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

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

(43) **International Publication Date**
**02 June 2022 (02.06.2022)**

WIPO | PCT

(10) **International Publication Number**
**WO 2022/110102 A1**

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(51) **International Patent Classification:**
*D21H 21/18* (2006.01) *C08F 220/56* (2006.01)
*D21H 17/49* (2006.01) *C08F 222/38* (2006.01)
*D21H 17/50* (2006.01) *C08F 226/02* (2006.01)
*D21H 17/47* (2006.01) *C08F 220/06* (2006.01)
*C08L 33/26* (2006.01) *C08F 8/28* (2006.01)

(21) **International Application Number:**
PCT/CN2020/132621

(22) **International Filing Date:**
30 November 2020 (30.11.2020)

(25) **Filing Language:** English

(26) **Publication Language:** English

(71) **Applicant: ECOLAB USA INC.** [US/US]; 1 Ecolab Place, St. Paul, Minnesota 55102-1390 (US).

(72) **Inventors: ZHANG, Jinming**; 1-3F Of Building C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai 201206 (CN). **ZHANG, Meng**; 1-3F Of Building C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai 201206 (CN). **DONG, Qun**; 1-3F Of Building C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai 201206 (CN). **CHEN, Zhi**; 1-3F Of Building C, Jinqiao Science Park, No. 255 Guiqiao Road, Pudong, Shanghai 201206 (CN).

(74) **Agent: BEIJING PAT SF INTELLECTUAL PROPERTY AGENCY CO. LTD**; 1110-11, A, Floor 11, Chengjian Plaza, 18 Beitaipingzhuang Road, Haidian District, Beijing 100088 (CN).

(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, IT, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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,

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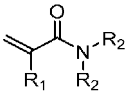
(54) **Title:** ANIONIC GLYOXALATED POLYACRYLAMIDE



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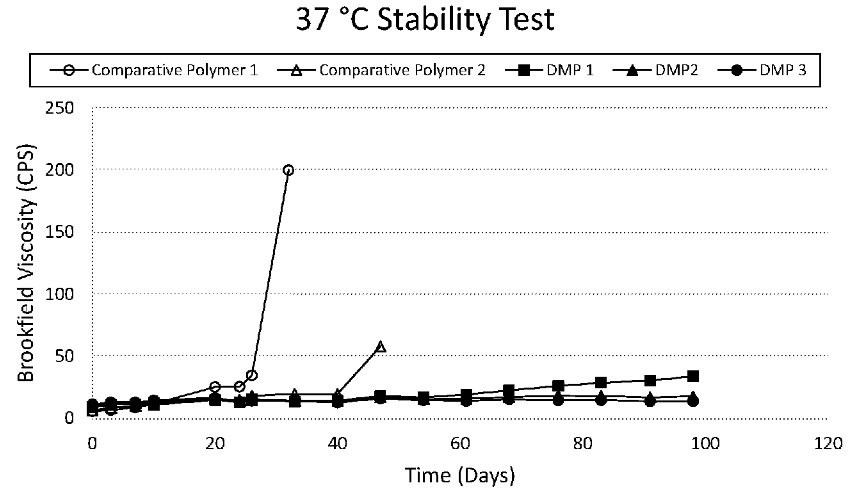


FIG. 3

(57) **Abstract:** A dialdehyde-modified polymer mixture is provided. The dialdehyde-modified polymer mixture comprises a solvent and a dialdehyde modified polymer comprising: (a) a polymer backbone comprising: (i) one or more monomer unit (s) derived from a monomer of Formula I, wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (ii) about 10 mol%to about 50 mol%of one or more anionic monomer unit (s), and (b) a dialdehyde modification to the polymer backbone, wherein the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0. A method of making the dialdehyde-modified polymer is also provided.

*[Continued on next page]*

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).

**Published:**

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

# ANIONIC GLYOXALATED POLYACRYLAMIDE

## BACKGROUND OF THE INVENTION

**[0001]** Glyoxalated polyacrylamides (“GPAMs”) are used in the papermaking process as strength aids, playing a role in enhancing paper strength properties such as, for example, dry tensile strength, wet tensile strength, temporary wet tensile strength, ring crush, burst, and Scott bond. Treatment of a paper sheet precursor with a GPAM strength aid can improve certain properties of the finished product and/or the papermaking process. Treatment with a GPAM strength aid can, for example, allow for increased ash content in the finished paper, boost strength properties of the finished paper, increase retention during the papermaking process, and improve dewatering efficiency during the papermaking process.

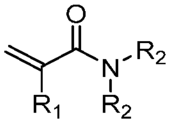
**[0002]** Conventionally, GPAM polymer products are prepared by reacting a polyacrylamide polymer backbone with an excess amount of glyoxal under basic conditions, *e.g.*, a pH of about 9 (see, for example, U.S. Patent Application Publication 2017/0002519, “the ’519 publication”). When the acrylamide-based polymer reaches the desired degree of glyoxalation, the glyoxalation process is retarded by reacting with an acid until the reaction reaches a pH of 3 or less (quenching). However, quenching does not completely terminate the glyoxalation reaction as demonstrated by the continued increase in the molecular weight of GPAM polymers after quenching. As a result, gelation of conventional GPAM polymers typically occur within about three weeks when stored at temperatures above 25 °C.

**[0003]** In order to combat the issue of instability, the ’519 publication provides a two-step method, where the polymer ingredients are stabilized at a low pH, and then shipped to the consumer for on-site preparation of the GPAM. Unfortunately, said two-step method requires marketing an unfinished product, and facilities on-site to prepare the GPAM strength aid.

**[0004]** Thus, there remains a need for shelf stable GPAMs that do not gel during storage.

## BRIEF SUMMARY OF THE INVENTION

**[0005]** A dialdehyde-modified polymer mixture is provided. The dialdehyde-modified polymer mixture comprises a solvent and a dialdehyde modified polymer comprising: (a) a polymer backbone comprising: (i) one or more monomer unit(s) derived from a monomer of Formula I:



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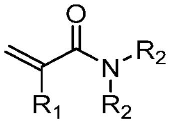
wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (ii) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s), and (b) a dialdehyde modification to the polymer backbone, wherein the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0.

**[0006]** A method of making a dialdehyde-modified polymer is further provided. The method comprises: (i) initiating a chemical reaction by treating a polymer backbone with a dialdehyde, wherein the polymer backbone comprises: (a) one or more monomer unit(s) derived from a monomer of Formula I:



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wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (b) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s) and (ii) quenching the chemical reaction by adjusting the pH until a pH of from about 4.0 to about 7.0 is reached.

**[0007]** The resulting dialdehyde-modified product is shelf stable and can be used for any application demanding an anionic dialdehyde-modified polymer (*e.g.*, the papermaking industry).

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0008]** FIG. 1 illustrates the viscosity results for Example 1.

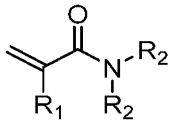
**[0009]** FIG. 2 illustrates the viscosity results for Example 2.

**[0010]** FIG. 3 illustrates the viscosity results for Example 3.

**[0011]** FIG. 4 illustrates the viscosity results for Example 4.

## DETAILED DESCRIPTION OF THE INVENTION

**[0012]** A dialdehyde-modified polymer mixture is provided. The dialdehyde-modified polymer mixture comprises a solvent and a dialdehyde modified polymer comprising: (a) a polymer backbone comprising: (i) one or more monomer unit(s) derived from a monomer of Formula I:



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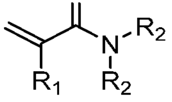
**[0013]** wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (ii) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s), and (b) a dialdehyde modification to the polymer backbone, wherein the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0.

**[0014]** The dialdehyde-modified polymer mixture comprises a solvent and a dialdehyde modified polymer. The solvent can be any suitable solvent, including, *e.g.*, water, ethanol, methanol, acetonitrile, etc., or a combination thereof. In certain embodiments of the mixture, the solvent is water. The water can be from any suitable source. For example, the water can be tap water, deionized water, distilled water, ground water, waste water, white water, etc. In some embodiments, the mixture further comprises a solvent other than water. The solvent can be any suitable solvent (*e.g.*, ethanol, methanol, acetonitrile, etc., or a combination thereof).

**[0015]** The dialdehyde-modified polymer comprises a polymer backbone. As used herein, the phrase “polymer backbone” refers to any polymer comprising (i) one or more monomer unit(s) derived from a monomer of Formula I and (ii) one or more anionic monomer unit(s). Accordingly, the polymer backbone can be considered a copolymer comprising one or more monomer unit(s) derived from a monomer of Formula I and one or more anionic monomer unit(s). Thus, the polymers described herein are considered anionic.

**[0016]** The polymer backbone can exist as any suitable copolymer. For example, the polymer backbone copolymer can exist as an alternating copolymer, random copolymer, block copolymer, graft copolymer, linear copolymer, branched copolymer, cyclic copolymer, or a combination thereof. The polymer backbone copolymer can contain any suitable number of differing monomer units. For example, the polymer backbone copolymer can contain 2 different monomer units, 3 different monomer units, 4 different monomer units, 5 different monomer units, or 6 different monomer units. The polymer backbone can comprise the one or more monomer unit(s) derived from a monomer of Formula I and the one or more anionic monomer unit(s) in any suitable concentration and any suitable proportion such that the polymer backbone comprises at least 10 mol% of the one or more anionic monomer unit(s).

**[0017]** The polymer backbone comprises one or more monomer unit(s) derived from a monomer of Formula I:



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wherein $R_1$ is H or $C_1$-$C_4$ alkyl (*e.g.*, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, or *tert*-butyl) and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group. As used herein, “derived” when referring to a monomer unit, means that the monomer unit has substantially the same structure of a monomer from which it was made. For example, when a carbon-carbon double bond of a terminal olefin is transformed to a carbon-carbon single bond during the process of polymerization.

