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(54) PROCESS CHEMICAL FOR USE IN THE PRODUCTION OF PAPER OR BOARD

PROZESSCHEMIKALIE ZUR VERWENDUNG BEI DER HERSTELLUNG VON PAPIER ODER KARTON

SUBSTANCE CHIMIQUE DE TRAITEMENT À UTILISER DANS LA PRODUCTION DE PAPIER OU DE CARTON

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Description

Field of the Invention

[0001] The present invention relates process chemicals obtained by controlled radical polymerization technique or by controlled photopolymerization technique. These polymers can be used in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine. These polymers are especially useful as coagulants or fixatives for the binding of disturbing substances to the fibres in the production of paper or board.

Background of the Invention

[0002] US Patent Publication 5 676 796 disclose a process for producing paper comprising forming a thick stock cellulosic suspension, flocculating the thick stock by adding a synthetic water soluble polymeric material, then diluting the flocculated thick stock to form a thin stock, and subsequently adding a coagulant to the thin stock followed by draining to form a sheet. A preferred flocculant polymer is a copolymer of acrylamide and dimethylaminoethyl acrylate quaternised with methyl chloride, and a preferred coagulant polymer is poly diallyl dimethyl ammonium chloride (polyDADMAC).

[0003] US Patent Publication 5 194 120 discloses a process for producing paper comprising adding a cationic polymer and an amorphous metal silicate material to a furnish followed by introducing the furnish to the headbox of a paper machine. A preferred cationic polymer is a tertiary or quaternary amine derivative of polyadrylamide.

[0004] US Patent Publication 4 980 025 discloses a process for producing paper comprising adding separately to an aqueous paper pulp a cationic polyacrylamide and a sol comprising anionic colloidal particles, followed by forming and drying the aqueous paper pulp. The process is claimed to improve drainage and retention.

[0005] EP Patent Publication 1 266 092 B1 discloses a process for producing paper comprising adding retention aids to the stock passing to the paper machine headbox, the stock is directed to the wire, the stock is dewatered to form a paper web, and the paper web is dried. The retention aids comprise a solution of a water-soluble cationic polymer which is a copolymer of acrylamide or methacrylamide and a cationic monomer, and in the form of a suspension, a microparticle mixture containg a swellable clay and a colloidal synthetic metal silicate.

[0006] WO 03/046024 discloses aqueous dispersions of polymers of N-vinyl carboxylic acid amides that contain as stabilizers cross-linked graft polymers. The aqueous dispersions are produced by radical polymerization of N-vinyl carboxylic acid amides in an aqueous medium in the presence of said stabilizer. The aqueous dispersions can be used for example as fixing agents in the production of paper.

[0007] WO 01/34909 discloses a flocculation system for flocculating a cellulosic suspension in the production of paper. The flocculation system comprises a siliceous material and an anionic branched water soluble polymer. The flocculation system may additionally comprise a water soluble cationic polymer.

[0008] WO 2006/087344 discloses aqueous dispersions of predominantly anionically charged polyelectrolyte complexes comprising an anionic polymer and a cationic polymer. The polyelectrolyte is produced by radical polymerization of an ethylenically unsaturated monomer in an aqueous medium in the presence of a water soluble cationic polymer. The aqueous dispersions can be used for example as retention agents in the production of paper.

[0009] The present invention is focussed on a different type of polymers being obtained by controlled radical polymerization or by controlled photopolymerization.

[0010] A control radical process has characteristics of a living polymerization system in that it is capable of controlling the molecular weight and the molecular weight distribution of the resultant polymer.

[0011] Free radical polymerization is the most widespread method of polymerization of vinylic monomers. Free radical polymerizations are chain reactions in which every polymer chain grows by addition of a monomer to the terminal free radical reactive site called "active center". The addition of the monomer to this site induces the transfer of the active center to the newly created chain end. Free radical polymerization is charactherized by many attractive features, such as applicability for a wide range of polymerizable groups, as well as tolerance to many solvents, small amount of impurities and many functional groups present in the monomers. However, classical free radical polymerization has some limitations, inherent to its mechanism. In particular, it is difficult to control molar masses and polydispersities as well as to introduce defined end-groups, or to prepare special macromolecular architectures such as block copolymers. In order to overcome these limitations, new strategies in free radical polymerization have emerged, often referred to as "controlled" free radical polymerization. Characteristically, these methods use reagents to transform reversibly the propagating radicals into a dormant species. So, in average, the polymer chains grow simultaneously, and no more one after the other. Thus, chain growth and monomer consumption takes place at a comparable rate. Process that have received most attention are: i) nitroxide-mediated radical polymerization (NMRP), ii) Atom Transfer Radical Polymerization (ATRP), catalysed by transition metal complexes, and more recently iii) polymerization via Reversible Addition-Fragmentation chain Transfer (RAFT) or Macromolecular Design via Interchange of Xanthates (MADIX) in the case of xanthates are used as chain transfer agents. Whithin these methods, the first two ones are based on reversibly blocking the growing polymer radical, whereas the last one is based on degenerative chain transfer. The RAFT process seems to be well adapted to numerous classes of monomers, solvents, functional moieties and to a large temperature window.

[0012] Reference may in particular be made, as examples of "controlled" radical polymerization processes, to:

> WO 98/58974, WO 00/75207 and WO 01/42312 discloses processes for radical polymerization controlled by control agents of xanthate type.
>
> WO 98/01478 discloses a process for radical polymerization controlled by control agents of dithioester type. The produced polymers can be used in the fields of coatings, imaging, electronics, plastics, adhesives and sealants.
>
> WO 99/03894 discloses a polymerization in the presence of nitroxide precursors.
>
> WO 99/31144 discloses a process for radical polymerization controlled by control agents of dithiocarbamate type.
>
> WO 02/26836 discloses a process for radical polymerization controlled by control agents of dithiocarbazate type.
>
> WO 02/10223 discloses a process for radical polymerization controlled by control agents of dithiophosphoro ester type.
>
> WO 96/30421 disclosed a polymerization process based on atom transfer radical polymerization (ATRP).

