weight. Those water-soluble polymer components are not cross-linked at all or only cross-linked to a very limited amount. By contrast, the respective polymer components of the polymer obtained by the process according to the present invention having a rather high molecular weight contain a rather high amount of cross-linking. Said polymer components with a rather high molecular weight are nearly or completely insoluble in water and only more or less swellable in water. Furthermore, only a rather limited amount of crosslinker has to be employed for producing the polymers obtained by the process according to the present invention.

When assessing the shear dilution, it is important that an inverse dispersion containing the polymers obtained by the process according to the present invention, after being added to the aqueous formulation like a fabric softener, where the phase inversion from a water in oil to an oil in water system is taking place, in its basic state is viscous and thick whereas it is thin upon stirring. The improved shear dilution has a positive effect on the life and properties of pumps during the production of the aqueous fabric softener, promotes convenient dosage for the consumer and promotes the residue-free use of the fabric softener, especially in the washing machines which have an automatic dosing device. The inverse dispersions containing the polymers obtained by the process according to the invention improve the stability of the corresponding formulation. Also in the aqueous formulation containing the inventive polymer after phase inversion the settling or creaming of additionally added particles like vesicles, different soap phases, microcapsules, silicon particles, aluminium flakes or other particles is effectively prevented, irrespective of whether they are within the order of magnitude of nanometers, micrometers or millimeters. Moreover, they have the advantages that any redispersion required as well as the thickening effect are achieved very quickly.

Embodiments of the process according to the present invention in which the polymers present in the inverse dispersion are prepared using little amount of crosslinker is likewise associated with advantages.

Due to the relatively high amount of water-soluble polymer components of the polymer, resoiling during a washing operation is reduced. Consequently, the article to be washed, even after repeated washing operations, has clean fibers which have been free effectively of soil particles, such that graying has been minimized. Only very slight, if any, adhesion or redistribution of soil particles/polymers on the washed articles is observed, which can then be removed in the next washing cycle avoiding an accumulation effect. Also in that phase of the process, it is advantageous to employ the polymers together with a stabilizing agent containing one or more hydrophobic chains with more than 30 carbon atoms in order to apparently supporting the stabilization of the dispersed solid particles, especially by employing those stabilizing agents with longer hydrophilic B blocks.

A further advantage of the polymers or inverse dispersions, respectively, prepared by the inventive process is manifested in surfactant-containing formulations because a high thickening performance and/or marked shear dilution are achieved in these formulations even at low thickener concentrations (< 1% by weight of inverse dispersion related to the total weight of the formulation).

A further advantage of the polymers or inverse dispersions, respectively, prepared by the inventive process is manifested in fabric softeners having the above-mentioned advantages in the rheology. But the additional advantage is the high storage stability of aqueous fabric softeners formulations if they contain the inventive polymer. Furthermore the effectiveness of such fabric softeners is highly improved as the inventive polymers induce the more quantitative deposition of the softening components and the fragrance on the laundry during the last processing step in the washing machine.

Within the context of the present invention, the term “polymer” means the entirety of all polymer components of the respective polymer. The polymer components may also be designated as individual polymer components, individual polymers, polymer molecules or individual polymer molecules. The (individual) polymer components differ in respect of their (individual) molecular weight. The molecular weight of an (individual) polymer component may be influenced, for example, by the amount of crosslinker employed within the respective polymerization process. By consequence, each polymer (known in the state of the art) has a molecular weight distribution since it contains a plurality of polymer components/individual polymer molecules. However, the polymers according to the present invention have an at least bimodal molecular weight distribution (as further specified within the context of the present invention).

In the context of the present invention, the term “at least bimodal molecular weight distribution” means that the molecular weight distribution within the polymer according to the present invention may be bimodal, trimodal, tetramodal or pentamodal, or it may contain an even higher modality. The modality of the molecular weight distribution of the polymers according to the present invention is determined by the number of (main) peaks. Unless indicated otherwise, the peaks are determined/measured by an average sedimentation coefficient. Only those peaks are considered for determination of the respective modality, which contribute to an amount of more than 1%, preferably of more than 5%, to the total amount of polymer (main peaks). In other words, rather small peaks in the baseline having a very low signal to noise ratio are not considered as a peak when determining the modality of the respective polymer. In case a peak, such as the first peak (P1) is split into two or more peaks (P1.1, P1.2, ... P1.X), said peaks (P1.1, P1.2, ... P1.X) may overlap. For example, if the first peak (P1) is split into the two peaks P1.1 and P1.2, but there is only one second peak (P2), the respective polymer is trimodal in respect of the peaks (P1) and (P2) and bimodal in respect of peak (P1). Within the context of the present invention, it is also possible to obtain polymers with an at least trimodal molecular weight distribution having at least one first peak (P1), at least one second peak (P2) and additionally at least one third peak with an average sedimentation coefficient outside the respective values of the peaks (P1) and (P2), for example with an average sedimentation coefficient in the range of 150 to 300 Sved. The determination of the modality and the average sedimentation coefficient in the unit of Svedberg (Sved) is carried out according to P. Schuck, ‘Size-distribution analysis of macromolecules by sedimentation velocity ultracentrifugation and Lamm equation modeling’, Biophysical Journal 78, (3) (2000), 1606-1619.

In the context of the present invention, the definitions such as C_1-C_{30}-alkyl, as defined, for example, below for the R_9 radical in formula (I), mean that this substituent (radical) is an alkyl radical having a carbon atom number from 1 to 30. In other words, the respective alkyl radical is derived from alkanes by removal of a hydrogen atom from any carbon atom according to the general formula $-C_nH_{2n+1}$, wherein n is any integer from 1 to 30 (in case of, for example, C_1-C_{30}-alkyl). The alkyl radical may be either linear or branched and optionally cyclic. Preferably, the alkyl radical is linear or branched. Alkyl radicals which have both a cyclic and a linear component are likewise covered by this definition. The same also applies to other alkyl radicals, for example a C_1-C_4-alkyl radical or a C_{16}-C_{22}-alkyl radical. The alkyl radicals may optionally also be mono- or polysubstituted by functional groups such as amino, quaternary ammonium, hydroxyl, halogen, aryl or heteroaryl. Unless stated otherwise, the alkyl radicals preferably do not have any functional groups as substituents. Examples of alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, 2-ethylhexyl, tert-butyl (tert-Bu/t-Bu), cyclohexyl, octyl, stearyl or behenyl.

The present invention is specified further hereinafter:

Within the inventive process, the polymer is obtained by polymerization of the following monomer components a) and b) and optionally c).

The monomer component a) used is at least one anionic monomer and and/or at least one nonionic monomer. Anionic monomers as such and nonionic monomers as such are known to persons skilled in the art.

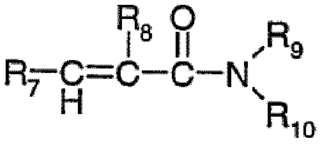
If at least one anionic monomer is present in component a), it is preferably selected from acrylic acid, methacrylic acid, itaconic acid, maleic acid or a salt thereof, preferably selected from an alkali metal salt and/or a fluoro salt of said acids, more preferably selected from Na or Li acrylate, Na or Li methacrylate, Na or Li trifluorboroacrylate and/or Na or Li trifluorboromethacrylate, most preferably selected from Li acrylate or Li trifluorboroacrylate.

If component a) comprises at least one anionic monomer, the at least one anionic monomer is preferably present in component a) in an amount of at least 50% by weight, more preferably at least 75% by weight and most preferably at least 90% by weight, in each case based on the total weight of component a).

In one embodiment of the present invention, monomer component a) comprises 100% by weight of at least one anionic monomer.

If at least one nonionic monomer is present in component a), apart from the nitrogen-containing monomers described below, such as, for example, the compounds according to formula (I), esters of the anionic monomers described above are also suitable as nonionic monomers. Such nonionic monomers are preferably the methyl or ethyl esters of acrylic acid or methacrylic acid such as ethyl acrylate or methyl acrylate. Preference is also given to the corresponding dimethylamino-substituted esters such as dimethylaminoethyl (meth)acrylate.

Preferably, the nonionic monomer according to monomer component a) in the polymer is selected from N-vinylpyrrolidone, N-vinylimidazole, an associative monomer or a compound of the formula (I)



$$R_7-\underset{H}{C}=\overset{R_8}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-N\begin{matrix}R_9\\R_{10}\end{matrix}$$

(I)

where
R_7 is H or $C_1 - C_4$ – alkyl,
R_8 is H or methyl, and
R_9 and R_{10} are each independently H or $C_1 - C_{30}$– alkyl.

Preferred compounds of the formula (I) include acrylamide, methacrylamide or dialkylaminoacrylamide, most preferably acrylamide.

The at least one nonionic monomer according to monomer component a) in the polymer preferably comprises at least one associative monomer.

Associative monomers as such are known to those skilled in the art. Suitable associative monomers are described, for example, in WO 2009/019225. Associative monomers are also described as surfactant monomers.

Preferably, the associative monomer in the polymer is selected from a compound of the formula (II)

$$R\text{-}O\text{-}(CH_2\text{-}CHR'\text{-}O)_n\text{-}CO\text{-}CR''{=}CH_2 \qquad \text{(II)}$$

where
R is $C_1 - C_{50}$ – alkyl, preferably $C_1 - C_{30}$ – alkyl, especially $C_1 - C_{22}$– alkyl,
R' is H or $C_1 - C_4$ – alkyl, preferably H,
R" is H or methyl,
n is an integer from 0 to 500, preferably 3 to 100, especially 20 to 50.

More preferably, the at least one associative monomer used is a compound of the formula (II) in which

R is C_1-C_{22}-alkyl,
R‘ is H,
R“ is H or methyl and
n is 20 to 50.

Compounds of the formula (II) are commercially available in solution, for example under the Plex 6954 O name from Evonik Röhm GmbH. These are methacrylates of fatty alcohol ethoxylates. A suitable fatty alcohol ethoxylate is, for example, the commercially available Lutensol® AT 25 (BASF SE, Ludwigshafen, Germany).

The R radical in the compounds of the formula (II) may also be present as a mixture of radicals with different chain lengths, such as C_{16} and C_{18}. One example thereof is C_{16}-C_{18}-fatty alcohol-(ethylene glycol)$_{25}$-ether methacrylate, where both C_{16} and C_{18} fatty alcohol radicals (in non-negligible amounts) are present as a mixture. In contrast, for example, in the compounds (of the formula (II)) behenyl-25 methacrylate and cetyl-25 methacrylate, the particular R radical is not present as a mixture but as a C_{22} or C_{16} chain. Other chain lengths occur only in the form of impurities. The number "25" in these compounds of the formula (II) represents the size of the variables n.

In one embodiment of the present invention, the nonionic monomer according to monomer component a) in the polymer preferably contains at least two different associative monomers according to formula (I), wherein in the first monomer R is C_1-C_3-alkyl, preferably methyl, and n is an integer from 40 to 50, preferably 45, and in the second monomer R is C_{16}-C_{22}-alkyl, preferably C_{18}-alkyl, and n is an integer from 20 to 30, preferably 25.

If component a) comprises at least one nonionic monomer, the at least one nonionic monomer is preferably present in component a) in an amount of at least 0.5% by weight, more preferably at least 10% by weight and most preferably at least 15% by weight, in each case based on the total weight of component a). It is also preferred that the at least one nonionic monomer is preferably present in component a) in an amount of not more than 50 % by weight, more preferably not more than 30 % by weight, most preferably not more than 25 % by weight, in each case based on the total weight of component a).

In another embodiment of the present invention, monomer component a) comprises 100% by weight of at least one nonionic monomer.