**[0018]** Each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$. As used herein, the terms “independent” and “independently,” when referring to one or more constituent (*e.g.*, $R_2$), means that each substituent is individually selected from the list and can be the same or different. For example, if constituent $R_2$ appears more than once in a formula and $R_2$ is independently selected from a recited list, then each $R_2$ may be the same or different and selected from the recited list. As used herein, “linear or branched $C_1$-$C_{10}$ aliphatic group” refers to a saturated, unsaturated, branched, straight-chained, cyclic, or a combination thereof aliphatic group having from 1 to 10 carbon atoms (*i.e.*, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms). An exemplary list of linear or branched $C_1$-$C_{10}$ aliphatic groups is methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, *n*-pentyl, *sec*-pentyl, *neo*-pentyl, hexyl, etc. In some embodiments, the linear or branched $C_1$-$C_{10}$ aliphatic group is further substituted with one or more heteroatoms (*e.g.*, O, S, N, and/or P).

**[0019]** As used herein, the term “substituted” means that one or more hydrogens on the designated atom or group are replaced with another group provided that the designated atom's normal valence is not exceeded. For example, when the substituent is oxo (*i.e.*, =O), then two hydrogens on the carbon atom are replaced. Combinations of substituents are permissible provided that the substitutions do not significantly adversely affect synthesis or use of the dialdehyde-modified polymer.

**[0020]** In some embodiments, the monomer of Formula I is acrylamide, methacrylamide, ethylacrylamide, N-methyl acrylamide, N-butyl acrylamide, or any combination thereof. In certain embodiments, the monomer of Formula I is acrylamide and/or methacrylamide. In preferred embodiments, the monomer of Formula I is acrylamide.

**[0021]** The polymer backbone can comprise the one or more monomer unit(s) derived from a monomer of Formula I in any suitable concentration such that the polymer backbone comprises at least 10 mol% of the one or more anionic monomer unit(s) (*i.e.*, the polymer backbone comprises 90 mol% or less of the one or more monomer unit(s) derived from a monomer of Formula I). The polymer backbone can comprise about 40 mol% or more of the one or more monomer unit(s) derived from a monomer of Formula I, for example, about 50 mol% or more, about 60 mol% or more, about 65 mol% or more, about 70 mol% or more, or about 75 mol% or more. Alternatively, or in addition, the polymer backbone can comprise about 90 mol% or less, for example, about 88 mol% or less, about 85 mol% or less, about 80 mol% or less, about 75 mol% or less, about 70 mol% or less, about 65 mol% or less, about 60 mol% or less, about 55 mol% or less, or about 50 mol% or less. Thus, the polymer backbone can comprise the one or more monomer unit(s) derived from a monomer of Formula I in a concentration bounded by any two of the aforementioned endpoints. The polymer backbone can comprise from about 40 mol% to about 90 mol% of the one or more monomer unit(s) derived from a monomer of Formula I, for example, from about 50 mol% to about 90 mol%, from about 60 mol% to about 90 mol%, from about 65 mol% to about 90 mol%, from about 70 mol% to about 90 mol%, from about 75 mol% to about 90 mol%, from about 50 mol% to about 88 mol%, from about 60 mol% to about 88 mol%, from about 65 mol% to about 88 mol%, from about 70 mol% to about 88 mol%, from about 75 mol% to about 88 mol%, from about 50 mol% to about 85 mol%, from about 60 mol% to about 85 mol%, from about 65 mol% to about 85 mol%, from about 70 mol% to about 85 mol%, from about 75 mol% to about 85 mol%, from about 50 mol% to about 80 mol%, from about 60 mol% to about 80 mol%, from about 65 mol% to about 80 mol%, from about 70 mol% to about 80 mol%, or from about 75 mol% to about 80 mol%.

**[0022]** The polymer backbone comprises one or more anionic monomer unit(s). The one or more anionic monomer unit(s) can be any suitable anionic monomer unit derived from any suitable anionic monomer. In some embodiments, the anionic monomer unit is derived from a monomer selected from 2-acrylamido-2-methylpropane sulfonic acid (“AMPS”), 2-acrylamido-2-methylbutane sulfonic acid (“AMBS”), [2-methyl-2-[(1-oxo-2-propenyl)amino]propyl]-phosphonic acid, methacrylic acid, acrylic acid, salts thereof, and combinations thereof. In certain embodiments, the anionic monomer unit is derived from methacrylic acid and/or acrylic acid. In preferred embodiments, the anionic monomer unit is derived from acrylic acid.

**[0023]** The polymer backbone can comprise the one or more anionic monomer unit(s) in any suitable concentration such that the polymer backbone comprises at least 10 mol% of the one or more anionic monomer unit(s). The polymer backbone can comprise about 10 mol% or more of the one or more anionic monomer unit(s), for example, about 12 mol% or more, about 15 mol% or more, or about 20 mol% or more. Alternatively, or in addition to, the polymer backbone can comprise about 60 mol% or less the one or more anionic monomer unit(s), for example, about 50 mol% or less, about 40 mol% or less, about 30 mol% or less, or about 25 mol% or less. Thus, the polymer backbone can comprise the one or more anionic monomer unit(s) in a concentration bounded by any two of the aforementioned endpoints. The polymer backbone can comprise from about 10 mol% to about 60 mol% of the one or more anionic monomer unit(s), for example, from about 10 mol% to about 50 mol%, from about 10 mol% to about 40 mol%, from about 10 mol% to about 30 mol%, from about 10 mol% to about 25 mol%, from about 12 mol% to about 60 mol%, from about 12 mol% to about 50 mol%, from about 12 mol% to about 40 mol%, from about 12 mol% to about 30 mol%, from about 12 mol% to about 25 mol%, from about 15 mol% to about 60 mol%, from about 15 mol% to about 50 mol%, from about 15 mol% to about 40 mol%, from about 15 mol% to about 30 mol%, from about 15 mol% to about 25 mol%, from about 20 mol% to about 60 mol%, from about 20 mol% to about 50 mol%, from about 20 mol% to about 40 mol%, from about 20 mol% to about 30 mol%, or from about 20 mol% to about 25 mol%.

**[0024]** The polymer backbone can be synthesized by any suitable polymerization method. For example, the polymer backbone can be made through free radical polymerization, addition polymerization, cationic polymerization, anionic polymerization, emulsion polymerization, solution polymerization, suspension polymerization, precipitation polymerization, or a combination thereof. In certain embodiments, polymerization occurs through free radical polymerization.

**[0025]** Generally, the polymer backbone has a weight average molecular weight of from about 1 kDa to about 100 kDa. The polymer backbone can have a weight average molecular weight of about 100 kDa or less, for example, about 80 kDa or less, about 50 kDa or less, about 40 kDa or less, about 30 kDa or less, or about 20 kDa or less. Alternatively, or in addition, the polymer backbone can have a weight average molecular weight of about 1 kDa or more, for example, about 2 kDa or more, about 5 kDa or more, about 10 kDa or more, about 15 kDa or more, or about 20 kDa or more. Thus, the polymer backbone can have a weight average molecular weight bounded by any two of the aforementioned endpoints. For example, the polymer backbone can have a weight average molecular weight of from about 1 kDa to about 100 kDa, from about 1 kDa to about 60 kDa, from about 1 kDa to about 50 kDa, from about 1 kDa to about 40 kDa, from about 1 kDa to about 30 kDa, from about 1 kDa to about 20 kDa, 2 kDa to about 100 kDa, from about 2 kDa to about 50 kDa, from about 2 kDa to about 40 kDa, from about 2 kDa to about 30 kDa, from about 2 kDa to about 20 kDa, from about 5 kDa to about 100 kDa, from about 5 kDa to about 50 kDa, from about 5 kDa to about 40 kDa, from about 5 kDa to about 30 kDa, or from about 5 kDa to about 20 kDa.

**[0026]** Weight average molecular weight can be determined by any suitable technique. While alternate techniques are envisioned, in some embodiments, the weight average molecular weight is determined using size exclusion chromatography (SEC) equipped with a set of TSKgel PW columns (TSKgel Guard+ GMPW+GMPW+G1000PW), Tosoh Bioscience LLC, Cincinnati, Ohio) and a Waters 2414 (Waters Corporation, Milford, Massachusetts) refractive index detector or a DAWN HELEOS II multi-angle light scattering (MALS) detector (Wyatt Technology, Santa Barbara, California). Moreover, the weight average molecular weight is determined from either calibration with polyethylene oxide/polyethylene glycol standards ranging from

150-875,000 Daltons or directly using light scattering data with known refractive index increment (“dn/dc”).

**[0027]** The polymer backbone is modified with a dialdehyde to form a dialdehyde-modified polymer. As used herein, “dialdehyde-modified” refers to a polymer (*e.g.*, a polyacrylamide copolymer) comprising monomer units that have been modified with a chemical compound containing at least two aldehydes (*e.g.*, two aldehydes). Any suitable monomer unit can be dialdehyde-modified. In an embodiment, for example, acrylamide can be dialdehyde-modified. The dialdehyde can be any suitable chemical compound with at least two aldehydes (*e.g.*, two aldehydes). For example, the dialdehyde can be glyoxal, malondialdehyde, succinic dialdehyde, or glutaraldehyde. In a preferred embodiment, the dialdehyde is glyoxal.

