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TITLE

BETA-AMINO ESTER COMPOUNDS AND USES THEREOF

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention is directed to compositions and methods for treating hair, and in particular to methods and compositions for imparting thickness, volume, texture and definition, which permit improved styling.

DESCRIPTION OF RELATED ART

[0002] Hair treatment products on the market typically use commercial polymers to impart volume, texture, definition and thickness. People with fine or thin hair regularly use “volumizing” products in the form of shampoos, conditioners, styling sprays, creams, gels, or mousses in an effort to increase the volume and body of their hair. Many of these materials are polyvinylpyrrolidone/ polyvinyl acetate (PVP/VA) combinations. These materials create volume in hair by binding multiple hair fibers together in spot-welds, such that a droplet of the product lands on a section of the hair thereby linking a hair fiber back on itself and/or linking two or more fibers, creating stiffer hair, more resistant to, for example, falling flat on the head. This technology suffers from several drawbacks, as the visual benefits obtained do not last and the hair is left feeling

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stiff or crunchy. Thus, it is desired to identify and develop compositions that achieve these results with greater ease of use, less heaviness and less feeling of sticky residue, that do not impart a crunchy or stiff feeling to the hair, and which impart shine and softness to the hair as well as volume and thickness.

[0003] Preparation of poly(β -amino esters) from conjugate addition of bis(secondary amines) or primary amines to a bis(acrylate ester) is described in U.S. Patent Nos. 6,998,115 and 7,427,394, and related applications, the disclosures of which are incorporated herein by reference in their entirety. Many of the compounds within the scope of the disclosure are said to be biodegradable and biocompatible and said to be useful in a variety of drug delivery systems. However, use in cosmetics is not contemplated in these patents.

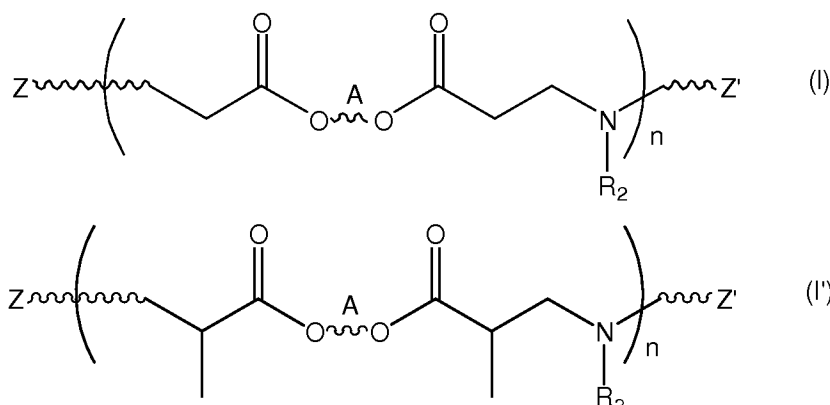
SUMMARY OF THE INVENTION

[0004] Whereas advances in the art typically involve new formulations of known compounds, the inventors herein have brought real innovation to the field of hair treatment at the compound level, developing new molecular entities for use in styling hair. Of particular interest are hair styling compositions that avoid reliance on conventional high-molecular weight PVP/VA compounds, that provide a lighter, more natural feel, while still providing thickness, texture, volume and definition.

[0005] In one aspect, the invention involves the use of the compounds such as are disclosed in US Patent Nos. 7,427,394 and 6,998,115; US Patent Application Publication Nos. US 2004/0071654 and US 2005/0265961; and International Application Nos. WO 02/31025; WO 04/106411 and WO 07/143659 with a cosmetically acceptable carrier in a composition for treatment of hair. The disclosure of each of the aforesaid patents and published applications is incorporated by reference herein.