In one embodiment, monomer component a) contains at least one anionic monomer and optionally at least one nonionic monomer in order to obtain an anionic polymer. Within the context of the present invention, the term “anionic polymer” means that the respective monomer component a) (employed for obtaining said anionic polymer by polymerization) contains at least 10 % by weight, more preferably at least 50 % by weight, even more preferably at least 75 % by weight of at least one anionic monomer (in each cased based on the total weight of component a)). This means that within the context of the present invention an anionic polymer is also obtained in case monomer component a) contains further monomers, such as nonionic monomers, even in an amount up to 90 % by weight. It is also preferred that monomer component a) does not contain any further monomers besides anionic monomers and optionally nonionic monomers. An anionic polymer is, of course, also obtained if monomer component a) comprises 100 % by weight of at least one anionic monomer.

In another embodiment, monomer component a) contains at least one nonionic monomer and optionally at least one anionic monomer in order to obtain a nonionic polymer. Within the context of the present invention, the term “nonionic polymer” means that the respective monomer component a) (employed for obtaining said nonionic polymer by polymerization) contains at least 90 % by weight, more preferably at least 95 % by weight, even more preferably at least 98 % by weight of at least one nonionic monomer (in each cased based on the total weight of component a)). This means that within the context of the present invention a nonionic polymer is also obtained in case monomer component a) contains further monomers, such as anionic monomers, even in an amount up to 10 % by weight. It is also preferred that monomer component a) does not contain any further monomers besides nonionic monomers and optionally anionic monomers. A nonionic polymer is, of course, also obtained if monomer component a) comprises 100 % by weight of at least one nonionic monomer.

It is also preferred within the context of the present invention that monomer component a) does not comprise any further monomers besides at least one anionic monomer and/or at least one nonionic monomer.

In a preferred embodiment, component a) comprises from 20 to 100% by weight, preferably 30 to 100% by weight, more preferably 40 to 100% by weight of at least one anionic monomer and from 0 to 80% by weight, preferably 0 to 70% by weight, more preferably 0 to 60% by weight of at least one nonionic monomer, in each case based on the total weight of component a). If a nonionic monomer is present, it is preferably at least one associative monomer.

In another embodiment of the present invention, the monomer component a) contains at least one anionic monomer and at least one nonionic monomer.

The monomer component b) used is at least one crosslinker. Suitable crosslinkers are known to those skilled in the art.

Preferably, the crosslinker in the polymer is selected from divinylbenzene; tetraallylammonium chloride; allyl acrylates; allyl methacrylates; diacrylates and dimethacrylates of glycols or polyglycols; butadiene; 1,7-octadiene; allylacrylamides or allylmethacrylamides; bisacrylamidoacetic acid; N,N'-methylenebisacrylamide; polyol polyallyl ethers such as polyallyl sucrose or pentaerythritol triallyl ether; pentaerythrityl triacrylate; pentaerythrityl tetraacrylate; 1,1,1-trimethylolpropane tri(meth)acrylate; the ethoxylated compounds thereof or a mixture thereof.

Most preferably the crosslinker is selected from N,N’-methylenebisacrylamide, pentaerythrityl triacrylate or pentaerythrityl tetraacrylate.

In one embodiment according to the present invention, the crosslinker in the polymer is a trifunctional monomer, a tretrafunctional monomer or a mixture thereof. Preferably, the crosslinker of this embodiment is selected from tetraallylammonium chloride; allyl acrylates; allyl methacrylates; and tri- and tetramethacrylates of polyglycols; or polyol polyallyl ethers such as polyallyl sucrose or pentaerythritol triallyl ether, ditrimethylolpropane tetraacrylate, pentaerythrityl tetraacrylate, pentaerythrityl tetramethacrylate, pentaerythrityl triacrylate, pentaerythrityl triacrylate, ethoxylated, triethanolamine trimethacrylate, 1,1,1-trimethylolpropane triacrylate, 1,1,1-trimethylolpropane triacrylate, ethoxylated, trimethylolpropane tris(polyethylene glycol ether) triacrylate, 1,1,1-trimethylolpropane trimethacrylate, tris-(2-hydroxyethyl)-1,3,5-triazine-2,4,6-trione triacrylate, tris-(2-hydroxyethyl)-1,3,5-triazine-2,4,6-trione trimethacrylate, dipentaerythrityl pentaacrylate, 3-(3-{[dimethyl-(vinyl)-silyl]-oxy}-1,1,5,5-tetramethyl-1,5-divinyl-3-trisiloxanyl)-propyl methacrylate, dipentaerythritol hexaacrylate, 1-(2-propenyloxy)-2,2-bis[(2-propenyloxy)-methyl]-butane, trimethacrylic acid-1,3,5-triazin-2,4,6-triyltri-2,1-ethandiyl ester, glycerine triacrylate, propoxylated, 1,3,5-triacryloylhexahydro-1,3,5-triazine, 1,3-dimethyl-1,1,3,3-tetravinyldisiloxane, pentaerythrityl tetravinyl ether, 1,3-dimethyl-1,1,3,3-tetravinyldisiloxane, (ethoxy)-trivinylsilane, (Methyl)-trivinylsilane, 1,1,3,5,5-pentamethyl-1,3,5-trivinyltrisiloxane, 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, 1,3,5-trimethyl-1,3,5-trivinyltrisilazane, tris-(2-butanone oxime)-vinylsilane, 1,2,4-trivinylcyclohexane, trivinylphosphine, trivinylsilane, methyltriallylsilane, pentaerythrityl triallyl ether, phenyltriallylsilane, triallylamine, triallyl citrate, triallyl phosphate, triallylphosphine, triallyl phosphite, triallylsilane, 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, trimellitic acid triallyl ester, trimethallyl isocyanurate, 2,4,6-tris-(allyloxy)-1,3,5-triazine, 1,2-Bis-(diallylamino)-ethane, pentaerythrityl tetratallate, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, tris-[(2-acryloyloxy)-ethyl]-phosphate, vinylboronic anhydride pyridine, 2,4,6-trivinylcyclotriboroxanepyridine, tetraallylsilane, tetraallyloxysilane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasilazane. More preferably, the crosslinker of this embodiment is selected alkyltrimethylammonium chloride, pentaerythrityl triacrylate, pentaerythrityl tetraacrylate, tetrallylammonium chloride, 1,1,1-trimethylolpropane tri(meth)acrylate, or a mixture thereof. These more preferred compounds can also be ethoxylated.

It is generally preferred within the present invention that the crosslinker contains more than two reactive groups and/or is used in an amount of 10 to 500 ppm, preferably 30 to 490 ppm, more preferably 50 to 400 ppm, even more preferably less than 375 ppm, related to the total amount of polymer.

In the preparation of the polymer by polymerization, at least one chain transfer agent may optionally be present as monomer component c). Suitable chain transfer agents are known to those skilled in the art. Preferably, the chain transfer agent in the polymer is selected from mercaptans, lactic acid, formic acid, isopropanol or hypophosphites. More preferably, the chain transfer agent is selected from mercaptans, isopropanol or sodium hypophosphite. Most preferably, the chain transfer agent is sodium hypophosphite. It is furthermore preferred that at least one chain transfer agent is employed within the polymerization for obtaining the polymer.

In one preferred embodiment according to the present invention, the inventive process for obtaining the polymer is carried out by polymerization of the monomer components a), b) and optionally c) as defined above.

In another embodiment according to the present invention, the inventive process for obtaining the polymer is carried out by polymerization of the monomer components a), b) and c) as defined above.

Within all embodiments according to the present invention, the inventive process for obtaining the polymer may be carried out by additional polymerization of further monomer components which do not fall under the definition of the monomer components a), b) and c) as defined above. However, it is preferred that no further monomer components, which do not fall under the definition of the monomer components a), b) and c) as defined above, are employed within the inventive polymerization process for obtaining the polymer.

The polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) with an average sedimentation coefficient of ≤ 100 Sved and with at least one second peak (P2) with an average sedimentation coefficient of ≥ 1000 Sved.

Preferably, the polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) with an average sedimentation coefficient of ≤ 50 Sved and with at least one second peak (P2) with an average sedimentation coefficient of ≥ 10 000 Sved.

It is also preferred that the first peak (P1) has an average sedimentation coefficient of ≤ 15 Sved, more preferably in the range of 4 to 10 Sved, most preferably in the range of 5.5 to 8.5 Sved.

Furthermore, it is also preferred that the second peak (P2) has an average sedimentation coefficient of ≥ 14 000 Sved, more preferably in the range of 15 000 to 50 000 Sved, most preferably in the range of 16 000 to 22 000 Sved. The range of 16 000 to to 22 000 Sved is most preferably obtained in case for polymers obtainable by a polymerization without employing any chain transfer agent (monomer component c)). However, in case such a chain transfer agent is employed during polymerization, the second peak (P2) has most preferably an average sedimentation coefficient in the range of 16 000 to 42 000 Sved.

It is also preferred that the first peak (P1) has a weight average peak maximum of ≥ 400 000 g/mol, preferably in the range of 410 000 to 1 000 000 g/mol, most preferably in the range of 420 000 to 750 000 g/mol. This is preferably the case for polymers obtainable by a polymerization without employing any chain transfer agent (monomer component c)).

In another embodiment, it is also preferred that the first peak (P1) has a weight average peak maximum of ≥ 50 000 g/mol, preferably in the range of 55 000 to 800 000 g/mol, most preferably in the range of 60 000 to 750 000 g/mol. This is preferably the case for polymers obtainable by a polymerization with employing a chain transfer agent (monomer component c)).

In respect of the at least bimodal molecular weight distribution (as defined above) of the polymer according to the present invention, it is also possible in one embodiment of the present invention that the first peak (P1) is split into at least two peaks (P1.1, P1.2, ... P1.X) and the weight average sum of said peaks (P1.1, P1.2, ... P1.X) has a sedimentation coefficient of ≤ 10 Sved, more preferably ≤ 8 Sved. Analogously to the above disclosed connection with the first peak (P1), the second peak (P2) may also be split into at least two peaks (P2.1, P2.2, ... P2.X).

Furthermore, it is preferred that the polymer has an at least trimodal molecular weight distribution, in particular a trimodal or tetramodal molecular weight distribution.

The polymer components covered by the first peak (P1) are, as already described above, water-soluble polymer components since the respective polymer components have a rather low molecular weight.

The solubility of the polymer is determined by methods known to those skilled in the art, for example, by admixing the polymer present in the inventive inverse dispersion with a defined amount of water (see, for example, EP-A 343 840 or preferably the above mentioned determination method of the sedimentation coefficient in the unit of svedberg (Sved) according to P. Schuck).

It is preferred that the amount of polymer components covered by the first peak (P1) of the polymer is between 5 to 95% by weight, preferably between 25 and 90% by weight, more preferably between 35 and 75% by weight, most preferably between 50 and 60% by weight, related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

In one embodiment of the present invention, it is also preferred that the water-soluble polymer components of the polymer are ≥ 25% by weight related to the total amount of polymer.

Furthermore, it is preferred that the water-soluble polymer components of the polymer are between 25 to 90% by weight, preferably between 35 and 75% by weight, more preferably between 50 and 60% by weight, related to the total amount of polymer.

In one embodiment of the present invention, it is preferred that

i) the anionic monomer according to monomer component a) in the polymer is selected from Li acrylate or Li trifluorboroacrylate, and/or

ii) the nonionic monomer according to monomer component a) in the polymer contains at least two different associative monomers according to formula (I), wherein in the first monomer R is C_1-C_3-alkyl, preferably methyl, and n is an integer from 40 to 50, preferably 45, and in the second monomer R is C_{16}-C_{22}-alkyl, preferably C_{18}-alkyl, and n is an integer from 20 to 30, preferably 25.