**[0028]** The dialdehyde-modified polymer can comprises any suitable amount of the dialdehyde modification. Without wishing to be bound by any particular theory, it is believed that the amount of dialdehyde modification has an impact on the viscosity of the dialdehyde-modified polymer, such that as the amount of dialdehyde modification increases, the viscosity increases. Accordingly, it is believed that quenching the dialdehyde modification reaction with an acid until reaching a pH of greater than about 4.0 significantly decreases the rate of the glyoxalation reaction during storage, thereby increasing the shelf life of the resulting dialdehyde-modified polymer. In some embodiments, the dialdehyde-modified polymer comprises from about 0.1 mol% to about 20 mol% (*e.g.*, from about 0.1 mol% to about 15 mol%, from about 0.1 mol% to about 10 mol%, from about 0.1 mol% to about 7 mol%, from about 0.1 mol% to about 5 mol%, from about 1 mol% to about 20 mol%, from about 1 mol% to about 15 mol%, from about 1 mol% to about 10 mol%, from about 1 mol% to about 7 mol%, or from about 1 mol% to about 5 mol%) of the dialdehyde modification. In certain embodiments, the dialdehyde-modified polymer comprises from about 0.1 mol% to about 10 mol% of the dialdehyde modification.

**[0029]** The dialdehyde-modified polymer can have any suitable weight average molecular weight. Generally, the dialdehyde-modified polymer has a weight average molecular weight of from about 10 kDa to about 10,000 kDa. The dialdehyde-modified polymer can have a weight average molecular weight of about 10,000 kDa or less, for example, about 8,000 kDa or less, about 6,000 kDa or less, about 5,000 kDa or less, about 4,000 kDa or less, about 2,000 kDa or less, or about 1,000 kDa or less. Alternatively, or in addition, the dialdehyde-modified polymer can have a weight average molecular weight of about 10 kDa or more, for example, about 100 kDa or more, about 200 kDa or more, about 300 kDa or more, about 400 kDa or more, about 500 kDa or more, or about 750 kDa or more. Thus, the dialdehyde-modified polymer can have a weight average molecular weight bounded by any two of the aforementioned endpoints. For example, the dialdehyde-modified polymer can have a weight average molecular weight of from about 10 kDa to about 10,000 kDa, from about 10 kDa to about 5,000 kDa, from about 100 kDa to about 10,000 kDa, from about 100 kDa to about 5,000 kDa, from about 100 kDa to about 1,000 kDa, from about 100 kDa to about 2,000 kDa, from about 200 kDa to about 1,000 kDa, from about 300 kDa to about 1,000 kDa, from about 400 kDa to about 1,000 kDa, from about 500 kDa to about 1,000 kDa, from about 750 kDa to about 1,000 kDa, from about 750 kDa to about 2,000 kDa, from about 750 kDa to about 4,000 kDa, from about 750 kDa to about 6,000 kDa, from about 750 kDa to about 8,000 kDa, from about 750 kDa to about 10,000 kDa, from about 200 kDa to about 2,000 kDa, or from about 500 kDa to about 2,000 kDa. In certain embodiments, the dialdehyde-modified polymer has a weight average molecular weight of from about 100 kDa to about 2,000 kDa.

**[0030]** The dialdehyde-modified polymer mixture can comprise any suitable amount of the dialdehyde-modified polymer, referred to as “solids content.” In some embodiments, the mixture comprises from about 1 wt.% to about 40 wt.% (*e.g.*, from about 1 wt.% to about 30 wt.%, from about 1 wt.% to about 25 wt.%, from about 1 wt.% to about 20 wt.%, from about 1 wt.% to about 15 wt.%, from about 1 wt.% to about 10 wt.%, from about 2 wt.% to about 30 wt.%, from about 2 wt.% to about 25 wt.%, from about 2 wt.% to about 20 wt.%, from about 2 wt.% to about 15 wt.%, from about 2 wt.% to about 10 wt.%, from about 5 wt.% to about 40 wt.%, from about 5 wt.% to about 30 wt.%, from about 5 wt.% to about 25 wt.%, from about 5 wt.% to about 20 wt.%, from about 5 wt.% to about 15 wt.%, or from about 5 wt.% to about 10 wt.%) solids content. In certain embodiments, the mixture comprises from about 5 wt.% to about 25 wt.% solids content.

**[0031]** The dialdehyde-modified polymer mixture can have any suitable pH so long as the method for making the dialdehyde-modified polymer includes the step of quenching the chemical (e.g., glyoxalation) reaction by adjusting the pH until a pH of from about 4.0 to about 7.0 is reached. Without wishing to be bound by any particular theory, it is believed that the improved stability of the dialdehyde-modified polymer described herein is a result of quenching the chemical (e.g., glyoxalation) reaction by adjusting the pH until reaching a pH of greater than about 4.0 (*e.g.*, greater than about 4.5 or greater than about 5.0). In some embodiments, the pH is further adjusted after quenching the chemical (e.g., glyoxalation) reaction by adjusting the pH until reaching a pH of greater than about 4.0 (*e.g.*, greater than about 4.5 or greater than about 5.0). Generally, the pH of the dialdehyde modified polymer is not adjusted after quenching the chemical (e.g., glyoxalation) reaction by adjusting the pH until reaching a pH of greater than about 4.0 (*e.g.*, greater than about 4.5 or greater than about 5.0). Accordingly, the dialdehyde-modified polymer mixture can have a pH of about 4.0 or greater (*e.g.*, about 4.5 or greater or about 5.0 or greater). In some embodiments, the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0 (*e.g.*, from about 4.1 to about 7.0, from about 4.2 to about 7.0, from about 4.3 to about 7.0, from about 4.4 to about 7.0, from about 4.5 to about 7.0, from about 4.6 to about 7.0, from about 4.7 to about 7.0, from about 4.8 to about 7.0, from about 4.9 to about 7.0, from about 5.0 to about 7.0, from about 5.1 to about 7.0, from about 5.2 to about 7.0, from about 5.3 to about 7.0, from about 5.4 to about 7.0, from about 5.5 to about 7.0, from about 6.0 to about 7.0, from about 4.5 to about 6.5, from about 4.5 to about 6.0, from about 4.5 to about 5.5, from about 5.0 to about 6.5, from about 5.0 to about 5.5, from about 5.5 to about 6.5, or from about 5.5 to about 6). In certain embodiments, the dialdehyde-modified polymer mixture has a pH of from about 4.5 to about 7.0. In other embodiments, the dialdehyde-modified polymer mixture has a pH of from about 5.0 to about 7.0.

**[0032]** The dialdehyde-modified polymer mixture can have any suitable Brookfield viscosity as measured using an aqueous solution containing the dialdehyde-modified polymer. For example, the dialdehyde-modified polymer, as an 8 wt.% solution in deionized water, can have a Brookfield viscosity of about 50 cps or less, about 45 cps or less, about 40 cps or less, about 35 cps or less, about 30 cps or less, about 25 cps or less, or about 20 cps or less. Alternatively, or in addition, the dialdehyde-modified polymer, as an 8 wt.% solution in deionized water, can have a Brookfield viscosity of about 0.5 cps or more, for example, about 1 cp or more, about 2 cps or more, about 3 cps or more, about 4 cps or more, about 5 cps or more, or about 10 cps or more. Thus, the dialdehyde-modified polymer, as an 8 wt.% solution in deionized water, can have a Brookfield viscosity bounded by any two of the aforementioned endpoints. For example, the dialdehyde-modified polymer, as an 8 wt.% solution in deionized water, can have a Brookfield viscosity of from about 0.5 cps to about 50 cps, from about 1 cp to about 50 cps, from about 2 cps to about 50 cps, from about 3 cps to about 50 cps, from about 4 cps to about 50 cps, from about 5 cps to about 50 cps, from about 10 cps to about 50 cps, from about 0.5 cps to about 30 cps, from about 1 cp to about 30 cps, from about 2 cps to about 30 cps, from about 3 cps to about 30 cps, from about 4 cps to about 30 cps, from about 5 cps to about 30 cps, from about 10 cps to about 30 cps, from about 0.5 cps to about 45 cps, from about 0.5 cps to about 40 cps, from about 0.5 cps to about 35 cps, from about 0.5 cps to about 30 cps, from about 0.5 cps to about 25 cps, from about 0.5 cps to about 20 cps, from about 1 cp to about 20 cps, from about 5 cps to about 20 cps, from about 1 cp to about 40 cps, from about 5 cps to about 40 cps, or from about 10 cps to about 20 cps.

**[0033]** The viscosity can be measured by any suitable method. For example, the viscosity can be measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm.

**[0034]** Typically, the dialdehyde-modified polymer described herein has improved stability, as measured by Brookfield viscosity, as compared to an identical dialdehyde-modified polymer (*i.e.*, identical monomer units, identical concentration of monomer units, and identical degree of dialdehyde modification) that has been synthesized by quenching a chemical (e.g., glyoxalation) reaction by adjusting the pH until reaching a pH of less than 4.0. For example, the viscosity of an aqueous mixture containing a dialdehyde-modified polymer quenched by adjusting the pH until reaching a pH of greater than about 4.0 and a viscosity of 5 cps will increase less rapidly than the viscosity of the same dialdehyde-modified polymer quenched by adjusting the pH until reaching a pH of less than 4.0 and a viscosity of 5 cps.

**[0035]** The stability of the dialdehyde-modified polymer can be assessed by the dialdehyde-modified polymer's ability to maintain a Brookfield viscosity of less than about 50 cps. In some embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps over the span of at least 100 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 25 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm.

**[0036]** In some embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps over the span of at least 50 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 30 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm. In some embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps over the span of at least 75 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 30 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm. In certain embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps the span of at least 100 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 30 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm.

**[0037]** In some embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps over the span of at least 40 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 37 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm. In some embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps over the span of at least 50 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 37 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm. In certain embodiments, the dialdehyde-modified polymer has a Brookfield viscosity of from about 0.5 cps to about 50 cps the span of at least 60 days from synthesis when stored as an 8 wt.% solution in deionized water in a polyethylene bottle in an oven at 37 °C, as measured by a Brookfield viscometer at about 25 °C and a rotation speed of 60 rpm.