[0013] Additionally US 6 812 291 discloses a process for the prepration of block polymers by controlled radical polymerization from dithiocarbamate compounds by thermal initiation.

[0014] Although there are a number of RAFT chain transfer agents, only few of them are water soluble. The present invention preferably uses water soluble chain transfer agents having a specific composition resulting in a polymer having desired properties, such as narrow molecular weight distribution.

[0015] An object of the invention is to improve the process for producing paper or board by providing an improved process chemical of the above type.

Summary of the Invention

[0016] According to the present invention it has been found that polymers obtained by controlled radical polymerization technique from an ethylenically unsaturated monomer, a chain transfer agent, and an initiator in a liquid medium preferably using heat to make radicals or by controlled photopolymerization technique from an ethylenically unsaturated monomer and a photoiniferter in a liquid medium preferably using UV light to make radicals, are useful as process chemicals in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine.

Detailed description of the Invention

[0017] Thus, the present invention provides a process for producing paper or board from an aqueous fibre suspension, which process comprises adding a process chemical to the aqueous fibre suspension, feeding the obtained aqueous fibre suspension to the headbox of a paper or board machine, feeding the aqueous fibre suspension from the headbox to a wire, dewatering the aqueous fibre suspension on the wire to form a paper or board web, and drying the paper or board web, said process chemical being a polymer obtained by controlled radical polymerization technique, which is Reversible Addition-Fragmentation Chain Transfer (RAFT), Macromolecular Design via Interchange of Xanthates (MADIX), Atom Transfer Radical Polymerization (ATRP) or nitroxide-mediated radical polymerization (NMRP), from an ethylenically unsaturated monomer, a chain transfer agent, and an initiator in a liquid medium or by controlled photopolymerization technique from an ethylenically unsaturated monomer and a photoiniferter in a liquid medium.

[0018] Typical ethylenically unsaturated monomers include a,β-ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, itaconic anhydride, crotonic acid, fumaric acid, citraconic acid, etc.; styrenesulfonic acid, vinylsulfonic acid and the like; salts of these (alkali metal salts, ammonium salts, amine salts, etc.); acid anhydrides such as maleic anhydride, and half esters thereof with straight or branched alcohols; amino group-containing (meth)acrylate such as dimethylaminoethyl meth(acrylate), dimethylaminopropyl (meth)acrylate, diethylaminoethyl (meth)acrylate, {2-[(meth)acryloyloxy]ethyl]trimethylammonium chloride, diallyldimethylammonium chloride etc.; (meth)acrylamide, α-ethyl(meth)acrylamide, N-butoxymethyl-(meth)acrylamide, N,N-dimethylacrylamide, N-metylacrylamide and acryloylmorpholine, hydrochlorides and acetates of these, and so forth.

Preferred monomers are acrylamide, acrylic acid, dimethyl acrylamide, 2-(dimethylamino)ethyl methacrylate, [2-(acryloyloxy)ethyl]trimethylammonium chloride, 2-(methacryloyloxy)ethyl]trimethylammonium chloride and diallyldimethylammonium chloride.

[0019] In the controlled radical polymerization technique preferred chain transfer agents are compounds having a segment having the formula

-X-C(=S)-S- I

wherein X is C, O, N or S.

[0020] Such chain trasfer agents are for example S,S'-bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate, 4-cyanopentanoic acid dithiobenzoate (CPA) and 2-(2-methyl-2-thiobenzoylsulfanylpropionylimino)ethanesulfonate. In order to increase the solubility of the CPA its salts can be used, for example sodium salt.

[0021] The compounds can thus be utilized to control free radical polymerization to give narrow molecular weight distributions and to control the molecular weight of the polymer. The control means also that block polymers can be made from the previously synthetized homopolymers that have been made according to invention. These homopolymers can be used as chain transfer agent.

[0022] The molar ratio of the chain transfer agent to monomer is preferably from 0.0005 to 0.025, more preferably from 0.001 to 0.01, and still more preferably from 0.001 to 0.005.

[0023] In the synthesis of the polymers of the invention, one measure of the control character of the reaction appears through the values of the polydispersity index PDI= M_w/M_n. Thus, the polydispersity index is a measure of the distribution of molecular weights in a polymer and is the weight average molecular weight (M_w) divided by the number average molecular weight (M_n). The PDI is preferably less than 2, more preferably less than 1.7 for the polymers prepared according to the invention.

[0024] The polymerization of monomers can be made in any suitable solvent of solvent mixture. Suitable solvents include water, alcohol (e.g. methanol, ethanol, n-propanol, isopropanol or butanol), ether (e.g. diethyl ether, anisole or tetrahydrofuran), dimethyl sulphoxide, dimethyl formamide, acetone, acetonitrile, hexamethylphosphoramide, acetic acid, formic acid, hydrocarbon (e.g. hexane, cyclohexane, benzene or toluene), methylene chloride, chloroform and ethyl acetate. Preferably the liquid medium wherein the polymerization is carried out comprises water.

[0025] The synthesis of S,S'-bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate has been described in Macromolecules 2002, 35, 6754-6756. John T. Lai, Debby Filla, and Ronald Shea. "Functional Polymers from Novel Carboxylic-Terminated Trithiocarbonates as Highly Efficient RAFT Agents". The synthesis of CPA has been described in Macromolecules 2001, 34, 2248-2256. Yoshiro Mitsukami, Michael S. Donovan, Andrew B. Lowe, and Charles L. McCormick. "Water-Soluble Polymers. 81. Direct Synthesis of Hydrophilic Styrenic-Based Homopolymers and Block Copolymers in Aqueous Solution via RAFT" and the synthesis of 2-(2-methyl-2-thiobenzoylsulfanylpropionylimino)ethanesulfonate has been described in Macromolecules 2005, 38, 3601-3614. Murat Mertoglu, André Laschewsky, K. Skrabania, and Christoph Wieland. "New Water Soluble Agents for Reversible Addition-Fragmentation Chain Transfer Polymerization and Their Application in Aqueous Solutions".