[0006] Thus, in one aspect, the invention is a hair treatment composition comprising a compound according to formula (I) or (I') in a cosmetically acceptable carrier:

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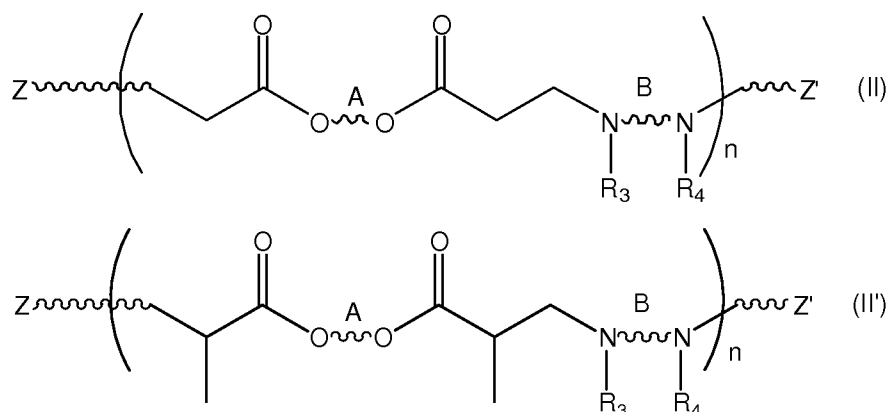
[0007] In formula (I) and (I'), n is an integer between 1 and 10,000; and Z and Z' , together with the atoms to which they are attached, represent acrylate, methacrylate or amino end groups.

[0008] The substituent R_2 is the residue of a primary amine starting material, which may be reacted with a diacrylate or dimethacrylate starting material, to form the compound according to formula (I) or (I'), as described in greater detail below. For example, R_2 may be selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxy, alkylthioether, siloxyl, and thiohydroxyl groups.

[0009] A is a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxy, alkylthioether, and thiol groups; wherein said substituents may join to form one or more rings.

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[0010] Alternatively, a bis(amine) is used as a starting material and is reacted with the diacrylate or dimethacrylate starting material so that the hair treatment composition comprises a compound according to formula (II) or (II').



[0011] In formula (II) and (II'), A, n, Z and Z' are as defined for formula (I); R₃ and R₄ are defined as for R₂ in Formula (I); and B and A are, independently, a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl, aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxyl, alkylthioether, and thiol groups.

[0012] In another aspect of the invention, oligomers are provided which have β-amino ester monomer units bonded to blocks of repeating monomer units (such as polybutadiene blocks). In particular, it has now been found that compounds having a β-amino ester moiety and a rubber moiety in novel and useful hair treatment compositions avoid the drawbacks of the volumizing products known in the prior art.

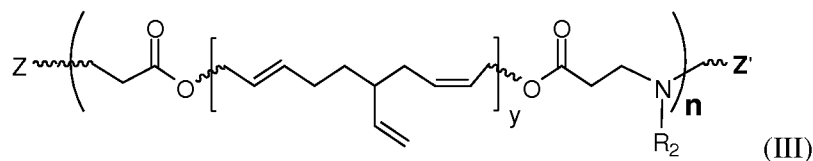
[0013] Without wishing to be bound by any particular theory, it is believed that the β-amino ester compounds disclosed herein bind to the hair fibers to increase inter-fiber friction and produce benefits not delivered through conventional technology. The inventive composition increase friction in hair while allowing hair fibers to remain free to move, allowing for a more natural feel. In addition, the inventive compositions afford longer lasting and re-shapeable hair styles. Fibers are free to separate and re-attach at different points, allowing for a more

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natural feel and movement. These effects are achieved according to the invention using the compositions and methods described herein. As a result, the present inventive compositions and methods are believed to avoid making the hair feel stiff or crunchy.

[0014] Thus, in this further aspect, the invention is a hair treatment composition comprising a compound according to formula (I) or formula (II) wherein A is a rubber moiety, such as, without limitation, a moiety made up of one or more units of butadiene, isoprene, chloroprene, styrene-butadiene, mixtures thereof, or variations thereof.

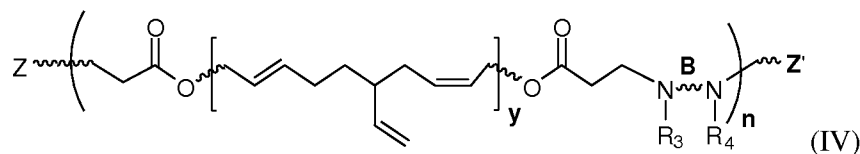
[0015] In preferred embodiments, a hair treatment composition according to the invention comprises a compound of formula (III) in a cosmetically acceptable carrier:



[0016] In the above formula (III), n is an integer between 1 and 10,000; y is an integer between 1 and 10,000; and R₂ is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups.