Preferably, the polymer is prepared by polymerization of

a) 20 to 99.99% by weight, preferably 95 to 99.95% by weight, related to the total amount of polymer, of at least one anionic monomer and/or at least one nonionic monomer,

b) 10 to 500 ppm, preferably 30 to 490 ppm, more preferably 50 to 400 ppm, even more preferably less than 375 ppm, related to the total amount of polymer, of at least one crosslinker,

c) 0 to 3% by weight, preferably 0.05 to 0.5% by weight, related to the total amount of polymer, of optionally at least one chain transfer agent.

The polymerization of the polymer according to the process of the present invention is carried out in two subsequent steps I) and II) with:

I) polymerization of monomer component a) and monomer component b),

II) polymerization of monomer component a), optionally monomer component c) and in the complete absence or in the presence of < 10 ppm (related to the total amount of polymer) of monomer component b),

wherein step II) is carried out after the polymerization of step I) is finished or step I) is carried out after the polymerization of step II) is finished.

The polymerization of steps I) and II) as such is known to the person skilled in the art. The above-described steps I) and II) can be carried out by any method known to the person skilled in the art. The order of carrying out the steps I) and II) can be freely chosen. It is even possible to carry out step I) and II) for several times as independent batches. However, it is preferred to first carry out step I) and, after the polymerization is finished, step II) follows.

It is preferred that the polymerization for obtaining the polymer according to the process of the present invention is carried out under consideration of at least one of the following options i) to v), wherein

i) step II) is carried out after the polymerization of step I) is finished, and/or

ii) step II) is carried out by polymerization of monomer component a) and monomer component c), preferably monomer component a) contains at least one anionic monomer and optionally at least one associative monomer, and/or

iii) monomer component b) is completely absent during the polymerization according to step II), and/or

iv) step I) is carried out by polymerization of monomer component a), 10 to 10.000 ppm, preferably 100 to 2000 ppm, more preferably 500 to 1000 ppm, (related to the total amount of polymer) of monomer component b) and optionally monomer component c), and/or

v) in step II), 5 to 95 % by weight, preferably 25 to 90 % by weight, more preferably between 35 and 75 % by weight, even more preferably between 50 and 60 % by weight of the polymer components covered by the first peak (P1) of the polymer are produced related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

The temperature of the individual steps I) and II) can be chosen freely and independently from each other. However, it is preferred that

i) step I) is initiated at a lower temperature than the temperature of step II), and/or

ii) step I) is carried out at a temperature in the range of -5 °C to 40 °C, preferably in the range of 20 °C to 30 °C, more preferably the temperature is kept constant during step I), and/or

iii) step II) is carried out at a temperature in the range of 70 °C to 120 °C, preferably in the range of 80 °C to 100 °C, more preferably the temperature is kept constant during step II), and/or

iv) step I) is started at a temperature in the range of -5 °C to 40 °C, preferably in the range of 15 °C to 25 °C, and heated-up by the exothermal polymerization under adiabatical conditions.

It is preferred that the polymerization in steps I) and II) is carried out by an emulsion polymerization, preferably by an inverse emulsion polymerization. It is also preferred that steps I) and II) as described above are carried out in the same polymerization vessel. Any vessel suitable for polymerization and known to the skilled person can be used, such as a glass vessel or a reactor.

It is also preferred that the inverse emulsion polymerization is followed by distillation by means of the liquid dispersion polymer technology.

Inverse emulsion polymerization is understood by the person skilled in the art generally to mean polymerization processes according to the following definition: the hydrophilic monomers are dispersed in a hydrophobic oil phase. The polymerization is effected directly in this hydrophilic monomer particle by addition of initiator.

In addition, it is preferred that, after the inverse emulsion polymerization and before the addition of activator (as defined below in more detail), at least a portion of water and at least a portion of the low-boiling constituents of the oil phase are distilled off, especially by means of LDP technology (Liquid Dispersion Polymer Technology). LDP technology as such is known to those skilled in the art; it is described, for example, in WO 2005/097834.

The information which follows, unless stated otherwise, applies to all kinds of emulsion polymerization (under consideration of step I) and/or step II) as defined above), for example to emulsion polymerization in water, which then constitutes the continuous phase, and especially also to inverse emulsion polymerization in which the hydrophobic oil phase constitutes the continuous phase. A suitable polymerization initiator is used for the polymerization. Redox initiators and/or thermally activatable free-radical polymerization initiators are preferred.

Suitable thermally activatable free-radical initiators or the oxidative component of the redox initiator pair are in particular those of the peroxy and azo type. These include hydrogen peroxide, peracetic acid, t-butyl hydroperoxide, di-t-butyl peroxide, dibenzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-2,5-bis(hydroperoxy)hexane, perbenzoic acid, t-butyl peroxypivalate, t-butyl peracetate, dilauroyl peroxide, dicapryloyl peroxide, distearoyl peroxide, dibenzoyl peroxide, diisopropyl peroxydicarbonate, didecyl peroxydicarbonate, dieicosyl peroxydicarbonate, di-t-butyl perbenzoate, azobisisobutyronitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, ammonium persulfate, potassium persulfate, sodium persulfate and sodium perphosphate.

The persulfates (peroxodisulfates), especially sodium persulfate, are most preferred.

In the performance of the emulsion polymerization, the initiator is used in a sufficient amount to initiate the polymerization reaction. The initiator is typically used in an amount of about 0.01 to 3% by weight, based on the total weight of the monomers used. The amount of initiator is preferably about 0.05 to 2% by weight and especially 0.1 to 1% by weight, based on the total weight of the monomers used.

The emulsion polymerization is effected typically at 0°C to 100°C. It can be performed either as a batch process or in the form of a feed process. In the feed method, at least a portion of the polymerization initiator and optionally a portion of the monomers are initially charged and heated to polymerization temperature, and then the rest of the polymerization mixture is supplied, typically over several separate feeds, one or more of which comprise the monomers in pure or emulsified form, continuously or stepwise while maintaining the polymerization. Preference is given to supplying the monomer in the form of a monomer emulsion. In parallel to the monomer supply, further polymerization initiator can be metered in.

In preferred embodiments, the entire amount of initiator is initially charged, i.e. there is no further metering of initiator parallel to the monomer feed.

In a preferred embodiment, the thermally activatable free-radical polymerization initiator is therefore initially charged completely and the monomer mixture, preferably in the form of a monomer emulsion, is fed in. Before the feeding of the monomer mixture is started, the initial charge is brought to the activation temperature of the thermally activatable free-radical polymerization initiator or a higher temperature. The activation temperature is considered to be the temperature at which at least half of the initiator has decomposed after one hour.

In another preferred preparation method, the polymer is obtained by polymerization of a monomer mixture in the presence of a redox initiator system. A redox initiator system comprises at least one oxidizing agent component and at least one reducing agent component, in which case heavy metal ions are preferably additionally present as a catalyst in the reaction medium, for example salts of cerium, manganese or iron (II).

Suitable oxidizing agent components are, for example, peroxides and/or hydroperoxides such as hydrogen peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, pinane hydroperoxide, diisopropylphenyl hydroperoxide, dicyclohexyl percarbonate, dibenzoyl peroxide, dilauroyl peroxide and diacetyl peroxide. Hydrogen peroxide and tert-butyl hydroperoxide are preferred.

Suitable reducing agent components are alkali metal sulfites, alkali metal dithionites, alkali metal hyposulfites, sodium hydrogensulfite, Rongalit C (sodium formaldehydesulfoxylate), mono- and dihydroxyacetone, sugars (e.g. glucose or dextrose), ascorbic acid and salts thereof, acetone bisulfite adduct and/or an alkali metal salt of hydroxymethanesulfinic acid. Sodium hydrogensulfite or sodium metabisulfite is preferred.

Suitable reducing agent components or catalysts are also iron(II) salts, for example iron(II) sulfate, tin(II) salts, for example tin(II) chloride, titanium(III) salts such as titanium(III) sulfate.

The amounts of oxidizing agent used are 0.001 to 5.0% by weight, preferably from 0.005 to 1.0% by weight and more preferably from 0.01 to 0.5% by weight, based on the total weight of the monomers used. Reducing agents are used in amounts of 0.001 to 2.0% by weight, preferably of 0.005 to 1.0% by weight and more preferably of 0.01 to 0.5% by weight, based on the total weight of the monomers used.

A particularly preferred redox initiator system is the sodium peroxodisulfate/sodium hydrogensulfite system, for example 0.001 to 5.0% by weight of sodium peroxodisulfate and 0.001 to 2.0% by weight of sodium hydrogensulfite, especially 0.005 to 1.0% by weight of sodium peroxodisulfate and 0.005 to 1.0% by weight of sodium hydrogensulfite, more preferably 0.01 to 0.5% by weight of sodium peroxodisulfate and 0.01 to 0.5% by weight of sodium hydrogensulfite.

A further particularly preferred redox initiator system is the t-butyl hydroperoxide/hydrogen peroxide/ascorbic acid system, for example 0.001 to 5.0% by weight of t-butyl hydroperoxide, 0.001 to 5.0% by weight of hydrogen peroxide and 0.001 to 2.0% by weight of ascorbic acid, especially 0.005 to 1.0% by weight of t-butyl hydroperoxide, 0.005 to 1.0% by weight of hydrogen peroxide and 0.005 to 1.0% by weight of ascorbic acid, more preferably 0.01 to 0.5% by weight of t-butyl hydroperoxide, 0.01 to 0.5% by weight of hydrogen peroxide and 0.01 to 0.5% by weight of ascorbic acid.

The polymer is preferably prepared by inverse emulsion polymerization, by first separately preparing an aqueous phase of the water-soluble components and an oil phase. Thereafter, the two phases are mixed with one another to obtain a water-in-oil dispersion. The mixture is polymerized by adding a redox initiator system; optionally, another, thermal initiator can subsequently be added or, if already present, thermally activated.

The aqueous phase comprises, for example, a chain transfer agent, a crosslinker, an anionic monomer and/or an nonionic monomer, and optionally further components. Suitable further components (as defined below in more detail) are, for example, complexing agents for salts such as pentasodium diethylenetriaminepentaacetic acid, or compounds which can be used to adjust the pH and/or stabilizing agents, such as citric acid.

The oil phase comprises, for example, an emulsifier, a stabilizer, a high-boiling oil, a low-boiling oil and/or optionally an associative monomer. In addition, the oil phase may optionally comprise a nonionic monomer.

In a preferred embodiment of the present invention, an associative monomer according to monomer component a) is added to the oil phase in the inverse emulsion polymerization.

In the inverse emulsion polymerization, the temperature can be kept constant or else it can rise. The rise in the temperature can be performed continuously or in stages. For example, the temperature can rise by 0.2 to 10°C per minute during the polymerization, preferably from 1 to 3°C per minute. The temperature rise is controlled by the rate of initiator addition. The starting temperature value may be 0 to 30°C, preferably 10 to 20°C.

In another embodiment of the present invention, the temperature in the inverse emulsion polymerization is kept constant (cold method); the temperature is 0 to 30°C, preferably 10 to 20°C. In a further embodiment of the present invention, the temperature is kept constant within a higher temperature range (hot method). The temperature in the polymerization is 40 to 150°C, preferably 70 to 120°C.

In a particularly preferred embodiment of the present invention, the temperature is kept constant during the inverse emulsion polymerization, the temperature being at least 40°C, preferably 50 to 90°C.