**[0038]** In some embodiments, the mixture further comprises or is used with any suitable conventional papermaking product. For example, the mixture further comprises or is used with one or more inorganic filler(s), dye(s), retention aid(s), drainage aid(s), or combinations thereof.

**[0039]** In some embodiments, the mixture further comprises or is used with one or more inorganic filler(s). The inorganic filler can be any suitable inorganic filler, capable of increasing opacity or smoothness, decreasing the cost per mass of the paper, or combinations thereof. For example, the mixture further comprises or is used with kaolin, chalk, limestone, talc, titanium dioxide, calcined clay, urea formaldehyde, aluminates, aluminosilicates, silicates, calcium carbonate (*e.g.*, ground and/or precipitated calcium carbonate), or combinations thereof.

**[0040]** In some embodiments, the mixture further comprises or is used with one or more dye(s). The dye can be any suitable dye, capable of controlling the coloration of paper. For example, the dye can be a direct dye, a cationic direct dye, acidic dye, basic dye, insoluble colored pigment, or combinations thereof.

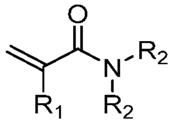
**[0041]** In some embodiments, the mixture further comprises or is used with one or more drainage and/or retention aid(s). The drainage and/or retention aids can be any suitable drainage and/or retention aids, capable of helping to maintain efficiency and drainage of the paper machine, while improving uniformity, and retaining additives. For example, the drainage and/or retention aid can be a cationic polyacrylamide ("PAM") polymer, an anionic polyacrylamide ("PAM") polymer, a cationic polyethylenimine ("PEI") polymer, polyamines, ammonium-based polymers (*e.g.*, polydiallyldimethylammonium chloride ("DADMAC"), colloidal silica, bentonite, polyethylene oxide ("PEO"), starch, polyaluminum sulfate, polyaluminum chloride, or combinations thereof.

**[0042]** In some embodiments, the mixture further comprises or is used with one or more coagulant(s). The coagulant can be any suitable coagulant. As it relates to the present application, "coagulant" refers to a water treatment chemical used in a solid-liquid separation stage to neutralize charges of suspended particles so that the particles can agglomerate. Generally, coagulants may be categorized as cationic, anionic, amphoteric, or zwitterionic. Furthermore, coagulants may be categorized as inorganic coagulants, organic coagulants, and blends thereof. Exemplary inorganic coagulants include, *e.g.*, aluminum or iron salts, such as aluminum sulfate, aluminum chloride, ferric chloride, ferric sulfate, polyaluminum chloride, and/or aluminum chloride hydrate. Exemplary organic coagulants include, *e.g.*, diallyldimethylammonium chloride ("DADMAC"), dialkylaminoalkyl acrylate and/or a dialkylaminoalkyl methacrylate, or their quaternary or acid salts.

**[0043]** In some embodiments, the mixture is used with one or more strength aid(s). The strength aid can be any suitable strength aid. For example, the strength aid can improve dry strength of the paper sheet, wet strength or rewetted strength of the paper sheet, wet web strength of the paper sheet, or a combination thereof. Exemplary strength aids include, *e.g.*, polyamidoamine-epichlorohydrin ("PAAE"), starch, cationic polyacrylamide ("PAM") polymer, an anionic polyacrylamide ("PAM") polymer, a cationic polyethylenimine ("PEI") polymer, polyamines, ammonium-based polymers (*e.g.*, polydiallyldimethylammonium chloride ("DADMAC"), and blends thereof.

**[0044]** In some embodiments, the mixture does not contain additional components known to stabilize conventional GPAM. For example, in certain embodiments, the mixture does not contain a second portion of dialdehyde (e.g., glyoxal) added after the step of quenching the chemical (e.g., glyoxalation) reaction by adjusting the pH until reaching a pH of greater than about 4.0. In certain embodiments, the mixture does not contain a buffer to stabilize the pH (e.g., to stabilize at a pH of less than about 4). For example, in certain embodiments, the mixture is free or substantially free of a weak acid or a weak base, such as citric acid with sodium citrate, disodium phosphate with citric acid, succinic acid with borax, acetic acid with sodium acetate, monopotassium phthalate with hydrochloric acid, bicarbonates, carbonate esters, complex carbonate salts of organic acids, hydrogen phosphates, phosphate esters, phosphinate esters, borates, borate esters, hydrogen sulfates, sulfinates, and sulfate esters. Other examples of buffers include potassium bicarbonate, potassium biphthalate, potassium bisulfate, potassium dihydrogen citrate, dipotassium hydrogen citrate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium hydrogen tartrate, potassium hydrogen oxolate, potassium hydrogen maleate, potassium hydrogen succinate, potassium hydrogen glutarate, potassium hydrogen adipate, potassium tetraborate, potassium pentaborate, potassium octaborate and all the corresponding sodium salts, and complex calcium carbonate salts of organic acids (such as octanoic acid, iso-octanoic acid, 2-ethyl hexanoic acid, hexanoic acid, and the like). In certain embodiments, the mixture is free or substantially free of aldehyde scavengers, such as, for example, lactic acid, malic acid, citric acid, and choline chloride.

**[0045]** A method of making a dialdehyde-modified polymer is further provided. The method comprises: (i) initiating a chemical reaction by treating a polymer backbone with a dialdehyde, wherein the polymer backbone comprises: (a) one or more monomer unit(s) derived from a monomer of Formula I:



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wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (b) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s) and (ii) quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH until a pH of from about 4.0 to about 7.0 is reached. As used herein, the phrase "chemical reaction" refers to the interaction between two molecules (*e.g.*, a polymer backbone and a dialdehyde or two polymer backbones comprising dialdehyde modifications). In certain embodiments, the chemical reaction is a glyoxalation reaction.

**[0046]** The method of making a dialdehyde-modified polymer comprises initiating a chemical reaction by treating a polymer backbone with a dialdehyde. As used herein, the term "treating" refers to a process of contacting a polymer backbone with a dialdehyde. The polymer backbone and the dialdehyde can be contacted by any suitable method (*e.g.*, pouring, mixing, dropping, etc., or a combination thereof) in any suitable solvent (*e.g.*, water, ethanol, methanol, acetonitrile, etc., or a combination thereof).

**[0047]** The step of initiating a chemical reaction by treating a polymer backbone with a dialdehyde can occur at any suitable pH. Typically, the step of initiating a chemical reaction by treating a polymer backbone with a dialdehyde occurs at a pH of at least about 7.0. For example, the step of initiating a chemical reaction by treating a polymer backbone with a dialdehyde can occur at a pH of from about 7.0 to about 14 (*e.g.*, from about 7.0 to about 13, from about 7.0 to about 12, from about 7.0 to about 11, from about 7.0 to about 10, from about 7.0 to about 9.0, from about 8.0 to about 12, from about 8.0 to about 11, from about 8.0 to about 10, from about 9.0 to about 14, or from about 9.0 to about 11). In some embodiments, the step of initiating a chemical reaction by treating a polymer backbone with a dialdehyde can occur at a pH of from about 8.0 to about 10. In certain embodiments, the step of initiating a chemical reaction by treating a polymer backbone with a dialdehyde can occur at a pH of about 9.0.

**[0048]** The method of making a dialdehyde-modified polymer comprises a quenching step with an acid, after initiating a chemical reaction by treating a polymer backbone with a dialdehyde. As used herein, the term "quenching" refers to a process of retarding the rate of a chemical (e.g., glyoxalation) reaction such that the degree of dialdehyde modification is substantially slowed or stopped (i.e., the rate of increase of the molecular weight and/or the viscosity is substantially reduced). Typically, the chemical (e.g., glyoxalation) reaction is quenched by adjusting the pH of the reaction mixture until it reaches a pH of from about 4.0 to about 7.0. As used herein, the terms “reach”, “reaches”, or “reaching”, when referring to the quenching pH, means the pH of the reaction mixture when the quenching process is discontinued. Typically, the glyoxalation reaction is quenched with an acid. The acid can be any suitable acid (*e.g.*, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, etc., or a combination thereof) used in any suitable amount such that the pH of the solution resulting from the step of quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH to about 4.0 to about 7.0. In certain embodiments of the methods provided herein, a suitable base (e.g., triethylamine, sodium hydroxide, potassium hydroxide, sodium bicarbonate, potassium carbonate, etc. or a combination thereof) may be used in combination with an acid to achieve the quenching pH of from about 4.0 to about 7.0.

**[0049]** The step of quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH of the reaction mixture (*e.g.*, the dialdehyde-modified polymer mixture) until reaching a pH of from about 4.0 to about 7.0. For example, the step of quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH of the reaction mixture can occur until reaching a pH of from about 4.0 to about 7.0, e.g., about 4.1 to about 7.0, about 4.2 to about 7.0, about 4.3 to about 7.0, about 4.4 to about 7.0, about 4.5 to about 7.0, about 4.6 to about 7.0, about 4.7 to about 7.0, about 4.8 to about 7.0, about 4.9 to about 7.0, about 5.0 to about 7.0, about 5.1 to about 7.0, about 5.2 to about 7.0, about 5.3 to about 7.0, about 5.4 to about 7.0, about 5.5 to about 7.0, about 6.0 to about 7.0, about 4.5 to about 6.5, about 4.5 to about 6.0, about 4.5 to about 5.5, about 5.0 to about 6.5, about 5.0 to about 5.5, about 5.5 to about 6.5, or about 5.5 to about 6.0. In certain embodiments, the step of quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH of the reaction mixture (*e.g.*, the dialdehyde-modified polymer mixture) until reaching a pH of from about 4.5 to about 7.0. In other embodiments, the step of quenching the chemical (*e.g.*, glyoxalation) reaction by adjusting the pH of the reaction mixture (*e.g.*, the dialdehyde-modified polymer mixture) until reaching a pH of from about 5.0 to about 7.0.