[0026] In the controlled radical polymerization technique the source of free radicals can be any suitable method of generating free radicals such as thermally induced method, redox initiating method, photochemical initiating method or high energy radiation such as electron beam, X- or gamma ray radiation. The initiating system is chosen such that under the reaction conditions, there is no substantial adverse interaction of the initiator, the initiating conditions or the initiating radicals with the transfer agent under the conditions of the procedure. The preferred method of generating free radicals is thermally induced method.

[0027] In the controlled radical polymerization typical thermal initiators are azo compund, peroxides or peroxyesters. The polymerization initiators are not limited to any particular species but may be any of the conventional initiators, inclusive redox initiators, azo initiators and peroxides. Among them, the azo initiators are preferred and, as specific examples thereof, there may be mentioned, among others, azonitrile compounds such as 2,2'-azobis(2-methylpropionitrile) (AIBN), azobisdimethylvalero-nitrile and azobisdimethylmethoxyvaleronitrile; azoamidine compounds such as 2,2'-azobis(methylpropionamidine)dihydrochloride (V-50), VA-041, VA-044 and VA-061 (V-50, VA-041, VA-044 and VA-061 are products of Wako Pure Chemical Industries , Ltd.); azoamide compounds such as VA-080, VA-086 and VA-088 (products of Wako Pure Chemical Industries , Ltd.); azoalkyl compounds such as azodi-tert-octane and azoditert-butane; cyanopropylazo-formamide, 4,4'-azobis(cyanovaleric acid), 4,4'-azobis(cyanopentanoic acid) dimethylazobismethyl propionate, azobishydroxymethylpropionitrile and the like. Preferred initiators are 2,2'-azobis(methylpropionamidine)dihydrochloride (V-50), and 4,4'-azobis(cyanopentanoic acid) or 4,4'-azobis(cyanovaleric acid).

[0028] One of these radical polymerization initiators for use in the present invention may be used alone, or two or more thereof may be used as a mixture.

[0029] The molar ratio of the radical polymerization initiator to the monomer is preferably from 0.0001 to 0.1, more preferably from 0.0005 to 0.05, still more preferably from 0.0005 to 0.01.

[0030] The polymerization process according to the present invention is performed under the conditions typical of conventional free-radical polymerization. Polymerizations are suitably carried out at temperatures in the range of 0 - 150 C°, preferably 20 - 120 C°, more preferably 60 - 90 C°. The pH can vary from 1 to 9, preferably from 4 to 7. Buffer solutions can also be used, especially in the polymerization of acrylamide.

[0031] In the controlled photopolymerization preferred photoiniferters are compounds having a segment having the formula

-N-C(=S)-S- II

[0032] Such photoiniferters are for example 2-(N,N-diethyldithiocarbamyl)isobutyric acid (DTCA) and 2-(N,N-dimethyldithiocarbamyl)isobutyric acid. In order to increase the solubility of the photoiniferter its salts cand be used, for example sodium salt.

[0033] One example of the synthesis of DTCA can be found from Journal of Polymer Science: Part A: Polymer Chemistry, Vol 42, 76-82, 2004. Koji Ishizu, Ruhul A. Khan, Yoshihiro Ohta, Masahito Furo. "Controlled Radical Polymerization of 2-hydroxyethyl methacrylate initiated by photofunctional 2-(N,N-diethyldithiocarbamyl)isobutyric acid".

[0034] The compounds can thus be utilized to control photo polymerization to give narrow molecular weight distributions and to control the molecular weight of the polymer. The control means also that block polymers can be made from the previously synthetized homopolymers that have been made according to invention. These homopolymers can be used as chain transfer agent. These compounds can be used as initators and chain transfer agent.

[0035] The molar ratio of the photoiniferter to the monomer is preferably from 0.0001 to 0.1, more preferably from 0.0005 to 0.05, still more preferably from 0.001 to 0.01.

[0036] The polymerization process according to the present invention is performed under the conditions typical of conventional photopolymerization. The radicals are preferably generated by UV irradiation. The UV intensities and radiation distances are the same as for conventional photopolymerization, for example 1000 - 4000 $\mu W/cm^2$ and 10-20 cm. Polymerizations are suitably carried out at temperatures in the range of 5 - 90 C°, preferably 20 - 70 C°, more preferably 20 - 50 C°.

[0037] The polymers of the invention can be homopolymers or copolymers. The copolymers can be block copolymers or multiblock copolymers, e.g. diblock, triblock copolymers.

[0038] The polymers of the invention to be used as process chemicals in the production of paper or board are cationic. It should, however, be understood that monomers or homopolymers used for building up cationic block copolymers can be anionic.

[0039] Block copolymer can be made from a homopolymer that has been made according this invention. In the embodiment wherein a chain transfer agent is used, the homopolymer works as a chain transfer agent and is called here macro-CTA (macrochain transfer agent). Correspondingly, in the embodiment wherein a photoiniferter is used, the homopolymer works as a macro-photoiniferter. The block copolymers can be made in similar process conditions as making homopolymers.

[0040] The polymers typically have a molecular weight (M_w) in the range of about 1000 to about 1 000 000. More preferably in the range of about 10 000 to about 400 000 still more preferably in the range of about 10 000 to 100 000.

[0041] According to the invention the polymer is preferably added to the aqueous fibre suspension in an amount of about 25 to 10 000 g/ ton, more preferably about 50 to 1 000 g/ton of dry matter of the aqueous fibre suspension.