If, in the context of the present invention, the temperature is kept constant in a polymerization, especially in an inverse emulsion polymerization, this means that the temperature is kept at a constant value from the start of the polymerization. Variations of +/- 5°C, preferably +/- 2°C and especially +/- 1°C during the polymerization process are considered to be a constant temperature (based on the desired constant temperature value). The temperature is kept constant until the polymerization has ended, which is preferably the case after a conversion of more than 90% of the monomers used, more preferably more than 95% by weight and especially preferably at full conversion (100% by weight). The temperature can be kept constant by removing the heat of reaction which arises by cooling. The start of the polymerization is normally the addition of the polymerization initiator, preferably the addition of a redox initiator system. Normally, the system is first heated to the desired temperature and a constant temperature is awaited while stirring. Subsequently, the polymerization initiator is added, as a result of which the polymerization process commences. In one embodiment of the present invention, the temperature is kept constant at a value above the melting point of the associative monomer used.

It is even more preferred,

i) in both steps I) and II), an aqueous phase and an oil phase are employed, and/or

ii) the aqueous phase in step I) contains at least one anionic monomer, at least one crosslinker and optionally at least one nonionic monomer, and/or

iii) the oil phase in step I) and/or step II) contains at least one stabilizing agent, at least one low-boiling oil, at least one high-boiling oil and optionally at least one associative monomer, and/or

iv) the aqueous phase in step II) contains at least one anionic monomer, optionally at least one nonionic monomer, and optionally at least one chain transfer agent, and/or

v) in step II), the mixture of the aqueous phase and the oil phase is completely added to the polymerization vessel (batch reaction) and afterwards the initiators are added continuously, and/or

vi) in step II), the mixture of the aqueous phase and the oil phase is continuously added to the polymerization vessel (continuous reaction) and the initiators are added prior to said mixture or the initiators are added continuously and in parallel to said mixture into the polymerization vessel.

It is also preferred that in step II) ≥ 5 %, preferably ≥ 25 %, most preferably ≥ 50 % by weight of the polymer components covered by the first peak (P1) of the polymer are produced related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

In a preferred embodiment of the present invention, the polymer is obtained by polymerization of

a) at least one anionic monomer and/or at least one nonionic monomer (monomer component a),

b) at least one crosslinker (monomer component b),

c) optionally at least one chain transfer agent (monomer component c),

wherein the polymer has an at least trimodal molecular weight distribution with i) at least one first peak (P1) with an average sedimentation coefficient of ≤ 10 Sved, wherein the first peak (P1) is splitted into at least two peaks (P1.1, P1.2, ... P.X) and with ii) at least one second peak (P2) with an average sedimentation coefficient of ≥ 10.000 Sved, and the polymer components covered by the first peak (P1) of the polymer are between 25 to 90 % by weight, related to the sum of polymer components covered by the first peak (P1) and the second peak (P2),

and wherein the polymerization is carried out in two subsequent steps I) and II) with:

I) polymerization of monomer component a) and monomer component b),

II) polymerization of monomer component a), optionally monomer component c) and in the complete absence or in the presence of < 10 ppm (related to the total amount of polymer) of monomer component b),

wherein step II) is carried out after the polymerization of step I) is finished and wherein in step II) between 25 to 90 % by weight of the polymer components covered by the first peak (P1) of the polymer are produced related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

Within this embodiment it is more preferred that

i) monomer component a) comprises at least one anionic monomer and at least one nonionic monomer, and/or

ii) monomer component b) is employed during the polymerization according to step I) in an amount of 30 to 490 ppm, more preferably 50 to 400 ppm, (related to the total amount of polymer) and monomer component b) is completely absent during the polymerization according to step II), and/or

iii) monomer component c) is present, and/or

iv) the first peak (P1) has an average sedimentation coefficient in the range of 5.5 to 8.5 Sved and the second peak (P2) has an average sedimentation coefficient in the range of 16 000 to 22 000 Sved.

Within this embodiment it is even more preferred that

i) the anionic monomer is Na or Li acrylate, Na or Li methacrylate, and the at least one nonionic monomer is acrylamide or at least one associative monomer selected from a compound of the formula (II), and/or

ii) monomer component b) is selected from N,N'-methylenebisacrylamide, pentaerythrityl triacrylate or pentaerythrityl tetraacrylate, and/or

iii) monomer component c) is selected from mercaptans, isopropanol or sodium hypophosphite.

The present invention further provides a process (as defined above), wherein an inverse dispersion comprises the at least one polymer as defined above. Methods for producing such an inverse dispersion are also described in context with the (inverse) emulsion polymerization.

The inverse dispersion may further comprise at least one oil (phase), at least one activator, at least one stabilizing agent, optionally at least one complexing agent and optionally additional additives. Preferably, the inverse dispersion is a water-in-oil emulsion.

Activators, stabilizing agents (stabilizers) such as emulsifiers, oils such as low-boiling oils and high-boiling oils and/or any further components as such, which may be present within the inventive inverse dispersion, are known to those skilled in the art. These compounds can be used individually or in the form of mixtures.

Activators as such are known in principle to those skilled in the art. Suitable activators are preferably surfactants, for example anionic, nonionic, cationic and/or amphoteric surfactants, which are disclosed, for example, in WO 2009/019225. Preference is given to using anionic and/or nonionic surfactants.

The nonionic surfactants used are preferably fatty alcohol alkoxylates. Fatty alcohol alkoxylates are also referred to as polyalkylene glycol ethers. Preferred fatty alcohol alkoxylates are alkoxylated, advantageously ethoxylated, especially primary alcohols having preferably 8 to 18 carbon atoms and an average of 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or branched, preferably 2-methyl-branched, or may comprise linear and methyl-branched radicals in a mixture, as typically present in oxoalcohol radicals. Especially preferred are, however, alcohol ethoxylates with linear radicals formed from alcohols of native or technical origin with 12 to 18 carton atoms, for example formed from coconut alcohol, palm alcohol, tallow fat alcohol or oleyl alcohol - or mixtures as derivable, for example, from castor oil - and an average of 2 to 8 EO per mole of alcohol. The preferred ethoxylated alcohols include, for example, C_{12}-C_{14}-alcohols with 3 EO, 4 EO or 7 EO, C_9-C_{11}-alcohol with 7 EO, C_{13}-C_{15}-alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C_{12}-C_{18}-alcohols with 3 EO, 5 EO or 7 EO and mixtures thereof such as mixtures of C_{12}-C_{14}-alcohol with 3 EO and C_{12}-C_{18}-alcohol with 7 EO. The degrees of ethoxylation reported are statistical averages which may be an integer or a fraction for a specific product. Preferred alcohol ethoxylates have a narrow homolog distribution (narrow range ethoxylates, NRE). In addition to these nonionic surfactants, it is also possible to use fatty alcohols with more than 12 EO. Examples thereof are tallow fat alcohol with 14 EO, 25 EO, 30 EO or 40 EO. It is also possible to use nonionic surfactants comprising

EO and PO groups together in a molecule. In this context, it is possible to use block copolymers with EO-PO block units or PO-EO block units, but also EO-PO-EO copolymers or PO-EO-PO copolymers. It will be appreciated that it is also possible to use mixed-alkoxylation nonionic surfactants in which EO and PO units are not present in blocks but in random distribution. Such products are obtainable by simultaneous action of ethylene oxide and propylene oxide on fatty alcohols.

In addition, further nonionic surfactants used may also be alkyl glycosides or alkyl polyglycosides. Alkyl glycosides or alkyl polyglycosides are generally understood by the person skilled in the art to mean compounds composed of at least one alkyl fragment and at least one sugar or polysugar fragment. The alkyl fragments preferably derive from fatty alcohols having a carbon atom number of 12 to 22, and the sugar fractions preferably from glucose, sucrose or sorbitan.

For example, it is possible to use alkyl glycosides of the general formula (1)

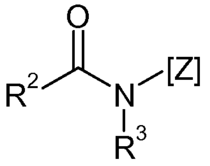
$$R^1O(G)_x \qquad (1)$$

in which R^1 is a primary straight-chain or methyl-branched, especially 2-methyl-branched, aliphatic radical having 8 to 22 and preferably 12 to 18 carbon atoms, and G is a glycoside unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization x, which specifies the distribution of monoglycosides and oligoglycosides, is any number between 1 and 10; x is preferably 1.2 to 1.4.

A further class of nonionic surfactants used with preference, which are used either as the sole nonionic surfactant or in combination with other nonionic surfactants, is that of alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters, as described, for example, in Japanese patent application JP 58/217598, or which are preferably prepared by the process described in international patent application WO-A-90/13533.

Nonionic surfactants of the amine oxide type may also be suitable, for example N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type. The amount of these nonionic surfactants is preferably not more than that of the ethoxylated fatty alcohols, especially not more than half thereof.

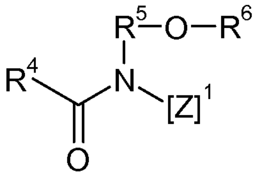
Further suitable surfactants are polyhydroxy fatty acid amides of the formula (2),



(2)

in which $R^2C(=O)$ is an aliphatic acyl radical having 6 to 22 carbon atoms, R^3 is hydrogen, an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms, and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances, which can be obtained typically by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of the formula (3)



(3)

in which R^4 is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R^5 is a linear, branched or cyclic alkylene radical having 2 to 8 carbon atoms or an arylene radical having 6 to 8 carbon atoms, and R^6 is a linear, branched or cyclic alkyl radical or an aryl radical, or an oxyalkyl radical having 1 to 8 carbon atoms, preference being given to C_1-C_4-alkyl or phenyl radicals, and $[Z]^1$ is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of this radical. $[Z]^1$ is preferably obtained by reductive amination of a sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy- or N-aryloxy-substituted compounds can then be converted to the desired polyhydroxy fatty acid amides, for example, according to WO-A-95/07331 by reaction with fatty acid methyl esters in the presence of an alkoxide as a catalyst.

The anionic surfactants used are, for example, those of the sulfonate and sulfate type. Useful surfactants of the sulfonate type include alkylbenzenesulfonates, preferably C_9-C_{13}-alkylbenzenesulfonates, olefinsulfonates, i.e. mixtures of alkene- and hydroxyalkanesulfonates, and disulfonates as obtained, for example, from C_{12}-C_{18}-monoolefins with terminal or internal double bonds by sulfonation with gaseous sulfur trioxide and subsequent alkaline or acidic hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, preferably secondary alkanesulfonates, which are obtained, for example, from C_{12}-C_{18}-alkanes by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization. Equally suitable are also the esters of α-sulfone fatty acids (ester sulfonates), for example the α-sulfonated methyl esters of hydrogenated coconut fatty acids, palm kernel fatty acids or tallow fatty acids.

Further suitable anionic surfactants are sulfonated fatty acid glyceryl esters. Fatty acid glyceryl esters are understood to mean the mono-, di- and triesters, and mixtures thereof as obtained in the preparation by esterification of a monoglycerol with 1 to 3 mol of fatty acid or in the transesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred sulfonated fatty acid glyceryl esters are the sulfonation products of saturated fatty acids having 6 to 22 carbon atoms, for example of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

Further suitable anionic surfactants are fatty alcohol sulfates, for example alk(en)yl sulfates. Preferred alk(en)yl sulfates are the alkali metal and especially the sodium salts of the sulfuric monoesters of the C_{12}-C_{18} fatty alcohols, for example of coconut fatty alcohol, tallow fatty alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, or of the C_{10}-C_{20} oxo alcohols and those monoesters of secondary alcohols of these chain lengths. Additionally preferred are alk(en)yl sulfates of the chain length mentioned which comprise a synthetic straight-chain alkyl radical produced on a petrochemical basis, which have analogous degradation behavior to the equivalent compounds based on fatty-chemical raw materials. In the interests of washing technology, preference is given to the C_{12}-C_{16}-alkyl sulfates and C_{12}-C_{15}-alkyl sulfates, and also C_{14}-C_{15}-alkyl sulfates. Suitable anionic surfactants are also 2,3-alkyl sulfates, which are prepared, for example, according to US patents 3,234,258 or 5,075,041 and can be obtained as commercial products from Shell Oil Company under the DAN® name.