[0017] Alternatively, a hair treatment composition according to the invention may comprise a compound according to formula (IV) in a cosmetically suitable carrier, wherein y, n, Z, Z', B, R₃ and R₄ are all defined as set forth above with respect to formulas (I), (II) and (III):

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[0018] Methods according to the invention comprise the step of contacting scalp hair with the composition containing a compound according to any of formulas (I) through (IV) in a cosmetically acceptable carrier, as described in greater detail in the detailed description that follows.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] The advantages of the compositions and formulations according to the invention are brought about by incorporating specific β -amino ester moieties and specific linking moieties according to the invention. In some cases (not to be construed as limiting), the formulations have been adapted for shaping hair. It has been found that some of these compositions afford the user the ability not only to shape the hair, but the ability to reshape a style after it has been significantly altered (after a night's sleep for example). The methods and specific examples of reacting diacrylates and amines, and the compounds and functional results achieved thereby, are described in greater detail in the following detailed description of the invention.

Definitions

[0020] Definitions of specific functional groups and chemical terms are described in more detail below. For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed., and specific functional groups are generally defined as described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in *Organic Chemistry*, Thomas Sorrell, University Science Books, Sausalito (1999), the entire contents of which are incorporated herein by reference.

[0021] Unless expressly stated otherwise, the compounds and groups described herein may be substituted with any number of substituents or functional moieties permitted by the valences of the respective compound or group. In general, the

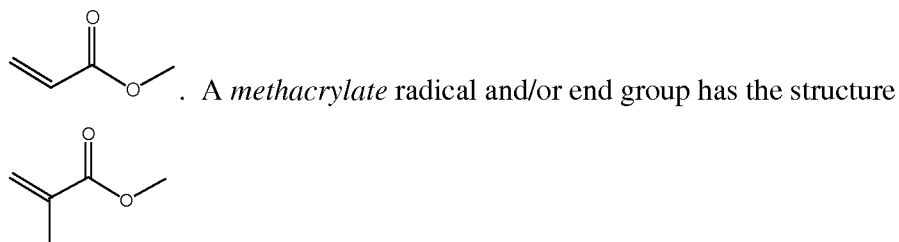
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term “substituted” whether preceded by the term “optionally” or not, and substituents contained in formulas of this invention, refer to the replacement of hydrogen atoms in a given structure with a specified substituent. Unless stated otherwise, when more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. As used herein, the term “substituted” is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. For purposes of this invention, heteroatoms such as nitrogen, oxygen or sulfur, may be bonded to hydrogen atoms or be substituted with any permissible substituents of organic compounds described herein which satisfy the valencies of the heteroatoms.

[0022] Where a carbon atom in a chain may be replaced with a heteroatom, this is also sometimes referred to as a “substitution.”

[0023] The term *acyl* as used herein refers to a group having the general formula $-C(O)R$, where R is alkyl, alkenyl, alkynyl, aryl, carbocyclic, heterocyclic, or aromatic heterocyclic. An example of an acyl group is acetyl.

[0024] As used herein, an *acrylate* radical, and/or end group has the structure



[0025] The term *aliphatic*, as used herein, includes both saturated and unsaturated, straight chain (*i.e.*, unbranched), branched, acyclic, cyclic, or polycyclic aliphatic hydrocarbons, which are optionally substituted with one or more functional groups. As will be appreciated by one of ordinary skill in the art, “aliphatic” is intended herein to include, but is not limited to, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, and cycloalkynyl moieties.