[0042] According to the invention the process chemical can function as a coagulant or fixative for the binding of disturbing substances to the fibres.

[0043] According to the invention chemicals conventionally used in paper and board manufacture, such as fillers and/or functional additives, can be added to the aqueous fibre suspension prior to the headbox. Such chemicals and the adequate amounts thereof are well-known to the man skilled in the art.

[0044] The aqueous fibre suspension to be treated by the invention can comprise a chemical pulp, mechanical pulp, chemo-mechanical pulp, recycled fibres or a mixture thereof.

[0045] The invention also relates to the use of a polymer obtained by controlled radical polymerization technique from an ethylenically unsaturated monomer, a chain transfer agent, and an initiator in a liquid medium, as a process chemical in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine. The polymers are as described above.

[0046] Additionally the invention relates to the use of a polymer obtained by controlled photopolymerization technique from an ethylenically unsaturated monomer and a photoiniferter in a liquid medium, as a process chemical in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine. The polymers are as described above.

[0047] Following examples illustrate the invention, however, without limiting the scope thereof.

Examples

Example 1

Synthesis of poly{[2-(Methacryloxy)ethyl]trimethylammonium chloride}

[0048] 8.31 g of 75% solution of [2-(methacryloxy)ethyl]trimethylammonium chloride, (30 mmol), 0.044 g of S,S'-bis (α,α'-dimethyl-α"-acetic acid) trithiocarbonate (0.157 mmol) and 8.8 mg of 4,4'-azobis-(cyanopentanoic acid) (0.031 mmol) were placed in a 250 ml round-bottom flask with a magnetic stirring bar. 30 ml of water was added and the reaction mixture was deoxygenated by three freeze-evaquate-thaw cycles. Polymerization was carried out in 60°C and it was stopped after 24 hours by adding inhibitor 4-methoxyphenol (0.31 mmol). The product was purified by dialysis and freeze dried. Mw by GPC was 16 500 g/mol and the PDI was 1.6.

Example 2

Synthesis of poly{[2-(Methacryloxy)ethyl]trimethylammonium chloride}

[0049] 13.85 g of 75% solution of [2-(methacryloxy)ethyl]trimethylammonium chloride, (50 mmol), 0.049 g of ,S'-bis (α,α'-dimethyl-α"-acetic acid) trithiocarbonate (0.174 mmol) and 9.7 mg of 4,4'-azobis-(cyanopentanoic acid) (0.035 mmol) were placed in a 250 ml round-bottom flask with a magnetic stirring bar. 46.5 ml of water was added and the reaction mixture was deoxygenated by three freeze-evaquate-thaw cycles. Polymerization was carried out in 60°C and it was stopped after 19 hours by adding inhibitor 4-methoxyphenol (0.35 mmol). The product was precipitated twice from water into acetone/ethanol (50:50). Mw by GPC was 26 100 g/mol and the PDI was 1.46.

Example 3

Synthesis of poly[2-(Dimethylamino)ethyl methacrylate]

[0050] 6.385 g of 98 % 2-(Dimethylamino)ethyl methacrylate (39.8 mmol), 0.0583 g sodium salt of 4-cyanopentanoic acid dithiobenzoate, (0.207 mmol) and 6.8 mg of 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.0414 mmol) were placed in a 250 ml round-bottom flask with a magnetic stirring bar. 13.4 ml of anisole was added. The reaction mixture was deoxygenated by three freeze-evaquate-thaw cycles which was repeated three times. The mixture was heated to 70°C in an oil bath and the polymerization was stopped after 24 hours by cooling. The product was purified by precipitation into acetone. Mw by GPC was 9870 g/mol and the PDI was 1.16.

Example 4

Synthesis of poly(Dimethylacrylamide)

[0051] 9.9 g of dimethylacrylamide, 0.43 g of S,S'-bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate 0.22 g of 4,4'-azobis(4-cyanovaleric acid), 19 g of water were placed in a three-neecked flask provided with a condenser, a magnetic stirrer and a heating bath. The heat of the bath was maintained at 70ºC for 6 h. The product was purified by dialysis and freeze dried. Mw by GPC was 38100 g/mol and the PDI was 1.2.

Example 5

Synthesis of [poly(Dimethylacrylamide)]-[poly(Acrylamide)]-[poly(Dimethylacrylamide)]

[0052] 3.6 g of Poly(dimethylacrylamide) of the example 4 and 70 ml of water was added to a round-bottom flask and was left to dissolve overnight. 16 g of 50 % solution in water of acrylamide (113 mmol) and 5 mg of 4,4'-azobis(cyanopentanoic acid) (0.0187 mmol) were added with a small amount of water. The reaction mixture was deoxygenated by bubbling nitrogen. The flask was embedded in an oil bath thermostated to 70°C and the reaction was allowed to proceed for 8 h, after which it was stopped. The product was purified by dialysis against distilled water and following lyophilization. Mw by GPC was 160 000 g/mol and the PDI was 1.27.

Example 6

Synthesis of poly[2-(Dimethylamino)ethyl methacrylate]

[0053] 9.625 g of 98 % 2-(Dimethylamino)ethyl methacrylate (60 mmol), 0.0446 g of BDAT (0.158 mmol) and 5.2 mg of AIBN (0.032 mmol) were placed in a 250 ml round-bottom flask with a magnetic stirring bar. 30 ml of anisole was added and the reaction mixture was deoxygenated by three freeze-evaquate-thaw cycles. Polymerization was carried out in 70°C and it was stopped after 24 hours by adding inhibitor 4-methoxyphenol (0.31 mmol). The product was purified by precipitation twice from water into n-hexane. Mw by GPC was 15 500 g/mol and the PDI was 1.66.