Also suitable are the sulfuric monoesters of the straight-chain or branched C_7-C_{21}-alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C_9-C_{11} alcohols with an average of 3.5 mol of ethylene oxide (EO) or C_{12}-C_{18}-fatty alcohols with 1 to 4 EO.

Further suitable anionic surfactants are also the salts of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters, and which are monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. Preferred sulfosuccinates comprise C_8-C_{18}-fatty alcohol radicals or mixtures thereof. Especially preferred sulfosuccinates comprise a fatty alcohol radical which derives from ethoxylated fatty alcohols. Particular preference is given in turn to sulfosuccinates whose fatty alcohol radicals derive from ethoxylated fatty alcohols with narrow homolog distribution. It is likewise also possible to use alk(en)ylsuccinic acid with preferably 8 to 18 carbon atoms in the alk(en)yl chain or salts thereof.

Further suitable anionic surfactants are alkyl carboxylates, for example the sodium salts of saturated or unsaturated fatty acids, where the alkyl radical of the alkyl carboxylate is preferably linear.

In the context of the present invention, the activator is preferably selected from fatty alcohol alkoxylates, alkyl glycosides, alkyl carboxylates, alkylbenzenesulfonates, secondary alkanesulfonates and fatty alcohol sulfates, more preferably selected from fatty alcohol alkoxylates. One example of a preferred fatty alcohol alkoxylate is C_6-C_{17}(secondary)-poly(3-6)ethoxylate.

It is additionally preferred in the context of the present invention to use an activator which has a (relatively) high HLB (hydrophilic-lipophilic balance) value. The activator preferably has an HLB value of 7 to 18, more preferably of 8 to 15 and especially preferably of 9 to 13.

Activators with a high HLB value are preferably i) fatty alcohol alkoxylates formed from secondary alcohols or mixtures of alcohols having 12 to 18 carbon atoms and ethylene oxide or propylene oxide, and ii) alkyl glycosides formed from sucrose and C_8 to C_{22} fatty alcohols. Examples of such activators are the commercially available Synperonic 87K from Croda GmbH, Herrenpfad-Süd 33, 41334 Nettetal, Germany; Croduret 40 or other ethoxylated hydrogenated castor oils (ricinus oils) such as Etocas 40 or Crodesta F110, all from Croda.

In a further embodiment of the present invention, it is preferred to use a mixture of at least two activators, at least one activator having a high HLB value and at least one activator a low HLB value. The activator with a high HLB value preferably has a HLB value of > 12 to 20, and the activator with a low HLB value preferably has an HLB value of 1 to 12. In this embodiment, the activator with a high HLB value and the activator with a low HLB value may be present in any desired ratios known to those skilled in the art. Preferably, in the mixture, 20 to 50% by weight of activator with high HLB value and 50 to 80% by weight of activator with low HLB value are used. Additionally preferably, this ratio of activator with high HLB value to activator with low HLB value is adjusted such that the overall HLB value is 7 to 18, more preferably 8 to 15 and especially preferably 9 to 13.

In these mixtures of at least two activators, the activators with a high HLB value used are preferably alkyl glycosides or polyalkyl glycosides or polyalkyl oligoethylene oxide glycoside based on sucrose or sorbitan and C_8 to C_{22} fatty alcohols such as polyethylene glycol sorbitan monostearate or polyoxyethylene sorbitan monostearate. Examples of such activators are the commercially available Crillet 1, Crillet 3 or Crodesta F160, all obtainable from Croda. The activators used with a low HLB value are preferably alkyl glycosides formed from sucrose or sorbitan and C_8 to C_{22} fatty alcohols or fatty acids, such as sorbitan laurate or sorbitan stearate. Examples of such activators are the commercially available Crill 1, Crill 3 or Crodesta F10 from Croda.

According to the invention, the ratio of activator to the polymer is preferably > 10 : 100 [% by weight/% by weight], preferably 10.5 to 50 : 100 [% by weight/% by weight], more preferably 11.5 to 20 : 100 [% by weight/% by weight].

Suitable stabilizing agents are preferably emulsifiers such as polymeric emulsifiers. Typical emulsifiers are anionic emulsifiers, for example sodium laurylsulfate, sodium tridecyl ether sulfates, dioctylsulfosuccinate sodium salt and sodium salts of alkylaryl polyether sulfonates; and nonionic emulsifiers, for example alkylaryl polyether alcohols and ethylene oxide-propylene oxide copolymers. Sorbitan trioleate is likewise suitable as an emulsifier.

Preferred emulsifiers have the following general formula:

$$R\text{-}O\text{-}(CH_2\text{-}CHR'\text{-}O)_n\text{-}X$$

in which

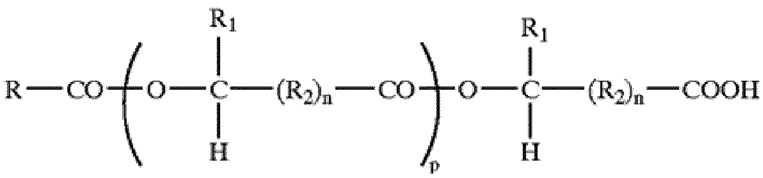
R is C_6-C_{30}-alkyl,
R′ is hydrogen or methyl,
X is hydrogen or SO_3M,
M is hydrogen or one alkali metal, and
n is an integer from 2 to 100.

Further suitable stabilizers are described, for example, in EP-A 172 025 or EP-A 172 724. Preferred stabilizers are copolymers of stearyl methacrylate and methacrylic acid.

According to this invention it is further preferred to employ having more than 30 carbon atoms, preferably more than 50 carbon atoms containing hydrophobic chains. The employment of such emulsifier as stabilizing agent is resulting in a dramatic increase of the stabilizing effect for the hydrophilic polymer particles dispersed in the hydrophobic continuous phase. In general are claimed for that purpose all emulsifiers or polymeric stabilizers containing more than 30 carbon atoms, preferably more than 50 carbon atoms in their hydrophobic chains. Optional this hydrophobic chain can be interrupted after every 6, preferred 10 or more carbon atoms by other atoms like oxygen, nitrogen, sulphur, phosphor or by groups like carbonate, isocyanate, carbamide, esters or others in an amount that they do not essentially disturb the hydrophobic character of the chain in order to get the low HLB-values as described below. Block-, graft- or comb-structure, preferably are based on polyhydroxystearic acid. In the block-structure the AB- or especially ABA-blocks are preferred. In the ABA block-structure the A block is preferably based on polyhydroxystearic acid and the B block on polyalkylene oxide.

The preferred concentration of these inventive stabilizing agents lies between 0.1 % and 10%, preferably between 1% to 5% by weight related to the total weight of the polymer.

The polymeric emulsifiers are more preferably a block copolymers having a general formula A-COO-B-OOC-A, in which B is the divalent residue of a water-soluble polyalkylene glycol and A is the residue of an oil-soluble complex monocarboxylic acid. Such polymeric emulsifiers, as well as the preparation thereof, have been disclosed in GB 2002400 and W09607689, the contents of which are herewith incorporated by reference. The emulsifiers, as described in GB2002400, are emulsifiers wherein A has a molecular weight of at least 500 and is the residue of an oil-soluble complex monocarboxylic acid, i.e. a fatty acid. These complex monocarboxylic acids may be represented by the general formula:

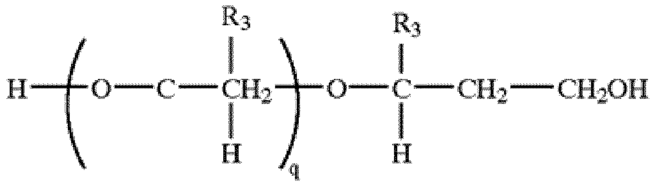


$$R-CO\left(O-\underset{H}{\overset{R_1}{C}}-(R_2)_n-CO\right)_p O-\underset{H}{\overset{R_1}{C}}-(R_2)_n-COOH$$

in which

R is hydrogen or a monovalent hydrocarbon or substituted hydrocarbon group;
R1 is hydrogen or a monovalent C1 to C24 hydro- carbon group;
R2 is a divalent C1 to C24 hydrocarbon group;
n is zero or 1;
p is an integer from zero to 200.

The units between the brackets in formula 1 may be all the same or they may differ in respect of R1, R2 and n. The quantity p will not normally have the same unique value for all molecules of the complex acid but will be statistically distributed about an average value lying within the range stated, as is commonplace in polymeric materials. Polymeric component B has a molecular weight of at least 500 and is the divalent residue of a water-soluble polyalkylene glycol having the general formula



$$H\left(O-C-\underset{H}{\overset{R_3}{CH_2}}\right)_q O-\underset{H}{\overset{R_3}{C}}-CH_2-CH_2OH$$

wherein

R3 is hydrogen or a C1 to C3 alkyl group;
q is an integer from 10 up to 500.

Most preferred emulsifiers used in the invention are e.g. PEG 30 Dipolyhydroxystearate. Another similar emulsifier for use with the invention are block copolymers (A-B-A) of polyethylene glycol and polyhydroxystearic acid with a mol weight of approximately 5000.

Furthermore the use of these ABA type block copolymers lead to water-in-oil emulsions having excellent stability during storage thus improving the shelf life of said emulsions. The resulting water-in-oil emulsions are stable and fluid at low temperatures, especially at 25° C.

Suitable high-boiling oils are, for example, 2-ethylhexyl stearate and hydroheated heavy naphtha, and suitable low-boiling oils are, for example, dearomatized aliphatic hydrocarbons or mineral oils of low viscosity.

In a preferred embodiment of the present invention, the inverse dispersion comprises at least one stabilizing agent wherein the stabilizing agent has one or more hydrophobic chains with more than 30 carbon atoms, preferably more than 50 carbon atoms, more preferably the stabilizing agent has an ABA block structure based on polyhydroxystearic acid as A block and polyalkylene oxide as B block.

The present invention further relates to a process for obtaining a thickener or deposition aid comprising at least one polymer as defined above or at least one inverse dispersion as defined above.

The present invention further relates to a polymer obtained by a polymerization process as described above.

The invention is illustrated hereinafter by the examples.

Examples

In the examples, the following abbreviations are used:

Monomers	
ACM	acrylamide
AA	acrylic acid
BEM	behenyl-25 methacrylate
MBA	methylene-bis-acrylamide (crosslinker)
TAAC	tetraallyl-ammonium chloride (crosslinker)
PETIA	pentaerythrityl tri/tetraacrylate (crosslinker)
TMPTA EOx	Trimethylolpropane tris(polyethylene glycol ether) triacrylate (TMPTA EOx) (crosslinker)

NaHP	sodium hypophosphite (chain transfer agent)
C16EO25MAc	C_{16}-C_{18}-fatty alcohol-(ethylene glycol)$_{25}$ ether methacrylate
Others	
Dehymuls LE	PEG 30 dipolyhydroxystearate
Wako V 59	2,2'-azobis(2-methylbutyronitrile)
pphm	parts per hundred parts of monomers [which corresponds to (10 to the power of 4) multiplied with (ppm related to total amount of polymer)]

General test methods

Unless stated otherwise, the following general test methods are used in the examples which follow:

Determination of viscosity in aqueous media

With reference to the methods according to DIN 51550, DIN 53018, DIN 53019, the Brookfield model DV II viscometer is used, unless stated otherwise within the following tables, at the speed of 10 or 60 revolutions per minute with the specified spindle no. 2, 3 or 6 to measure the viscosities reported in mPas.