**[0050]** A method of enhancing paper strength properties is also provided. The method comprises treating a paper sheet precursor with a dialdehyde-modified polymer(s) or mixture(s) described herein.

**[0051]** The method of enhancing paper strength properties comprises treating a paper sheet at any suitable pH. Generally, the overall treatment can have a pH of from about 4.0 or more, *e.g.*, about 4.5 or more, about 5.0 or more, about 5.5 or more, about 6.0 or more, about 6.5 or more, about 7.0 or more, about 7.5 or more, about 8.0 or more, or about 8.5 or more. Alternatively, or in addition, the treatment can have a pH of about 11 or less, *e.g.*, about 10.5 or less, about 10 or less, about 9.5 or less, or about 9.0 or less. Thus, the treatment can have a pH bounded by any two of the above endpoints recited. For example, the treatment can have a pH of from about 4.5 to about 9.0, *e.g.*, from about 5.0 to about 9.0, from about 5.5 to about 9.0, from about 6.0 to about 9.0, from about 6.5 to about 9.0, from about 7.0 to about 9.0, from about 7.5 to about 9.0, from about 8.0 to about 9.0, from about 8.5 to about 9.0, from about 8.5 to about 11, from about 8.5 to about 10.5, from about 8.5 to about 10, from about 8.5 to about 9.5, from about 8.5 to about 9.0, from about 4.0 to about 11, from about 7.0 to about 10, or about 8.0.

**[0052]** The dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to any suitable paper sheet precursor. As used herein, the term “paper sheet precursor” refers to any component of the papermaking process upstream of the point at which the fiber slurry begins being rolled into a paper sheet. Accordingly, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to pulp (*e.g.*, virgin pulp, recycled pulp, or a combination thereof), pulp slurry, cellulosic fibers, a solution used for any of the aforementioned components, and any combination thereof. The dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to the paper sheet precursor at any one or more of various locations during the papermaking process, up to and including a headbox. In some embodiments, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to the pulp slurry in a pulper, latency chest, reject refiner chest, disk filter or Decker feed or accept, whitewater system, pulp stock storage chests (either low density (“LD”), medium consistency (“MC”), or high consistency (“HC”)), blend chest, machine chest, headbox, save-all chest, paper machine whitewater system, or combinations thereof. In certain embodiments, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture is added to the headbox.

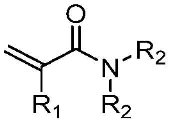
**[0053]** In some embodiments, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture is stored in the absence of fiber and added to the paper sheet precursor upstream of a wet end of a paper machine (*e.g.*, before the wet end). As used herein, the term "wet end" refers to any component of the papermaking process including the headbox and downstream thereof. Accordingly, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to any component of the papermaking process up to but not including the headbox. In certain embodiments, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture is added to a stock prep section of the paper machine. As used herein, "stock prep section" refers to any component of the papermaking process wherein the pulp is refined and/or blended. For example, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture can be added to the pulp stock storage chests (either low density ("LD"), medium consistency ("MC"), or high consistency ("HC")), blend chest, machine chest, save-all chest, or a combination thereof. In certain embodiments, the dialdehyde-modified polymer or dialdehyde-modified polymer mixture is added to pulp slurry upstream of a head box of a papermaking process.

**[0054]** In some embodiments, the pulp slurry comprises recycled fibers. The recycled fibers can be obtained from a variety of paper products or fiber containing products, such as paperboard, newsprint, printing grades, sanitary or other paper products. In some embodiments, these products can comprise, for example, old corrugated cardboard ("OCC"), old newsprint ("ONP"), mixed office waste ("MOW"), magazines, books, or a combination thereof. In some embodiments, the pulp slurry comprises virgin fibers. In embodiments comprising virgin fibers, the pulp can be derived from softwood, hardwood, or blends thereof. In certain embodiments, the virgin pulp can include bleached or unbleached Kraft, sulfite pulp or other chemical pulps, and groundwood ("GW") or other mechanical pulps such as, for example, thermomechanical pulp ("TMP").

**[0055]** The method of enhancing paper strength properties may enhance any suitable paper strength property. For example, treatment according to the methods described herein can, for example, allow for increased ash content in the finished paper, boost strength properties of the finished paper, increase retention during the papermaking process, and improve dewatering efficiency during the papermaking process.

**[0056]** The invention is further illustrated by the following embodiments.

**[0057]** (1) A dialdehyde-modified polymer mixture comprising a solvent and a dialdehyde modified polymer comprising: (a) a polymer backbone comprising: (i) one or more monomer unit(s) derived from a monomer of Formula I:



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wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (ii) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s), and (b) a dialdehyde modification to the polymer backbone, wherein the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0.

**[0058]** (2) The dialdehyde-modified polymer mixture of embodiment (1), wherein the one or more anionic monomer unit(s) is derived from a monomer selected from 2-acrylamido-2-methylpropane sulfonic acid (“AMPS”), 2-acrylamido-2-methylbutane sulfonic acid (“AMBS”), [2-methyl-2-[(1-oxo-2-propenyl)amino]propyl]-phosphonic acid, methacrylic acid, acrylic acid, salts thereof, and combinations thereof.

**[0059]** (3) The dialdehyde-modified polymer mixture of embodiment (1) or (2), wherein the anionic monomer unit is derived from acrylic acid.

**[0060]** (4) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(3), wherein the monomer of Formula I is acrylamide, methacrylamide, ethylacrylamide, N-methyl acrylamide, N-butyl acrylamide, or any combination thereof.

**[0061]** (5) The dialdehyde-modified polymer mixture of embodiment (4), wherein the monomer of Formula I is acrylamide.

**[0062]** (6) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(5), wherein the dialdehyde-modified polymer is modified with a dialdehyde selected from glyoxal, malondialdehyde, succinic dialdehyde, and glutaraldehyde.

**[0063]** (7) The dialdehyde-modified polymer mixture of embodiment (6), wherein the dialdehyde is glyoxal.

**[0064]** (8) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(7), wherein the dialdehyde-modified polymer mixture has a pH of from about 4.5 to about 7.0.

**[0065]** (9) The dialdehyde-modified polymer mixture of embodiment (8), wherein the dialdehyde-modified polymer mixture has a pH of from about 5.0 to about 7.0.

**[0066]** (10) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(9), wherein the polymer backbone comprises from about 12 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0067]** (11) The dialdehyde-modified polymer mixture of embodiment (10), wherein the polymer backbone comprises from about 15 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0068]** (12) The dialdehyde-modified polymer mixture of embodiment (11), wherein the polymer backbone comprises from about 20 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0069]** (13) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(12), wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 10 kDa to about 5,000 kDa.

**[0070]** (14) The dialdehyde-modified polymer mixture of embodiment (13), wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 100 kDa to about 2,000 kDa.

**[0071]** (15) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(14), wherein the polymer backbone has a weight average molecular weight of from about 2 kDa to about 50 kDa in the absence of the dialdehyde modification.

**[0072]** (16) The dialdehyde-modified polymer mixture of embodiment (15), wherein the polymer backbone has a weight average molecular weight of from about 5 kDa to about 20 kDa in the absence of the dialdehyde modification.

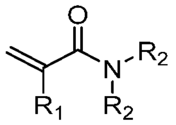
**[0073]** (17) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(16), wherein the dialdehyde-modified polymer mixture has a solids content of from about 1 wt.% to about 40 wt.%.

**[0074]** (18) The dialdehyde-modified polymer mixture of embodiment (17), wherein the solids content is from about 5 wt.% to about 25 wt.%.

**[0075]** (19) The dialdehyde-modified polymer mixture of any one of embodiments (1)-(18), wherein the dialdehyde-modified polymer mixture has a Brookfield viscosity of from about 5 cps to about 50 cps at a solids content of 8 wt.%.

**[0076]** (20) The dialdehyde-modified polymer mixture of embodiment (19), wherein the dialdehyde-modified polymer mixture has a Brookfield viscosity of from about 5 cps to about 30 cps at a solids content of 8 wt.%.

**[0077]** (21) A method of making a dialdehyde-modified polymer comprising: (i) initiating a chemical reaction by treating a polymer backbone with a dialdehyde, wherein the polymer backbone comprises: (a) one or more monomer unit(s) derived from a monomer of Formula I:



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wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and (b) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s) and (ii) quenching the chemical reaction by adjusting the pH until a pH of from about 4.0 to about 7.0 is reached.

**[0078]** (22) The method of embodiment (21), wherein the one or more anionic monomer unit(s) is derived from a monomer selected from 2-acrylamido-2-methylpropane sulfonic acid ("AMPS"), 2-acrylamido-2-methylbutane sulfonic acid ("AMBS"), [2-methyl-2-[(1-oxo-2-propenyl)amino]propyl]-phosphonic acid, methacrylic acid, acrylic acid, salts thereof, and combinations thereof.

**[0079]** (23) The method of embodiment (21) or (22), wherein the anionic monomer unit is derived from acrylic acid.

**[0080]** (24) The method of any one of embodiments (21)-(23), wherein the monomer of Formula I is acrylamide, methacrylamide, ethylacrylamide, N-methyl acrylamide, N-butyl acrylamide, or any combination thereof.

**[0081]** (25) The method of embodiment (24), wherein the monomer of Formula I is acrylamide.

**[0082]** (26) The method of any one of embodiments (21)-(25), wherein the dialdehyde-modified polymer is modified with a dialdehyde selected from glyoxal, malondialdehyde, succinic dialdehyde, and glutaraldehyde.

**[0083]** (27) The method of embodiment (26), wherein the dialdehyde is glyoxal.

**[0084]** (28) The method of any one of embodiments (21)-(27), wherein the pH is adjusted until a pH of from about 4.5 to about 7.0 is reached.

**[0085]** (29) The method of embodiment (28), wherein the pH is adjusted until a pH of from about 5.0 to about 7.0 is reached.