Example 7

Synthesis of {poly[2-(Methacryloxy)ethyl]trimethylammonium chloride]}-{poly(acrylamide)}

[0054] 6.34 g of 75% solution of [2-(methacryloxy)ethyl]trimethylammonium chloride, (22.9 mmol), 22.9 ml water and 44.3 mg of 2-(2-methyl-2-thiobenzoylsulfanylpropionylimino)ethan-sulfonate (0.12 mmol) were weighted in a round bottom flask with a magnetic stirring bar. The reaction mixture was deoxygenated by three freeze-evaquate-thaw cycles, after this the flask was immersed in an oil bath, 60º C, and allowed to warm up for 10 minutes. 6.7 mg of 4,4'-azobis-(cyanopentanoic acid) (0.024 mmol) was injected in the solution and the reaction was allowed to proceed.

[0055] The reaction was stopped after 24 h by injecting inhibitor to the reaction solution, and cooling the reaction solution to the room temperature. The poly[2-(methacryloxy)ethyl]trimethylammonium chloride] homopolymer was precipitated in acetone-ethanol (1:1) solution, dissolved in water and then dialyzed against water for 24 hours, and then freeze dried. Mw by GPC was 16 500 g/mol and the PDI was 1.52.

[0056] 1 g of poly[2-(methacryloxy)ethyl]trimethylammonium chloride] homopolymer from the previous reaction (macro chain transfer agent (macro-CTA)) and 11.8 ml of sodium acetate-acetic acid buffer solution having pH 5 was added to a round-bottom flask and the macro-CTA was left to dissolve overnight. 3.368 g of 50 % solution of acrylamide (0.0237 mol) and 1.9 mg of 4,4'-azobis(cyanopentanoic acid) (0.068 mmol) were added with a small amount of buffer solution. The reaction mixture was deoxygenated by three freeze-evacuate-thaw cycles. The flask was embedded in an oil bath thermostated to 70 °C and the reaction was allowed to proceed for 50 h, after which it was stopped. The {poly[2-(methacryloxy)ethyl]trimethylammonium chloride]}-{poly(acrylamide)} block copolymer was purified by precipitation in acetone. Mw by GPC was 22 600 g/mol and the PDI was 1.67.

Example 8

Synthesis of poly{[2-(Acryloyloxy)ethyl]trimethylammonium choride}

[0057] 9.6 g of 75% solution of [2-(acryloyloxy)ethyl]trimethylammonium choride, (49.8 mmol), 46.5 ml water and 0.0566g of S,S'-bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate (0.2 mmol), were weighted in a two necked round bottom flask, equipped with nitrogen in- and outlet and a septum. They were allowed to dissolve. After this, the solution was bubbled with nitrogen for 15 minutes, after which the flask was immersed in an oil bath, 60º C, and allowed to warm up for 10 minutes. 12.7 mg of 2,2'-azobis(methylpropionamidine)dihydrochloride (0.0468 mmol) was injected in the solution and the reaction was allowed to proceed 24 hours.

[0058] The reaction was stopped by injecting inhibitor (hydroquinone) to the reaction solution, opening the flask and cooling the reaction solution to the room temperature. The product was precipitated in acetone, dissolved in water and then dialyzed against water for 24 hours, and then freeze dried. The product was yellow. The weight average molecular weight determined by GPC-measurement was 57 000 g/mol.

Example 9

Synthesis of poly{[2-(Methacryloxy)ethyl]trimethylammonium chloride}

[0059] 20.8 g of 75% solution of [2-(methacryloxy)ethyl]trimethylammonium chloride (100 mmol), 0.43 g of sodium salt of 4-cyanopentanoic acid dithiobenzoate (0.524 mmol) and 0.029 g of 75 % 4,4'-azobis(4-cyanovaleric acid) (0.1 mmol) and 93 g of water were placed in a three-neecked flask provided with a condenser, a magnetic stirrer and a heating bath. The bath was kept at 70ºC for 6 h. The product was purified by dialysis and freeze dried. Mw by GPC was 34 200 g/mol.

Example 10

Synthesis of 2-(N,N-diethyldithiocarbamyl)isobutyric acid

[0060] To 100 mL of a solution of 0.1 mol 2-bromoisobutyric acid in acetone was added 0.12 mol N,N-diethyldithiocarbamate sodium salt, and the reaction mixture was stirred at 40 ºC for 8 h. The precipitated NaBr salt was removed by filtration, and acetone was evaporated from the reaction mixture. The crude mixture was dissolve in benzene, and insoluble N,N-diethyldithiocarbamate sodium salt was removed by filtration. Then the benzene solution was washed with water, and the organic extract was evaporated to dryness. The crude product was purified by silica column chromatography, eluting with 3:1 dichloromethane/hexane to yield 2-(N,N-diethyldithiocarbamyl)isobutyric acid as a white powder. The yield was 95 %.

Example 11

Synthesis of poly{[2-(Methacryloyloxy)ethyl]trimethylammonium chloride}

[0061] Photopolymerization of 8 g of 75 % solution of [2-(methacryloyloxy)ethyl]trimethylammonium chloride was carried out in 18 g of water initiated by 0.06 g of 2-(N,N-diethyldithiocarbamyl)isobutyric acid that was dissolved in 1 ml of methanol and neutralized with an equivalent molar amount of NaOH, at 35 ºC with UV irradiation time of 2 hours. After polymerization the polymer was recovered by precipitation with acetone.

Example 12

Synthesis of {poly(Acrylamide)}- {poly[2-(Methacryloyloxy)ethyl]-trimethylammonium chloride}

[0062] Photopolymerization of 12 g of 50 % water solution of acrylamide was carried out in 14 g water initiated by 0.06 g 2-(N,N-diethyldithiocarbamyl)isobutyric acid dissolved in 1 ml methanol neutralized with an equivalent molar amount of NaOH, and one drop diethylenetriaminepentaacetic acid, at 35 ºC water bath with UV irradiation time of 2 hours. After polymerization the homopolymer was recovered by precipitation.