Determination of viscosity at 25°C of 1wt% aqueous solution product (approximately 50wt% active polymer) - Brookfield viscosity is measured using a Brookfield DVII -fitted with a spindle 3 at 10rpm. The test is conducted in deionised water at 25°C. Initial viscosity is defined as the Brookfield viscosity measured within 35 minutes of making the sample.

Determination of viscosity at 25°C of an aqueous solution containing 0,4wt% product (approximatively 50wt% active polymer) and 100ppm calcium chloride - Brookfield viscosity is measured using a Brookfield DVII - fitted with a spindle 2 at 60rpm. The test is conducted in 100ppm calcium chloride solution in deionised water at 25°C. Initial viscosity is defined as the Brookfield viscosity measured within 2 hours of making the sample.

Assessing Phase and Brookfield viscosity stability

Brookfield viscosity is measured using a Brookfield DV-E viscometer fitted with a LV2 spindle at 60 RPM. The test is conducted in accordance with the instrument's instructions. Initial viscosity is defined as the Brookfield viscosity measured within 24 hours of making the sample. Samples are stored in glass jars with a screw cap lid and aged undisturbed in a constant temperature room maintained at 35 °C. Physical stability is assessed by visual observation of the product in the undisturbed glass jar. Products are deemed stable when no clear layer is observed at the bottom of the jar. Products are deemed unstable when a clear layer is observed at the bottom of the jar. Brookfield viscosity of the aged sample is measured after tipping the jar by hand to homogenize the sample.

Determining viscosity slope

Acidified water is prepared gravimetrically by adding about 0.1 ppm hydrochloric acid to deionized water. A series of aqueous polymer solutions are prepared to logarithmically span between 0.01 and 1 polymer weight percent of the polymer in said acidic water. Each polymer solvent solutions is prepared gravimetrically by mixing the polymer and solvent with a SpeedMixer DAC 150 FVZ-K (made by FlackTek Inc. of Landrum, South Carolina) for 1 minute at 2,500 RPM in a Max 60 cup or Max 100 cup to the target polymer weight percent of the aqueous polymer solution. Viscosity as a function of shear rate of each polymer solvent solutions is measured at 40 different shear rates using an Anton Paar rheometer with a DSR 301 measuring head and concentric cylinder geometry. The time differential for each measurement is logarithmic over the range of 180 and 10 seconds and the shear rate range for the measurements is 0.001 to 500 1/s (measurements taken from the low shear rate to the high shear rate).

Viscosities 0.2 Pa s and greater at a shear rate of 0.01 1/s as a function of polymer weight percent of the aqueous polymer solvent solution was fit using the equation $Y = bX^a$ wherein X was the polymer concentration in the solvent polymer solution, Y was the polymer solvent solution viscosity, b was the extrapolated solvent polymer solution viscosity when X is extrapolated to one weight percent and the exponent a is the polymer concentration viscosity scaling power, here defined as the viscosity slope, over the polymer concentration range where the exponent a is the highest value.

Use of the inventive polymers in standard formulation of fabric softeners

W3: Preparation of a methyltris(hydroxyethyl)ammonium ditallow fatty acid ester methosulfate, partly hydrogenated, fabric softener (active content 5.5%)

The fabric softener formulation has a pH of 2.7 and comprises 5.5% by weight of methyltris(hydroxyethyl)ammonium ditallow fatty acid ester methosulfate (partly hydrogenated) and 94.5% by weight of demineralized water.

Addition of 1wt% dispersion (approximately 50wt% active polymer) to fabric softener formulations W3.

The thickener is added gradually at room temperature to the particular fabric softener formulation and stirred until the formulation has homogenized.

The Brookfield viscosity is measured 2h after the preparation using the Brookfield model DV II viscometer at the speed of 10 revolutions per minute with the specified spindle no.6 reported in mPas. The results are compiled in Table 2.

Determination of the soluble and insoluble parts of the polymer using the analytical ultracentrifuge (AUC)

Sample preparation: the sample was diluted with distilled water to 2 g/l polymer and stirred with magnetic stirrer overnight. After that, this solution was diluted to 1 g/l using 0.2 M NaNO3 solution adjusted to pH 4 by HCL. Resulting solution (1 g/l polymer, 0.1 M NaNO3, pH 4) was equilibrated by stirring for 2 hours.

Sedimentation velocity runs have been recorded using a Beckman Optima XL-I (Beckman Instruments, Palo Alto, USA) with interference optical detection system (wavelength 675 nm) . The centrifugation speed was varied between 1000 rpm and 45,000 rpm.

The sedimentation coefficient, defined as a median value for each fraction, also named as “average sedimentation coefficient” and the concentration of one sedimenting fraction were determined using a standard analysis Software (SEDFIT) using the density and viscosity of the solvent, and a specific refractive index increment of the polymer. The sedimentation coefficient is in units of Sved (1 Sved = 10^{-13} seconds). The standard deviation for the determination of weight fraction and sedimentation coefficients of water soluble and crosslinked water-swellable polymers is 3%, 10% and up to 30% respectively. The weight percent of soluble polymer is based on the AUC value.

Determination of the molecular weight for the soluble part of the polymers using the analytical Field Flow Fractionation (FFF)

Sample preparation: the sample was diluted with distilled water to 2 g/l polymer and stirred with magnetic stirrer overnight. After that, this solution was diluted to 1 g/l using 0.2 M NaNO3 solution adjusted to pH 4 by HCL. Resulting solution (1 g/l polymer, 0.1 M NaNO3, pH 4) was equilibrated by stirring for 2 hours. In order to remove gel particles and oil this sample was centrifuged at 10000 rpm for 20 hours. The clear middle phase was taken out for the analysis with Field Flow Fractionation.

FFF equipment and measurements parameters: Eclipse AF4 (Wyatt) equipped with laser light scattering detector Heleos 2 and concentration (refractive index) detector R.I. Optilab T-Rex., long separation channel with spacer W 350µm, injection flow: 0.15ml/min, focus time: 3 min, membrane: Millipore reg. cellulose with molecular weight cut off 10kD. dn/dc value of 0.14 ml/g was used for the evaluation of the light scattering data (Zimm model). In the case the sample has still contained the traces of microgel this signal was not included into the evaluation range.

Fabric and Test Swatch Preparation Method

Fabrics are assessed under NA Top Load wash conditions using Kenmore FS 600 and/or 80 series washer machines. Wash Machines are set at: 32°C/15°C wash/rinse temperature, 6 gpg hardness, normal cycle, and medium load (64 liters). Fabric bundles consist of 2.5 kilograms of clean fabric consisting of 100% cotton. Test swatches are included with this bundle and comprise of 100% cotton Euro Touch terrycloth towels (purchased from Standard Textile, Inc. Cincinnati, OH). Bundles are stripped according to the Fabric Preparation-Stripping and Desizing procedure before running the test. Tide Free liquid detergent (1x recommended dose) is added under the surface of the water after the machine is at least half full. Once the water stops flowing and the washer begins to agitate, the clean fabric bundle is added. When the machine is almost full with rinse water, and before agitation has begun, the fabric care testing composition is slowly added (1x dose), ensuring that none of the fabric care testing composition comes in direct contact with the test swatches or fabric bundle. When the wash/rinse cycle is complete, each wet fabric bundle is transferred to a corresponding dryer. The dryer used is a Maytag commercial series (or equivalent) dryer, with the timer set for 55 minutes on the cotton/high heat/timed dry setting. This process is repeated for a total of three (3) complete wash-dry cycles. After the third drying cycle and once the dryer stops, 12 Terry towels from each fabric bundle are removed for actives deposition analysis. The fabrics are then placed in a constant Temperature/Relative Humidity (21˚C, 50% relative humidity) controlled grading room for 12-24 hours and then graded for softness and/or actives deposition.

The Fabric Preparation-Stripping and Desizing procedure includes washing the clean fabric bundle (2.5 Kg of fabric comprising 100% cotton) including the test swatches of 100% cotton EuroTouch terrycloth towels for 5 consecutive wash cycles followed by a drying cycle. AATCC (American Association of Textile Chemists and Colorists) High Efficiency (HE) liquid detergent is used to strip/de-size the test swatch fabrics and clean fabric bundle (1x recommended dose per wash cycle). The wash conditions are as follows: Kenmore FS 600 and/or 80 series wash machines (or equivalent), set at: 48˚C/48˚C wash/rinse temperature, water hardness equal to 0 gpg, normal wash cycle, and medium sized load (64 liters). The dryer timer is set for 55 minutes on the cotton/high/timed dry setting.

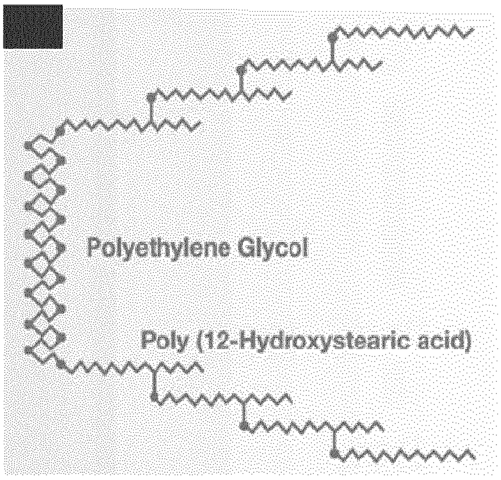
Silicone Measurement Method

Silicone is extracted from approximately 0.5 grams of fabric (previously treated according to the test swatch treatment procedure) with 12 mL of either 50:50 toluene:methylisobutyl ketone or 15:85 ethanol:methylisobutyl ketone in 20 mL scintillation vials. The vials are agitated on a pulsed vortexer for 30 minutes. The silicone in the extract is quantified using inductively coupled plasma optical emission spectrometry (ICP-OES). ICP calibration standards of known silicone concentration are made using the same or a structurally comparable type of silicone raw material as the products being tested. The working range of the method is 8 – 2300 µg silicone per gram of fabric. Concentrations greater than 2300 µg silicone per gram of fabric can be assessed by subsequent dilution. Deposition efficiency index of silicone is determined by calculating as a percentage, how much silicone is recovered, via the aforementioned measurement technique, versus how much is delivered via the formulation examples. The analysis is performed on terrycloth towels (EuroSoft towel, sourced from Standard Textile, Inc, Cincinnati, OH) that have been treated according to the wash procedure outlined herein.

Stabilizing agents used in the examples

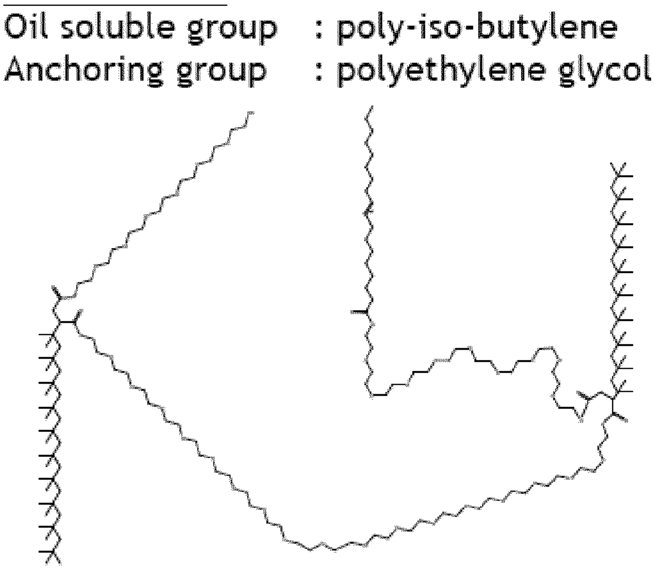
Stabilizing agent A (nonionic block copolymer): Polyglyceryl-dipolyhydroxystearate with CAS-Nr. 144470-58-6

Stabilizing agent B is a nonionic ABA-block copolymer with molecular weight of about 5000g/mol, and a hydrophobic lipophilic balance value (HLB) of 5 to 6, wherein the A block is based on polyhydroxystearic acid and and the B block on polyalkylene oxide.