**[0086]** (30) The method of any one of embodiments (21)-(29), wherein the polymer backbone comprises from about 12 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0087]** (31) The method of embodiment (30), wherein the polymer backbone comprises from about 15 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0088]** (32) The method of embodiment (31), wherein the polymer backbone comprises from about 20 mol% to about 50 mol% of the one or more anionic monomer unit(s).

**[0089]** (33) The method of any one of embodiments (21)-(32), wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 10 kDa to about 5,000 kDa.

**[0090]** (34) The method of embodiment (33), wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 100 kDa to about 2,000 kDa.

**[0091]** (35) The method of any one of embodiments (21)-(34), wherein the polymer backbone has a weight average molecular weight of from about 2 kDa to about 50 kDa in the absence of the dialdehyde modification.

**[0092]** (36) The method of embodiment (35), wherein the polymer backbone has a weight average molecular weight of from about 5 kDa to about 20 kDa in the absence of the dialdehyde modification.

**[0093]** (37) The method of any one of embodiments (21)-(36), wherein the dialdehyde-modified polymer has a Brookfield viscosity of from about 5 cps to about 50 cps at a solids content of 8 wt.% in water.

**[0094]** (38) The method of embodiment (37), wherein the dialdehyde-modified polymer has a Brookfield viscosity of from about 5 cps to about 30 cps at a solids content of 8 wt.% in water.

**[0095]** (39) Use of any one of the dialdehyde-modified polymer mixtures of embodiments (1)-(20) in treating a paper sheet precursor.

**[0096]** The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

## EXAMPLES

**[0097]** For each of the following examples, a polymer backbone comprising acrylamide and an anionic monomer unit or acrylamide and a cationic monomer unit is modified with a dialdehyde in an aqueous solution at a pH of about 9. Once the desired viscosity is reached, the dialdehyde-modification reaction is quenched with acid until the desired pH value is reached.

### EXAMPLE 1

**[0098]** This example demonstrates the effect that the quenching pH has on the stability of a resulting anionic glyoxalated polyacrylamide ("GPAM") polymer.

**[0099]** An aqueous solution containing an 88/12 mol% acrylamide/acrylic acid polymer was treated with glyoxal (48 wt.% in water) at a pH of about 9. Once the resulting glyoxalated polymer mixture had reached a viscosity of about 5.5 cps to about 11.5 cps, the reaction was quenched by adjusting the pH to 2.51 ("Comparative Polymer 1"), 3.57 ("Comparative Polymer 2"), 4.5 ("DMP 1"), 5.59 ("DMP 2"), and 6.47 ("DMP 3") with sulfuric acid. Samples (100 g) of the anionic GPAM polymers formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.51, 3.57, 4.5, 5.59, and 6.47 were individually stored, as an 8 wt.% solution in deionized water, in polyethylene bottles and placed at 25 °C. Their viscosity was monitored as a function of time using a Brookfield viscometer equipped with a #61 spindle at room temperature (*i.e.*, about 25 °C) and 60 rpm rotation speed, respectively. The results are set forth in FIG. 1.

**[0100]** As is apparent from the results set forth in FIG. 1, solutions of Comparative Polymer 1, Comparative Polymer 2, DMP 1, DMP 2, and DMP 3 maintain a Brookfield viscosity of less than about 25 cps for 100 days, demonstrating that Comparative Polymer 1, Comparative Polymer 2, DMP 1, DMP 2, and DMP 3 are stable at 25 °C for at least 100 days.

## EXAMPLE 2

**[0101]** This example demonstrates the effect that the quenching pH has on the stability of a resulting anionic glyoxalated polyacrylamide (“GPAM”) polymer.

**[0102]** An aqueous solution containing an 88/12 mol% acrylamide/acrylic acid polymer was treated with glyoxal (48 wt.% in water) at a pH of about 9. Once the resulting glyoxalated polymer mixture had reached a viscosity of about 5.5 cps to about 11.5 cps, the reaction was quenched by adjusting the pH to 2.51 (“Comparative Polymer 1”), 3.57 (“Comparative Polymer 2”), 4.5 (“DMP 1”), 5.59 (“DMP 2”), and 6.47 (“DMP 3”) with sulfuric acid. Samples (100 g) of the anionic GPAM polymers formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.51, 3.57, 4.5, 5.59, and 6.47 were individually stored, as an 8 wt.% solution in deionized water, in polyethylene bottles and placed at 30 °C. Their viscosity was monitored as a function of time using a Brookfield viscometer equipped with a #61 spindle at room temperature (*i.e.*, about 25 °C) and 60 rpm rotation speed, respectively. The results are set forth in FIG. 2.

**[0103]** As is apparent from the results set forth in FIG. 2, solutions of Comparative Polymer 2, DMP 1, DMP 2, and DMP 3 maintain a Brookfield viscosity of less than about 30 cps for 100 days, demonstrating that Comparative Polymer 2, DMP 1, DMP 2, and DMP 3 are stable at 30 °C for at least 100 days. However, a solution of Comparative Polymer 1, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.51, had a Brookfield viscosity that increased to about 50 cps after about 80 days, demonstrating that Comparative Polymer 1 is not stable at 30 °C. In addition, FIG. 2 shows that a solution Comparative Polymer 2, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 3.57, is beginning to show signs of instability at 100 days, as evidenced by the upward trend in the Brookfield viscosity.

**[0104]** These results show that a 12 mol% anionic GPAM polymer formed from quenching a glyoxalated polymer mixture by adjusting to a lower pH (*e.g.*, less than a pH of about 4) is less stable at 30 ° C.

## EXAMPLE 3

**[0105]** This example demonstrates the effect that the quenching pH has on the stability of a resulting anionic glyoxalated polyacrylamide ("GPAM") polymer.

**[0106]** An aqueous solution containing an 88/12 mol% acrylamide/acrylic acid polymer was treated with glyoxal (48 wt.% in water) at a pH of about 9. Once the resulting glyoxalated polymer mixture had reached a viscosity of about 5.5 cps to about 11.5 cps, the reaction was quenched by adjusting the pH to 2.51 ("Comparative Polymer 1"), 3.57 ("Comparative Polymer 2"), 4.5 ("DMP 1"), 5.59 ("DMP 2"), and 6.47 ("DMP 3") with sulfuric acid. Samples (100 g) of the anionic GPAM polymers formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.51, 3.57, 4.5, 5.59, and 6.47 were individually stored, as an 8 wt.% solution in deionized water, in polyethylene bottles and placed at 37 °C. Their viscosity was monitored as a function of time using a Brookfield viscometer equipped with a #61 spindle at room temperature (*i.e.*, about 25 °C) and 60 rpm rotation speed, respectively. The results are set forth in FIG. 3.

**[0107]** As is apparent from the results set forth in FIG. 3, solutions of DMP 1, DMP 2, and DMP 3 maintain a Brookfield viscosity of less than about 40 cps for 100 days, demonstrating that DMP 1, DMP 2, and DMP 3 are stable at 37 °C for at least 100 days. However, a solution of Comparative Polymer 1, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.51, and a solution of Comparative Polymer 2, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 3.57 had a Brookfield viscosity that increased to above 50 cps in less than about 50 days, demonstrating that Comparative Polymer 1 and Comparative Polymer 2 are not stable at 37 °C.

**[0108]** These results show that a 12 mol% anionic GPAM polymer formed from quenching a glyoxalated polymer mixture by adjusting to a lower pH (*e.g.*, less than a pH of about 4) is less stable at 37 °C.

## EXAMPLE 4

**[0109]** This example demonstrates the effect that the quenching pH has on the stability of a resulting cationic glyoxalated polyacrylamide ("GPAM") polymer.

**[0110]** An aqueous solution containing an 88/12 mol% acrylamide/diallyldimethylammonium chloride (“DADMAC”) polymer was treated with glyoxal (48 wt.% in water) at a pH of about 9. Once the resulting glyoxalated polymer mixture had reached a viscosity of about 22 cps to about 24 cps, the reaction was quenched by adjusting the pH to 2.8 (“Comparative Polymer 3”) and 5.3 (“Comparative Polymer 4”) with sulfuric acid. Samples (100 g) of the cationic GPAM polymers formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.8 and 5.3 were individually stored, as an 8 wt.% solution in deionized water, in polyethylene bottles and placed at 37 °C. Their viscosity was monitored as a function of time using a Brookfield viscometer equipped with a #61 spindle at room temperature (*i.e.*, about 25 °C) and 60 rpm rotation speed, respectively. The results are set forth in FIG. 4.

**[0111]** As is apparent from the results set forth in FIG. 4, the Brookfield viscosity of a solution of Comparative Polymer 3 and Comparative Polymer 4 increases drastically in less than 20 days. In addition, Comparative Polymer 4, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 5.3, is less stable than Comparative Polymer 3, which was formed from quenching the glyoxalated polymer mixture by adjusting the pH to 2.8, as demonstrated by the drastic increase in Brookfield viscosity of Comparative Polymer 4 after just 2 days. Such result follows an opposite trend than that shown for a 12 mol% anionic GPAM polymer.

**[0112]** All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

**[0113]** The use of the terms “a” and “an” and “the” and “at least one” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term “at least one” followed by a list of one or more items (for example, “at least one of A and B”) is to be construed to mean one item selected from the listed items (A or B) or any combination of two or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (*i.e.*, meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

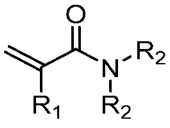
**[0114]** Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

CLAIM(S):

1. A dialdehyde-modified polymer mixture comprising a solvent and a dialdehyde modified polymer comprising:

(a) a polymer backbone comprising:

(i) one or more monomer unit(s) derived from a monomer of Formula I:



I

wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and

(ii) about 10 mol% to about 50 mol% of one or more anionic monomer unit(s), and

(b) a dialdehyde modification to the polymer backbone,

wherein the dialdehyde-modified polymer mixture has a pH of from about 4.0 to about 7.0.