[0063] Photopolymerization of 2.7 g of 75 % solution of [2-(methacryloyloxy)ethyl]-trimethylammonium chloride was carried out in 9.3 g water, initiated by 0.2 g of homopolymer from the previous step (macrophotoiniferter) at 35 ºC and under UV irradiation for 2 h. After polymerization the {poly(acrylamide)}- {poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride} was recovered by precipitation with acetone.

Example 13

Polymers as fixatives.

[0064] The purpose of the tests was to investigate the action of the polymers of the present invention as fixatives for TMP pulp. The polymers of examples 1,2 and 5 were used.

[0065] The pulp was a mixture comprising 80% of thermo mechanical pulp (TMP) and 20% of chemical softwood pulp.

[0066] Reference: polyepiamine, dry substance content 50% (trade name Fennofix 50).

[0067] Dilution of the fixative polymers: 200 mg of Fennofix 50 (= 100 mg dry substance) was diluted to 10 ml with water. Solutions of the other tested substances were made to the same dry substance concentration. A 0.4 % mixture was made from the pulp and the pH was adjusted to 5. The pulp was transferred into a 100 ml mixing vessel of a bar mixer (Braun 413 mixer), a dose of the fixative polymer was added to the pulp, and the pulp was treated with mixing blades for 10 seconds with full speed. The pulp was filtered through a filtration paper (Munktel grade NR 00R). The turbidity of the filtrates was determined immediately with a WTW Turbo555IR device, and the charge was determined with a Mütec PCD device, and the pH of the filtrates were determined with a Mettler Toledo MP 120 meter.

[0068] The doses of each fixative polymers were 0, 50, 100, 200 and 400 g per ton of dry matter of the aqueous fibre suspension. The test results are shown in following Table 1.

Table 1

	TURBIDITY NTU				
Polymer	0	50 g/ton	100 g/ton	200 g/ton	1400 g/ton
Example 1	823	644	583	377	146

(continued)

	TURBIDITY NTU				
Polymer	0	50 g/ton	100 g/ton	200 g/ton	1400 g/ton
Example 2	885	628	629	321	119
Example 3	835	664	646	220	76
Fennofix 50	837	700	562	379	183

[0069] The results clearly show that polymers prepared by the RAFT techniques work as fixative polymers.

Example 14

[0070] A second test was made as described in Example 13. The polymer of Example 5 was tested. The dose of the fixative polymers as dry substance was 100 g per ton of dry matter of the aqueous fibre suspension. The test results are shown in following Table 2.

Table 2

Polymer	Dosage g/ton	Turbidity (NTU)
No fixative	0	82
Example 5	100	43
Fennofix 50	100	57

Example 15

[0071] A third test was made as described in Example 13. The polymer of Example 6 was tested. The dose of the fixative polymers as dry substance was 800 g per ton of dry matter of the aqueous fibre suspension. The test results are shown in following Table 3.

Table 3

Polymer	Dosage q/ton	Turbidity (NTU)
No fixative	0	82
Example 6	800	10
Fennofix 50	800	12

Claims

1. A process for producing paper or board from an aqueous fibre suspension, which process comprises adding a process chemical to the aqueous fibre suspension, feeding the obtained aqueous fibre suspension to the headbox of a paper or board machine, feeding the aqueous fibre suspension from the headbox to a wire, dewatering the aqueous fibre suspension on the wire to form a paper or board web, and drying the paper or board web, said process chemical being a polymer obtained by controlled radical polymerization technique, which is Reversible Addition-Fragmentation Chain Transfer (RAFT), Macromolecular Design via Interchange of Xanthates (MADIX), Atom Transfer Radical Polymerization (ATRP) or nitroxide-mediated radical polymerization (NMRP), from an ethylenically unsaturated monomer, a chain transfer agent, and an initiator in a liquid medium or by controlled photopolymerization technique from an ethylenically unsaturated monomer and a photoiniferter in a liquid medium.

2. The process according to claim 1 wherein the liquid medium comprises an aqueous solution.

3. The process according to claim 1 or 2 wherein the radicals in the radical polymerization are generated by thermal means.

4. The process according to any of claims 1 to 3 wherein the chain transfer agent comprises a compound having a segment having the formula

-X-C(=S)-S- I

wherein X is C, O, N or S.

5. The process according to claim 4 wherein the chain transfer agent comprises S,S'-bis(α,α'-dimethyl-α"-acetic acid) trithiocarbonate, 4-cyanopentanoic acid dithio-benzoate (CPA) or a salt thereof or 2-(2-methyl-2-thiobenzoylsulfanylpropionylimino)-ethanesulfonate.

6. The process according to claim 1 or 2 wherein the photoiniferter comprises a compound having a segment having the formula

-N-C(=S)-S- II

7. The process according to claim 6 wherein the photoiniferter comprises 2-(N,N-diethyldithiocarbamyl)isobutyric acid or 2-(N,N-dimethyldithiocarbamyl)-isobutyric acid or a salt thereof.

8. The process according to any of claims 1 to 7 wherein the ethylenically unsaturated monomer comprises acrylamide, acrylic acid, dimethyl acrylamide, 2-(dimethylamino)ethyl methacrylate, [2-(acryloyloxy)ethyl]trimethylammonium chloride, 2-(methacryloyloxy)ethyl]trimethylammonium chloride or diallyldimethylammonium chloride.

9. The process according to any of claims 1 to 8 wherein the polymer comprises a homopolymer or copolymer.

10. The process according to claim 9 wherein the copolymer comprises a block copolymer or a multiblock copolymer.

11. The process according to any of claims 1 to 10 wherein the polymer has a molecular weight in the range of about 1000 to about 1 000 000, preferably 10 000 to 400 000, and more preferably 10 000 to 100 000.