Stabilizing agent C (nonionic block copolymer, Dehymuls LE): PEG-30 Dipolyhydroxystearate, with CAS-Nr. 70142-34-6

Stabilizing agent D (nonionic block copolymer): Alcyd Polyethylenglycol Poly-isobutene stabilizing surfactant with HLB 5-7



Comparative Example 1 (CE1)

Synthesis of the polymer

An aqueous phase of water soluble components is prepared by admixing together the following components:

1.19 g (0.19 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,

232.89 g (93.16 pphm) of water,

17.5 g (0.07 pphm) of methylene-bis-acrylamide (1% aqueous solution),

250.0 g (100 pphm) of acrylic acid, and

240.0 g (25.92 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase is prepared by admixing together the following components:

143.33 g (8.6 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)

162.96 g (12.3 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)

184.13 g (73.65 pphm) of 2-ethylhexyl stearate, and

3.75 g (1.5 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Polymerisation is effected by addition of a redox couple of sodium metabisulphite and tertiary butyl hydroperoxide stepwise such that is a temperature increase of 2°C/min.

After polymerisation are fed simultaneously 10.15g (0,25pphm) of tertiary butyl hydroperoxide (6.16% solution in solvent) and 11.98g (0,25pphm) of sodium metabisulphite (5.26% emulsion) for 120 min. (chem. deso.).

During this feeding heat or cool to 85°C.

Vacuum distillation is carried out to remove water and volatile solvent to give a final product of 50% polymer solids.

To this product addition is made of 40.0 g (16.0 pphm) of a fatty alcohol C13-C15 alkoxylate, (CAS No. 68131-39-5).

Example 1

Synthesis of the polymer

An aqueous phase (1) of water soluble components is prepared by admixing together the following components:

0.595g (0.095 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,

116.445 g (46.58 pphm) of water,

17.5 g (0.07 pphm) of methylene-bis-acrylamide (1% aqueous solution),

125.0 g (50 pphm) of acrylic acid, and
120.0 g (12.96 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (1) is prepared by admixing together the following components:
71.665 g (4.3 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
81.48 g (6.15 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
92.065 g (36.825 pphm) of 2-ethylhexyl stearate, and
1.875 g (0.75 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (1) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Polymerisation is effected by addition of a redox couple of sodium metabisulphite and tertiary butyl hydroperoxide stepwise such that is a temperature increase of 2°C/min.

After max. temperature is reached go on heating to 85°C.

Then the following mixture aqueous/oil phase (2) is fed continuously over 60 min.

An aqueous phase (2) of water soluble components is prepared by admixing together the following components:

0.595g (0.095 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,
116.445 g (46.58 pphm) of water,
125.0 g (50 pphm) of acrylic acid, and
120.0 g (12.96 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (2) is prepared by admixing together the following components:
71.665 g (4.3 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
81.48 g (6.15 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
92.065 g (36.825 pphm) of 2-ethylhexyl stearate, and
1.875 g (0.75 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (2) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Simultaneously are fed 10.15g (0,25pphm) of tertiary butyl hydroperoxide (6.16% solution in solvent) and 11.98g (0,25pphm) of sodium metabisulphite (5.26% emulsion) for 120 min. (polym. + chem. deso.)

Then vacuum distillation is carried out to remove water and volatile solvent to give a final product of 50% polymer solids.
To this product addition is made of 40.0 g (16.0 pphm) of a fatty alcohol C13-C15 alkoxylate, (CAS No. 68131-39-5).

Example 2
Synthesis of the polymer
An aqueous phase (1) of water soluble components is prepared by admixing together the following components:
0.893g (0.143 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,
187.65 g (75.06 pphm) of water,
17.5 g (0.07 pphm) of methylene-bis-acrylamide (1% aqueous solution),
187.5 g (75 pphm) of acrylic acid, and
180.0 g (19.44 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (1) is prepared by admixing together the following components:
107.498 g (6.45 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
122.22 g (9.225 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
138.098 g (5.238 pphm) of 2-ethylhexyl stearate, and
2.813 g (1.125 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (1) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Polymerisation is effected by addition of a redox couple of sodium metabisulphite and tertiary butyl hydroperoxide stepwise such that is a temperature increase of 2°C/min.

After max. temperature is reached go on heating to 85°C.

Then the following mixture aqueous/oil phase (2) is fed continuously over 60 min.

An aqueous phase (2) of water soluble components is prepared by admixing together the following components:

0.298 g (0.04 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,
62.55 g (25.02 pphm) of water,
62.5 g (25 pphm) of acrylic acid, and
60.0 g (6.48 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (1) is prepared by admixing together the following components:
71.665 g (4.3 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
81.48 g (6.15 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
92.065 g (36.825 pphm) of 2-ethylhexyl stearate, and
1.875 g (0.75 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (2) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Simultaneously are fed 10.15g (0,25pphm) of tertiary butyl hydroperoxide (6.16% solution in solvent) and 11.98g (0,25pphm) of sodium metabisulphite (5.26% emulsion) for 120 min. (polym. + chem. deso.)

Then vacuum distillation is carried out to remove water and volatile solvent to give a final product of 50% polymer solids.
To this product addition is made of 40.0 g (16.0 pphm) of a fatty alcohol C13-C15 alkoxylate, (CAS No. 68131-39-5).

Example 3

Synthesis of the polymer

An aqueous phase (1) of water soluble components is prepared by admixing together the following components:
0.298 g (0.04 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,
62.55 g (25.02 pphm) of water,
17.5 g (0.07 pphm) of methylene-bis-acrylamide (1% aqueous solution),
62.5 g (25 pphm) of acrylic acid, and
60.0 g (6.48 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (1) is prepared by admixing together the following components:

71.665 g (4.3 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
81.48 g (6.15 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
92.065 g (36.825 pphm) of 2-ethylhexyl stearate, and
1.875 g (0.75 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (1) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Polymerisation is effected by addition of a redox couple of sodium metabisulphite and tertiary butyl hydroperoxide stepwise such that is a temperature increase of 2°C/min.

After max. temperature is reached go on heating to 85°C.

Then the following mixture aqueous/oil phase (2) is fed continuously over 60 min.

An aqueous phase (2) of water soluble components is prepared by admixing together the following components:

0.893g (0.143 pphm) of a 40% aqueous solution of pentasodium diethylenetriaminepentaacetate,
187.65 g (75.06 pphm) of water,
187.5 g (75 pphm) of acrylic acid, and
180.0 g (19.44 pphm) of sodium hydroxide (50% aqueous solution).

An oil phase (2) is prepared by admixing together the following components:
107.498 g (6.45 pphm) of a PEG 30 Dipolyhydroxystearat (15% in solvent)
122.22 g (9.225 pphm) of a polymeric stabilizer (stearyl methacrylate-methacrylic acid copolymer: (18.87% in solvent)
138.098 g (5.238 pphm) of 2-ethylhexyl stearate, and
2.813 g (1.125 pphm) of dearomatised hydrocarbon solvent with a boiling point between 160°C and 190°C.

The two phases (2) are mixed together in a ratio of 40 parts oil phase to 60 parts aqueous phase under high shear to form a water-in-oil emulsion. The resulting water-in-oil emulsion is transferred to a reactor equipped with nitrogen sparge tube, stirrer and thermometer. The emulsion is purged with nitrogen to remove oxygen.

Simultaneously are fed 10.15g (0,25pphm) of tertiary butyl hydroperoxide (6.16% solution in solvent) and 11.98g (0,25pphm) of sodium metabisulphite (5.26% emulsion) for 120 min. (polym. + chem. deso.)

Then vacuum distillation is carried out to remove water and volatile solvent to give a final product of 50% polymer solids.
To this product addition is made of 40.0 g (16.0 pphm) of a fatty alcohol C13-C15 alkoxylate, (CAS No. 68131-39-5).

Examples 4 to 8

Examples 4 to 8 are carried out as outlined above for example 1 under consideration of the variations as depicted in tables 1 and 2 (below).

The following tables 1 and 2 depict the synthetic variations and the corresponding analytical data in respect of the working examples 1 to 8 as well as comparative example 1.

Table 1: Overview of all Examples

		Step I: Feed composition (crosslinked)			**Step II: Feed composition (soluble)**				remarks	
Example	Weight % ratio step I / step II	batch Acrylic acid (pphm)	Sodium hydroxide (mol % Acrylic acid)	Methylen bisacrylamide (pphm)	feed Acrylic acid (pphm)	Sodium hydroxide (mol % Acrylic acid)	Methylen bisacrylamide (pphm)	Sodiumhypo-phosphite (pphm)	Reaction temperature increase	Solid content (%)
CE1	100/0	100	75	0.07	--	--	--	--	2°/min.	51.2
1	50/50	50	75	0.07	50	75	--	--	2°/min.	52.4
2	75/25	75	75	0.07	25	75	--	--	2°/min.	51.7
3	25/75	25	75	0.07	75	75	--	--	2°/min.	52.1
4	50/50	50	75	0.21	50	75	--	0.10	2°/min.	51.3
5	50/50	50	75	0.21	50	75	--	0.20	2°/min.	50.3
6	50/50	50	75	0.07	50	75	--	0.10	2°/min.	52.3
7	50/50	50	75	0.21	50	75	--	0.40	2°/min.	51.9
8	50/50	50	75	0.42	50	75	--	0.05	2°/min.	52.9

In the above examples, the individual components as mentioned in the first line of table 1 are only employed within those examples, which contain a value within the respective box. In case a different component is used, the respective abbreviations are additionally mentioned in the respective box.

Table 2: Characterisation of examples from table 1

Example	*Viscosity (mPa*s) of 0.5% polymer in deionized water measured after 30 min. at room temperature*	*Sedimentation coefficient for water-soluble polymer component P1 (Sved)*	*Wt% for water-soluble polymer component (%)*	*Molecular weight for water-soluble polymer component P1 (g/mol)*	*Sedimentation coefficient for insoluble polymer component P2 (Sved)*	*Wt% for insoluble polymer component P2 (%)*
CE1	*3040*	*6.7*	*19*	*470000*	*14700*	*81*
1	*920*	*6.7*	*45*	*725000*	*21000*	*55*
2	*780*	*6.1*	*37*	*430000*	*20500*	*63*
3	*840*	*8.1*	*66*	*680000*	*16500*	*34*
4	*160*	*3.7*	*50*	*235000*	*35000*	*50*
5	*200*	*3.0*	*51*	*130000*	*32000*	*49*
6	*80*	*4.5*	*44*	*215000*	*33000*	*56*
7	*40*	*2.8*	*49*	*73000*	*37000*	*51*
8	*240*	*4.2*	*40*	*330000*	*41000*	*60*

In table 2, all values expressed in Sved are average sedimentation coefficients unless indicated otherwise. The values in % by weight for the respective peaks (P1) and (P2) are related to the sum of the peaks (P1) and (P2).