2. The dialdehyde-modified polymer mixture of claim 1, wherein the one or more anionic monomer unit(s) is derived from a monomer selected from 2-acrylamido-2-methylpropane sulfonic acid (“AMPS”), 2-acrylamido-2-methylbutane sulfonic acid (“AMBS”), [2-methyl-2-[(1-oxo-2-propenyl)amino]propyl]-phosphonic acid, methacrylic acid, acrylic acid, salts thereof, and combinations thereof.

3. The dialdehyde-modified polymer mixture of claim 1 or 2, wherein the anionic monomer unit is derived from acrylic acid.

4. The dialdehyde-modified polymer mixture of any one of claims 1-3, wherein the monomer of Formula I is acrylamide, methacrylamide, ethylacrylamide, N-methyl acrylamide, N-butyl acrylamide, or any combination thereof.

5. The dialdehyde-modified polymer mixture of claim 4, wherein the monomer of Formula I is acrylamide.

6. The dialdehyde-modified polymer mixture of any one of claims 1-5, wherein the dialdehyde-modified polymer is modified with a dialdehyde selected from glyoxal, malondialdehyde, succinic dialdehyde, and glutaraldehyde.

7. The dialdehyde-modified polymer mixture of claim 6, wherein the dialdehyde is glyoxal.

8. The dialdehyde-modified polymer mixture of any one of claims 1-7, wherein the dialdehyde-modified polymer mixture has a pH of from about 4.5 to about 7.0.

9. The dialdehyde-modified polymer mixture of claim 8, wherein the dialdehyde-modified polymer mixture has a pH of from about 5.0 to about 7.0.

10. The dialdehyde-modified polymer mixture of any one of claims 1-9, wherein the polymer backbone comprises from about 12 mol% to about 50 mol% of the one or more anionic monomer unit(s).

11. The dialdehyde-modified polymer mixture of claim 10, wherein the polymer backbone comprises from about 15 mol% to about 50 mol% of the one or more anionic monomer unit(s).

12. The dialdehyde-modified polymer mixture of claim 11, wherein the polymer backbone comprises from about 20 mol% to about 50 mol% of the one or more anionic monomer unit(s).

13. The dialdehyde-modified polymer mixture of any one of claims 1-12, wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 10 kDa to about 5,000 kDa.

14. The dialdehyde-modified polymer mixture of claim 13, wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 100 kDa to about 2,000 kDa.

15. The dialdehyde-modified polymer mixture of any one of claims 1-14, wherein the polymer backbone has a weight average molecular weight of from about 2 kDa to about 50 kDa in the absence of the dialdehyde modification.

16. The dialdehyde-modified polymer mixture of claim 15, wherein the polymer backbone has a weight average molecular weight of from about 5 kDa to about 20 kDa in the absence of the dialdehyde modification.

17. The dialdehyde-modified polymer mixture of any one of claims 1-16, wherein the dialdehyde-modified polymer mixture has a solids content of from about 1 wt.% to about 40 wt.%.

18. The dialdehyde-modified polymer mixture of claim 17, wherein the solids content is from about 5 wt.% to about 25 wt.%.

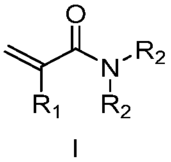
19. The dialdehyde-modified polymer mixture of any one of claims 1-18, wherein the dialdehyde-modified polymer mixture has a Brookfield viscosity of from about 5 cps to about 50 cps at a solids content of 8 wt.%.

20. The dialdehyde-modified polymer mixture of claim 19, wherein the dialdehyde-modified polymer mixture has a Brookfield viscosity of from about 5 cps to about 30 cps at a solids content of 8 wt.%.

21. A method of making a dialdehyde-modified polymer comprising:

(i) initiating a chemical reaction by treating a polymer backbone with a dialdehyde, wherein the polymer backbone comprises:

(a) one or more monomer unit(s) derived from a monomer of Formula I:



I

wherein $R_1$ is H or $C_1$-$C_4$ alkyl and each $R_2$ is independently selected from H or a linear or branched $C_1$-$C_{10}$ aliphatic group, and

(b) from about 10 mol% to about 50 mol% of one or more anionic monomer unit(s) and

(ii) quenching the chemical reaction by adjusting the pH until a pH of from about 4.0 to about 7.0 is reached.

22. The method of claim 21, wherein the one or more anionic monomer unit(s) is derived from a monomer selected from 2-acrylamido-2-methylpropane sulfonic acid (“AMPS”), 2-acrylamido-2-methylbutane sulfonic acid (“AMBS”), [2-methyl-2-[(1-oxo-2-propenyl)amino]propyl]-phosphonic acid, methacrylic acid, acrylic acid, salts thereof, and combinations thereof.

23. The method of claim 21 or 22, wherein the anionic monomer unit is derived from acrylic acid.

24. The method of any one of claims 21-23, wherein the monomer of Formula I is acrylamide, methacrylamide, ethylacrylamide, N-methyl acrylamide, N-butyl acrylamide, or any combination thereof.

25. The method of claim 24, wherein the monomer of Formula I is acrylamide.

26. The method of any one of claims 21-25, wherein the dialdehyde-modified polymer is modified with a dialdehyde selected from glyoxal, malondialdehyde, succinic dialdehyde, and glutaraldehyde.

27. The method of claim 26, wherein the dialdehyde is glyoxal.

28. The method of any one of claims 21-27, wherein the pH is adjusted until a pH of from about 4.5 to about 7.0 is reached.

29. The method of claim 28, wherein the pH is adjusted until a pH of from about 5 to about 7.0 is reached.

30. The method of any one of claims 21-29, wherein the polymer backbone comprises from about 12 mol% to about 50 mol% of the one or more anionic monomer unit(s).

31. The method of claim 30, wherein the polymer backbone comprises from about 15 mol% to about 50 mol% of the one or more anionic monomer unit(s).

32. The method of claim 31, wherein the polymer backbone comprises from about 20 mol% to about 50 mol% of the one or more anionic monomer unit(s).

33. The method of any one of claims 21-32, wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 10 kDa to about 5,000 kDa.

34. The method of claim 33, wherein the dialdehyde-modified polymer has a weight average molecular weight of from about 100 kDa to about 2,000 kDa.

35. The method of any one of claims 21-34, wherein the polymer backbone has a weight average molecular weight of from about 2 kDa to about 50 kDa in the absence of the dialdehyde modification.

36. The method of claim 35, wherein the polymer backbone has a weight average molecular weight of from about 5 kDa to about 20 kDa in the absence of the dialdehyde modification.

37. The method of any one of claims 21-36, wherein the dialdehyde-modified polymer has a Brookfield viscosity of from about 5 cps to about 50 cps at a solids content of 8 wt.% in water.

38. The method of claim 37, wherein the dialdehyde-modified polymer has a Brookfield viscosity of from about 5 cps to about 30 cps at a solids content of 8 wt.% in water.

39. Use of any one of the dialdehyde-modified polymer mixtures of claims 1-20 in treating a paper sheet precursor.

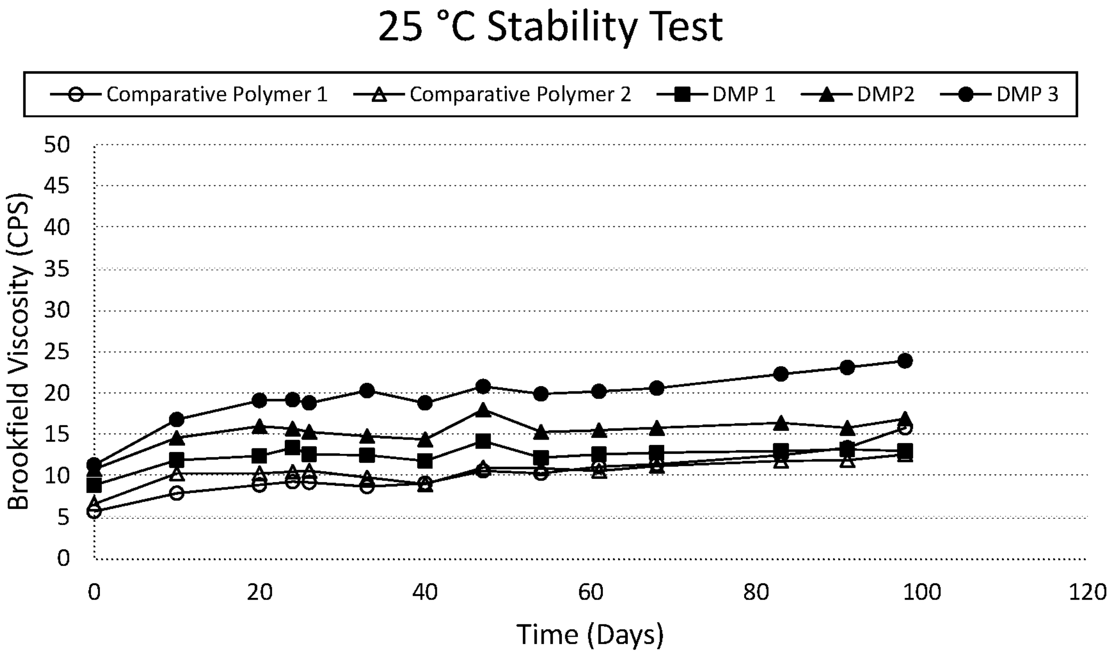

25 °C Stability Test
Comparative Polymer 1
Comparative Polymer 2
DMP 1
DMP2
DMP 3
Brookfield Viscosity (CPS)
0
5
10
15
20
25
30
35
40
45
50
Time (Days)
0
20
40
60
80
100
120