12. The process according to any of claims 1 to 11 wherein the polymer is added to the aqueous fibre suspension in an amount of about 25 to 10 000 g/ ton, preferably about 50 to 1 000 g/ton of dry matter of the aqueous fibre suspension.

13. The process according to any of claims 1 to 12 wherein the process chemical functions as a coagulant or fixative for the binding of disturbing substances to the fibres.

14. The process according to any of claims 1 to 13 wherein the aqueous fibre suspension comprises chemical pulp, mechanical pulp, chemo-mechanical pulp, recycled fibres or a mixture thereof.

15. Use of a polymer obtained by controlled radical polymerization technique, which is Reversible Addition-Fragmentation Chain Transfer (RAFT), Macromolecular Design via interchange of Xanthates (MADIX), Atom Transfer Radical Polymerization (ATRP) or nitroxide-mediated radical polymerization (NMRP), from an ethylenically unsaturated monomer, a chain transfer agent, and an initiator in a liquid medium, as a process chemical in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine.

16. Use of a polymer obtained by controlled photopolymerization technique from an ethylenically unsaturated monomer and a photoiniferter in a liquid medium, as a process chemical in the wet end of a paper or board machine in the production of paper or board for improving the runnability and productivity of the paper or board machine.

Patentansprüche

1. Verfahren zur Herstellung von Papier oder Karton aus einer wässrigen Fasersuspension, wobei das Verfahren Hinzufügen einer Prozesschemikalie zu der wässrigen Fasersuspension, Zuführen der erhaltenen wässrigen Fasersuspension zu dem Stoffauflauf einer Papier- oder Kartonmaschine, Zuführen der wässrigen Fasersuspension von dem Stoffauflauf zu einem Sieb, Entwässern der wässrigen Fasersuspension auf dem Sieb zum Bilden einer Papier- oder Kartonbahn und Trocknen der Papier- oder Kartonbahn umfasst, wobei die Prozesschemikalie ein

Polymer ist, erhalten durch ein geregeltes Radikalpolymerisationsverfahren, welches reversible Additions-Fragmentierungs-kettenübertragung (RAFT), Makromolekularkonstruktion mittels Austausch von Xanthogenaten (MADIX), Atomübertragungsradikalpolymerisation (ATRP) oder Nitroxid-vermittelte Radikalpolymerisation (NMRP) ist, aus einem ethylenisch ungesättigten Monomer, einem Kettenübertragungsreagens und einem Initiator in einem flüssigen Medium, oder durch ein geregeltes Photopolymerisationsverfahren aus einem ethylenisch ungesättigten Monomer und einem Photoiniferter in einem flüssigem Medium.

2. Verfahren nach Anspruch 1, wobei das flüssige Medium eine wässrige Lösung umfasst.

3. Verfahren nach Anspruch 1 oder 2, wobei die Radikale in der radikalischen Polymerisation thermisch erzeugt werden.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Kettenübertragungsreagens eine Verbindung umfasst, die eine Gruppe der Formel

-X-C(=S)-S- I

aufweist, wobei X C, O, N oder S ist.

5. Verfahren nach Anspruch 4, wobei das Kettenübertragungsreagens S,S'-Bis(α,α'-dimethyl-α"-essigsäure)trithiocarbonat, 4-Cyanopentansäuredithio-benzoat (CPA) oder ein Salz davon oder 2-(2-Methyl-2-thio-benzoylsulfanylpropionylimino)ethansulfonat umfasst.

6. Verfahren nach Anspruch 1 oder 2, wobei der Photoiniferter eine Verbindung umfasst, die eine Gruppe der Formel

-N-C(=S)-S- II

aufweist.

7. Verfahren nach Anspruch 6, wobei der Photoiniferter 2-(N,N-Diethyl-dithiocarbamyl)isobuttersäure oder 2-(N,N-Dimethyldithiocarbamyl)isobutter-säure oder ein Salz davon umfasst.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei das ethylenisch ungesättigte Monomer Acrylamid, Acrylsäure, Dimethylacrylamid, 2-(Dimethylamino)ethylmethacrylat, [2-(Acryloyloxy)ethyl]trimethylammonium-chlorid, [2-(Methacryloyloxy)ethyl]trimethylammoniumchlorid oder Diallyldimethylammoniumchlorid umfasst.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei das Polymer ein Homopolymer oder Copolymer umfasst.

10. Verfahren nach Anspruch 9, wobei das Copolymer ein Blockcopolymer oder ein Multiblockcopolymer umfasst.

11. Verfahren nach einem der Ansprüche 1 bis 10, wobei das Polymer ein Molekulargewicht in dem Bereich von etwa 1.000 bis etwa 1.000.000, bevorzugt 10.000 bis 400.000 und mehr bevorzugt 10.000 bis 100.000 aufweist.

12. Verfahren nach einem der Ansprüche 1 bis 11, wobei das Polymer zu der wässrigen Fasersuspension in einer Menge von etwa 25 bis 10.000 g/Tonne, bevorzugt von etwa 50 bis 1.000 g/Tonne an Trockensubstanz der wässrigen Fasersuspension hinzugefügt wird.

13. Verfahren nach einem der Ansprüche 1 bis 12, wobei die Prozesschemikalie als ein Koagulationsmittel oder Fixierungsmittel für das Binden von Störsubstanzen an die Fasern wirkt.

14. Verfahren nach einem der Ansprüche 1 bis 13, wobei die wässrige Fasersuspension chemischen Holzstoff, mechanischen Holzstoff, chemisch-mechanischen Holzstoff, recycelte Fasern oder eine Mischung davon umfasst.