Claims

1. A process for obtaining a polymer by polymerization of

   a) at least one anionic monomer and/or at least one nonionic monomer (monomer component a),

   b) at least one crosslinker (monomer component b),

   c) optionally at least one chain transfer agent (monomer component c),

   wherein the polymer has an at least bimodal molecular weight distribution with at least one first peak (P1) with an average sedimentation coefficient of ≤ 100 Sved and with at least one second peak (P2) with an average sedimentation coefficient of ≥ 1000 Sved, and

   wherein the polymerization is carried out in two subsequent steps I) and II) with:

   I) polymerization of monomer component a) and monomer component b),

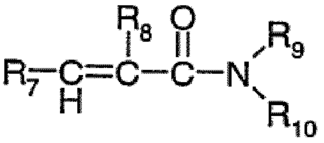
   II) polymerization of monomer component a), optionally monomer component c) and in the complete absence or in the presence of < 10 ppm (related to the total amount of polymer) of monomer component b),

   wherein step II) is carried out after the polymerization of step I) is finished or step I) is carried out after the polymerization of step II) is finished.

2. The process according to claim 1, wherein

   i) the anionic monomer according to monomer component a) in the polymer is selected from acrylic acid, methacrylic acid, itaconic acid, maleic acid or a salt thereof, preferably selected from an alkali metal salt and/or a fluoro salt of said acids, more preferably selected from Na or Li acrylate, Na or Li methacrylate, Na or Li trifluorboroacrylate~~,~~ and/or Na or Li trifluorborometh-acrylate, most preferably selected from Li acrylate or Li trifluorboroacrylate, and/or

   ii) the nonionic monomer according to monomer component a) in the polymer is selected from N-vinylpyrrolidone, N-vinylimidazole, an associative monomer or a compound of the formula (I)



$$R_7-\underset{H}{C}=\overset{R_8}{C}-\overset{O}{\overset{\|}{C}}-N\begin{smallmatrix}R_9\\R_{10}\end{smallmatrix}$$

(I)

where
R_7 is H or $C_1 - C_4$ – alkyl,
R_8 is H or methyl, and
R_9 and R_{10} are each independently H or $C_1 - C_{30}$– alkyl, and/or

iii) the crosslinker (monomer component b) in the polymer is selected from

divinylbenzene; tetraallylammonium chloride; allyl acrylates; allyl methacrylates; diacrylates and dimethacrylates of glycols or polyglycols; butadiene; 1,7-octadiene; allylacrylamides or allylmethacrylamides; bisacrylamidoacetic acid; N,N'-methylenebisacrylamide; polyol polyallyl ethers such as polyallyl sucrose or pentaerythritol triallyl ether; pentaerythrityl triacrylate; pentaerythrityl tetraacrylate; 1,1,1-trimethylolpropane tri(meth)acrylate; the ethoxylated compounds thereof or a mixture thereof, most preferably the crosslinker is selected from N,N'-methylenebisacrylamide, pentaerythrityl triacrylate or pentaerythrityl tetraacrylate, and/or

iv) the chain transfer agent (monomer component c) in the polymer is selected from mercaptans, lactic acid, formic acid, isopropanol or hypophosphites, more preferably the chain transfer agent is selected from mercaptans, isopropanol or sodium hypophosphite, most preferably the chain transfer agent is sodium hypophosphite.

3. The process according to claim 1 or 2, wherein the at least one nonionic monomer according to monomer component a) in the polymer comprises at least one associative monomer, preferably the associative monomer is selected from a compound of the formula (II)

$$R\text{-}O\text{-}(CH_2\text{-}CHR'\text{-}O)_n\text{-}CO\text{-}CR''\text{=}CH_2 \qquad (II)$$

where
R is $C_1 - C_{50}$ – alkyl, preferably $C_1 - C_{30}$ – alkyl, especially $C_1 - C_{22}$– alkyl,
R' is H or $C_1 - C_4$ – alkyl, preferably H,
R" is H or methyl,
n is an integer from 0 to 500, preferably 3 to 100, especially 20 to 50.

4. The process according to any of claims 1 to 3, wherein the polymerization is an emulsion polymerization, especially an inverse emulsion polymerization and/or steps I) and II) are carried out in the same polymerization vessel.

5. The process according to any of claims 1 to 4, wherein

   i) the first peak (P1) has a weight average peak maximum of ≥ 400 000 g/mol, preferably in the range of 410 000 to 1 000 000 g/mol, most preferably in the range of 420 000 to 750 000 g/mol, and/or

   ii) the first peak (P1) has an average sedimentation coefficient of ≤ 50 Sved, preferably ≤ 15 Sved, even more preferably in the range of 4 to 10 Sved, most preferably in the range of 5.5 to 8.5 Sved, and/or

   iii) the second peak (P2) has an average sedimentation coefficient of ≥ 10 000 Sved, preferably ≥ 14 000 Sved, even more preferably in the range of 15 000 to 50 000 Sved, most preferably in the range of 16 000 to 22 000 Sved, and/or

   iv) the polymer has an at least trimodal molecular weight distribution, and/or

   v) the water-soluble polymer components of the polymer are ≥ 25% by weight related to the total amount of polymer.

6. The process according to any of claims 1 to 5, wherein

   i) the anionic monomer according to monomer component a) in the polymer is selected from Li acrylate or Li trifluorboroacrylate, and/or

   ii) the nonionic monomer according to monomer component a) in the polymer contains at least two different associative monomers according to formula (I), wherein in the first monomer R is C_1-C_3-alkyl, preferably methyl, and n is an integer from 40 to 50, preferably 45, and in the second monomer R is C_{16}-C_{22}-alkyl, preferably C_{18}-alkyl, and n is an integer from 20 to 30, preferably 25.

7. The process according to any of claims 1 to 6, wherein the amount of polymer components covered by the first peak (P1) of the polymer are between 5 to 95 % by weight, preferably between 25 to 90% by weight, more preferably between 35 and 75% by weight, most preferably between 50 and 60% by weight, related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

8. The process according to claim 7, wherein in step II) ≥ 5 %, preferably ≥ 25 %, most preferably ≥ 50 % by weight of the polymer components covered by the first peak (P1) of the polymer are produced related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

9. The process according to any of claims 1 to 8, wherein

   i) step II) is carried out after the polymerization of step I) is finished, and/or

   ii) step II) is carried out by polymerization of monomer component a) and monomer component c), preferably monomer component a) contains at least one anionic monomer and optionally at least one associative monomer, and/or

   iii) monomer component b) is completely absent during the polymerization according to step II), and/or

   iv) step I) is carried out by polymerization of monomer component a), 10 to 10.000 ppm, preferably 100 to 2000 ppm, more preferably 500 to 1000 ppm, (related to the total amount of polymer) of monomer component b) and optionally monomer component c), and/or

   v) in step II), 5 to 95 % by weight, preferably 25 to 90 % by weight, more preferably between 35 and 75 % by weight, even more preferably between 50 and 60 % by weight of the polymer components covered by the first peak (P1) of the polymer are produced related to the sum of polymer components covered by the first peak (P1) and the second peak (P2).

10. The process according to any of claims 1 to 9, wherein

   i) in both steps I) and II), an aqueous phase and an oil phase are employed, and/or

   ii) the aqueous phase in step I) contains at least one anionic monomer, at least one crosslinker and optionally at least one nonionic monomer, and/or

   iii) the oil phase in step I) and/or step II) contains at least one stabilizing agent, at least one low-boiling oil, at least one high-boiling oil and optionally at least one associative monomer, and/or

iv) the aqueous phase in step II) contains at least one anionic monomer, optionally at least one nonionic monomer, and optionally at least one chain transfer agent, and/or

v) in step II), the mixture of the aqueous phase and the oil phase is completely added to the polymerization vessel (batch reaction) and afterwards the initiators are added continuously, and/or

vi) in step II), the mixture of the aqueous phase and the oil phase is continuously added to the polymerization vessel (continuous reaction) and the initiators are added prior to said mixture or the initiators are added continuously and in parallel to said mixture into the polymerization vessel.

11. The process according to any of claims 1 to 10, wherein

i) step I) is initiated at a lower temperature than the temperature of step II), and/or

ii) step I) is carried out at a temperature in the range of -5 °C to 40 °C, preferably in the range of 20 °C to 30 °C, more preferably the temperature is kept constant during step I), and/or

iii) step II) is carried out at a temperature in the range of 70 °C to 120 °C, preferably in the range of 80 °C to 100 °C, more preferably the temperature is kept constant during step II), and/or

iv) step I) is started at a temperature in the range of -5 °C to 40 °C, preferably in the range of 15 °C to 25 °C, and heated-up by the exothermal polymerization under adiabatical conditions.

12. The process according to any of claims 1 to 11, wherein an inverse dispersion comprises the at least one polymer.

13. The process according to claim 12, wherein the inverse dispersion comprises further:

at least one oil, at least one activator, at least one stabilizing agent, optionally at least one complexing agent and optionally additional additives.

14. The process according to claim 12 or 13, wherein the inverse dispersion is a water-in-oil emulsion.

15. The process according to claim 13 or 14, wherein the stabilizing agent has one or more hydrophobic chains with more than 30 carbon atoms, preferably more than 50 carbon atoms, more preferably the stabilizing agent has an ABA block structure based on polyhydroxystearic acid as A block and polyalkylene oxide as B block.

16. The process according to any of claims 4 to 15, wherein the inverse emulsion polymerization is followed by distillation by means of the liquid dispersion polymer technology.

17. A polymer obtained by a polymerization process according to any of claims 1 to 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/069683

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F2/32 C08F220/06
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2013/174621 A1 (BASF SE [DE]; BASF SCHWEIZ AG [CH]) 28 November 2013 (2013-11-28) cited in the application page 5 - page 8 page 21 - page 22 claims 1,4-6,14-17 -----	17 1-16
A	US 2004/115149 A1 (LOFFLER MATTHIAS [DE] ET AL) 17 June 2004 (2004-06-17) the whole document -----	1-17
A	WO 2013/068392 A1 (BASF SE [DE]; LEYRER REINHOLD J [DE]; ARISANDY CHRISTOFER [DE]; BENLAH) 16 May 2013 (2013-05-16) cited in the application the whole document ----- -/--	1-17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 13 August 2018	Date of mailing of the international search report 24/08/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Nikolai, Joachim

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/069683

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/068388 A1 (BASF SE [DE]; LEYRER REINHOLD J [DE]; ARISANDY CHRISTOFER [DE]; BENLAH) 16 May 2013 (2013-05-16) cited in the application the whole document -----	1-17

1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/069683

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013174621 A1	28-11-2013	BR 112014028928 A2	19-09-2017
		CA 2870646 A1	28-11-2013
		CN 104321349 A	28-01-2015
		EP 2666789 A1	27-11-2013
		EP 2852621 A1	01-04-2015
		JP 2015517599 A	22-06-2015
		KR 20150013862 A	05-02-2015
		RU 2014151608 A	10-07-2016
		WO 2013174621 A1	28-11-2013
US 2004115149 A1	17-06-2004	BR 0115806 A	16-09-2003
		DE 10059824 A1	13-06-2002
		EP 1339789 A2	03-09-2003
		ES 2238491 T3	01-09-2005
		JP 5377810 B2	25-12-2013
		JP 2002205936 A	23-07-2002
		US 2004115149 A1	17-06-2004
		WO 0244267 A2	06-06-2002
WO 2013068392 A1	16-05-2013	BR 112014011314 A2	09-05-2017
		CA 2853243 A1	16-05-2013
		CN 104093752 A	08-10-2014
		EP 2776478 A1	17-09-2014
		JP 2015504455 A	12-02-2015
		KR 20140089535 A	15-07-2014
		RU 2014123615 A	20-12-2015
		WO 2013068392 A1	16-05-2013
WO 2013068388 A1	16-05-2013	BR 112014011157 A2	09-05-2017
		CO 6950498 A2	20-05-2014
		EP 2776477 A1	17-09-2014
		RU 2014123616 A	20-12-2015
		WO 2013068388 A1	16-05-2013