FIG. 1

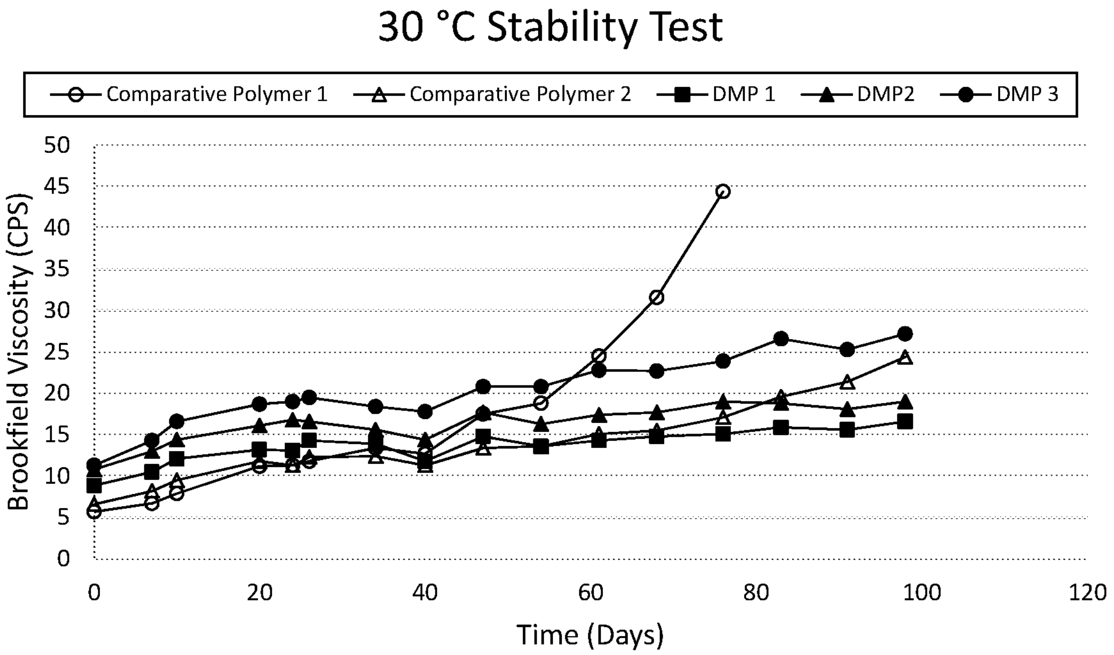

30 °C Stability Test
Comparative Polymer 1
Comparative Polymer 2
DMP 1
DMP2
DMP 3
Brookfield Viscosity (CPS)
0
5
10
15
20
25
30
35
40
45
50
Time (Days)
0
20
40
60
80
100
120

FIG. 2

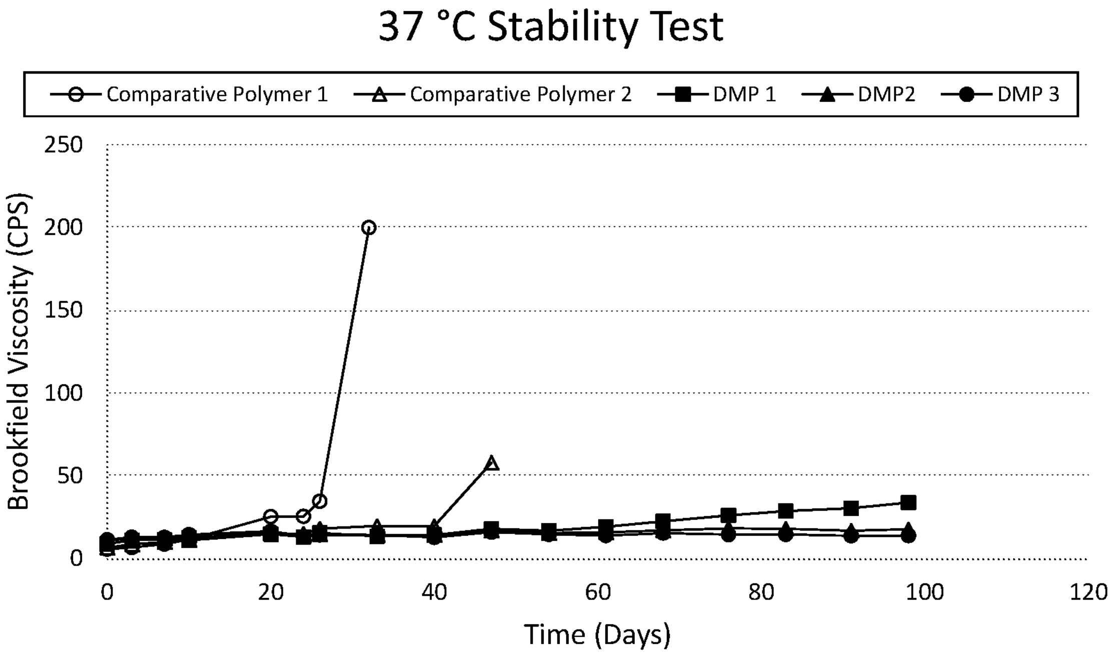

37 °C Stability Test
Comparative Polymer 1
Comparative Polymer 2
DMP 1
DMP2
DMP 3
Brookfield Viscosity (CPS)
250
200
150
100
50
0
0
20
40
60
80
100
120
Time (Days)

FIG. 3

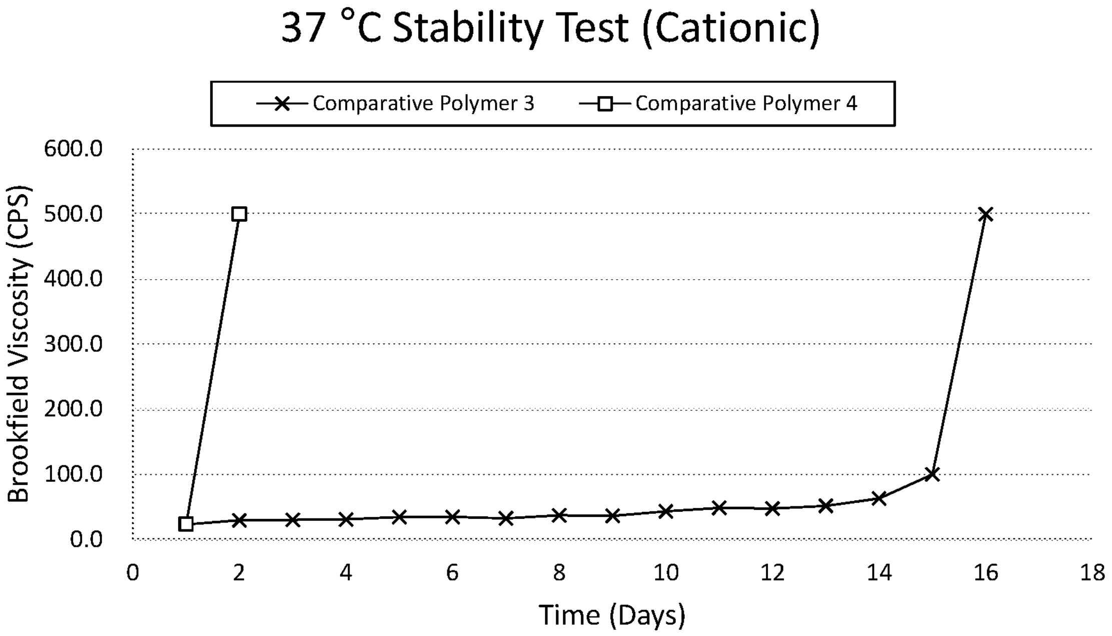

37 °C Stability Test (Cationic)
Comparative Polymer 3
Comparative Polymer 4
Brookfield Viscosity (CPS)
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0
2
4
6
8
10
12
14
16
18
Time (Days)

FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CN2020/132621**

## A. CLASSIFICATION OF SUBJECT MATTER

D21H 21/18(2006.01)i; D21H 17/49(2006.01)i; D21H 17/50(2006.01)i; D21H 17/47(2006.01)i; C08L 33/26(2006.01)i; C08F 220/56(2006.01)i; C08F 222/38(2006.01)i; C08F 226/02(2006.01)i; C08F 220/06(2006.01)i; C08F 8/28(2006.01)i

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)

D21H,C08L,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)

CNABS;CNTXT;CNKI;VEN;WOTXT;EPTXT;USTXT;JPTXT;STN;ISI Web of Science: polyacrylamide,anionic,ionic, solvent,paper,cellulose,strength+,intensif+, reinforce+,+acrylamide,+acrylic,sulfonic,phosphonic,glyoxal,+dialdehyde, succinic, glutaraldehyde,pH,quench+,stop+,reaction,adjust+,regulat+,control+, gel+,stabl+,stor+,molecular weight,solid,content,viscosity

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | CN 111936535 A (SPCM S A) 13 November 2020 (2020-11-13)<br>see description, paragraphs [0004]-[0028] | 1-39 |
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| X | CN 101553508 A (CIBA SC HOLDING AG) 07 October 2009 (2009-10-07)<br>see description, pages 3-5, example 1 | 1-39 |

☐ 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<br>**23 August 2021** | Date of mailing of the international search report<br>**09 September 2021** |
| Name and mailing address of the ISA/CN<br>**National Intellectual Property Administration, PRC**<br>**6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088**<br>**China** | Authorized officer<br>**ZHANG,Xi** |
| Facsimile No. **(86-10)62019451** | Telephone No. **010-62084387** |

# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

International application No.

**PCT/CN2020/132621**

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| | | EP 2788392 B1 | 21 February 2018 |
| | | CN 103987746 B | 20 April 2018 |
| | | US 8920606 B2 | 30 December 2014 |
| | | KR 20140100979 A | 18 August 2014 |
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