15. Verwendung eines Polymers, erhalten durch ein geregeltes Radikalpolymerisationsverfahren, welches reversible Additions-Fragmentierungskettenüber-tragung (RAFT), Makromolekularkonstruktion mittels Austausch von Xanthogenaten (MADIX), Atomübertragungsradikalpolymerisation (ATRP) oder Nitroxid-vermittelte Radikalpolymerisation (NMRP) ist, aus einem ethylenisch ungesättigten Monomer, einem Kettenübertragungsreagens und einem Initiator in einem flüssigen Medium, als eine Prozesschemikalie in der Nasspartie einer Papier- oder Kartonmaschine in der Herstellung von Papier oder Karton zur Verbesserung der Laufeigenschaft und Produktivität der Papier- oder

Kartonmaschine.

16. Verwendung eines Polymers, erhalten durch ein geregeltes Photopolymerisationsverfahren aus einem ethylenisch ungesättigten Monomer und einem Photoiniferter in einem flüssigem Medium, als eine Prozesschemikalie in der Nass-partie einer Papier- oder Kartonmaschine in der Herstellung von Papier oder Karton zur Verbesserung der Laufeigenschaft und Produktivität der Papier- oder Kartonmaschine.

Revendications

1. Procédé pour la production de papier ou de carton à partir d'une suspension aqueuse de fibres, lequel procédé comprend l'addition d'un produit chimique de procédé à la suspension aqueuse de fibres, l'introduction de la suspension aqueuse de fibres obtenue dans la caisse de tête d'une machine à papier ou à carton, l'introduction de la suspension aqueuse de fibres à partir de la caisse de tête vers un câble, la déshydratation de la suspension aqueuse de fibres sur le câble pour former une bande de papier ou de carton, et le séchage de la bande de papier ou de carton, ledit produit chimique de procédé étant un polymère obtenu par une technique de polymérisation radicalaire contrôlée, laquelle est un transfert de chaîne réversible par addition-fragmentation (RAFT), une conception macromoléculaire via l'échange de xanthates (MADIX), une polymérisation radicalaire par transfert d'atomes (ATRP) ou une polymérisation radicalaire en présence de nitroxydes (NMRP), à partir d'un monomère éthyléniquement insaturé, d'un agent de transfert de chaîne, et d'un initiateur dans un milieu liquide ou par une technique de photopolymérisation contrôlée à partir d'un monomère éthyléniquement insaturé et d'un photoiniferter dans un milieu liquide.

2. Procédé selon la revendication 1, dans lequel le milieu liquide comprend une solution aqueuse.

3. Procédé selon la revendication 1 ou 2, dans lequel les radicaux dans la polymérisation radicalaire sont produits par un moyen thermique.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel l'agent de transfert de chaîne comprend un composé présentant un segment ayant la formule

   -X-C(=S)-S- I

   où X est C, O, N ou S.

5. Procédé selon la revendication 4, dans lequel l'agent de transfert de chaîne comprend du trithiocarbonate de S,S'-bis(acide α,α'-diméthyl-α''-acétique), du dithio-benzoate d'acide 4-cyanopentanoïque (CPA) ou un sel de ceux-ci ou le 2-(2-méthyl-2-thiobenzoylsulfanylpropionylimino)-éthanesulfonate.

6. Procédé selon la revendication 1 ou 2, dans lequel le photoiniferter comprend un composé présentant un segment ayant la formule

   -N-C(=S)-S- II

7. Procédé selon la revendication 6, dans lequel le photoiniferter comprend de l'acide 2-(N,N-diéthyldithiocarbamyl)-isobutyrique ou de l'acide 2-(N,N-diméthyldithiocarbamyl)-isobutyrique ou un sel de ceux-ci.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le monomère éthyléniquement insaturé comprend de l'acrylamide, de l'acide acrylique, du diméthylacrylamide, du méthacrylate de 2-(diméthylamino)éthyle, du chlorure de [2-(acryloyloxy)éthyl]-triméthylammonium, du chlorure de [2-(méthacryloyloxy)éthyl]triméthylammonium ou du chlorure de diallyldiméthylammonium.

9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel le polymère comprend un homopolymère ou un copolymère.

10. Procédé selon la revendication 9, dans lequel le copolymère comprend un copolymère séquencé ou un copolymère multi-séquencé.

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel le polymère présente une masse moléculaire

dans l'intervalle d'environ 1 000 à environ 1 000 000, de préférence de 10 000 à 400 000, et encore mieux de 10 000 à 100 000.

12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel le polymère est ajouté à la suspension aqueuse de fibres dans une quantité d'environ 25 à 10 000 g/tonne, de préférence d'environ 50 à 1 000 g/tonne de matières sèches de la suspension aqueuse de fibres.

13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel le produit chimique de procédé fonctionne comme un coagulant ou un fixateur pour la liaison de substances gênantes par rapport aux fibres.

14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel la suspension aqueuse de fibres comprend une pâte à papier chimique, une pâte à papier mécanique, une pâte à papier chimico-mécanique, des fibres recyclées ou un mélange de celles-ci.

15. Utilisation d'un polymère obtenu par une technique de polymérisation radicalaire contrôlée, laquelle est un transfert de chaîne réversible par addition-fragmentation (RAFT), une conception macromoléculaire via l'échange de xanthanes (MADIX), une polymérisation radicalaire par transfert d'atomes (ATRT) ou une polymérisation radicalaire en présence de nitroxydes (NMRP), à partir d'un monomère éthyléniquement insaturé, d'un agent de transfert de chaîne, et d'un initiateur dans un milieu liquide, comme un produit chimique de procédé dans l'extrémité humide d'une machine à papier ou à carton dans la production de papier ou de carton pour améliorer la fonctionnabilité et la productivité de la machine à papier ou à carton.

16. Utilisation d'un polymère obtenu par une technique de polymérisation contrôlée à partir d'un monomère éthyléniquement insaturé et d'un photoiniferter dans un milieu liquide, comme un produit chimique de procédé dans l'extrémité humide d'une machine à papier ou à carton dans la production de papier ou de carton pour améliorer la fonctionnabilité et la productivité de la machine à papier.

REFERENCES CITED IN THE DESCRIPTION

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