[0026] The term *alkyl* as used herein refers to a saturated, straight- or branched-chain hydrocarbon radicals derived from a hydrocarbon containing between one

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and twenty carbon atoms by removal of a single hydrogen atom. In some embodiments, the alkyl group contains 1-10 carbon atoms. In another embodiment, the alkyl group contains 1-8 carbon atoms. In still other embodiments, the alkyl group contains 1-6 carbon atoms. In yet another embodiment, the alkyl group contains 1-4 carbons. Examples of alkyl radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, sec-pentyl, iso-pentyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, sec-hexyl, n-heptyl, n-octyl, n-decyl, n-undecyl, dodecyl, and the like, which may bear one or more substituents. As used herein, the term “alkyl” includes straight, branched and cyclic alkyl groups. An analogous convention applies to other generic terms such as “alkenyl”, “alkynyl”, and the like. Furthermore, as used herein, the terms “alkyl”, “alkenyl”, “alkynyl,” and the like, encompass both substituted and unsubstituted groups. In certain embodiments, as used herein, “lower alkyl” is used to indicate those alkyl groups (cyclic, acyclic, substituted, unsubstituted, branched or unbranched) having 1-6 carbon atoms.

[0027] The term *alkoxy* as used herein refers to a saturated (*i.e.*, alkyl-O-) or unsaturated (*i.e.*, alkenyl-O- and alkynyl-O-) group attached to the parent molecular moiety through an oxygen atom. In certain embodiments, the alkyl, alkenyl or alkynyl group contains 1-20 aliphatic carbon atoms. In certain other embodiments, the alkyl, alkenyl, and alkynyl groups employed in the alkoxy groups of the invention contain 1-8 aliphatic carbon atoms. In still other embodiments, the alkyl group contains 1-6 aliphatic carbon atoms. In yet other embodiments, the alkyl group contains 1-4 aliphatic carbon atoms. Examples include, but are not limited to, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, *tert*-butoxy, *i*-butoxy, *sec*-butoxy, neopentoxy, n-hexoxy, and the like.

[0028] The term *alkenyl* denotes a monovalent group derived from a hydrocarbon moiety having at least one carbon-carbon double bond by the removal of a single hydrogen atom. In certain embodiments, the alkenyl group employed in the invention contains 1-20 carbon atoms. In some embodiments, the alkenyl group employed in the invention contains 1-10 carbon atoms. In another embodiment, the alkenyl group employed contains 1-8 carbon atoms. In still other embodiments, the alkenyl group contains 1-6 carbon atoms. In yet

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another embodiments, the alkenyl group contains 1-4 carbons. Alkenyl groups include, for example, ethenyl, propenyl, butenyl, 1-methyl-2-buten-1-yl, and the like.

[0029] The term *alkynyl* as used herein refers to a monovalent group derived from a hydrocarbon having at least one carbon-carbon triple bond by the removal of a single hydrogen atom. In certain embodiments, the alkynyl group employed in the invention contains 1-20 carbon atoms. In some embodiments, the alkynyl group employed in the invention contains 1-10 carbon atoms. In another embodiment, the alkynyl group employed contains 1-8 carbon atoms. In still other embodiments, the alkynyl group contains 1-6 carbon atoms. Representative alkynyl groups include, but are not limited to, ethynyl, 2-propynyl (propargyl), 1-propynyl, and the like.

[0030] The term *alkylamino*, *dialkylamino*, and *trialkylamino* as used herein refers to one, two, or three, respectively, alkyl groups, as previously defined, attached to the parent molecular moiety through a nitrogen atom. The term *alkylamino* refers to a group having the structure $\text{-NHR}'$ wherein R' is an alkyl group, as previously defined; and the term *dialkylamino* refers to a group having the structure $\text{-NR}'\text{R}''$, wherein R' and R'' are each independently selected from the group consisting of alkyl groups. The term *trialkylamino* refers to a group having the structure $\text{-NR}'\text{R}''\text{R}'''$, wherein R' , R'' , and R''' are each independently selected from the group consisting of alkyl groups. In certain embodiments, the alkyl group contain 1-20 aliphatic carbon atoms. In certain other embodiments, the alkyl group contains 1-10 aliphatic carbon atoms. In yet other embodiments, the alkyl group contains 1-8 aliphatic carbon atoms. In still other embodiments, the alkyl group contain 1-6 aliphatic carbon atoms. In yet other embodiments, the alkyl group contain 1-4 aliphatic carbon atoms. Additionally, R' , R'' , and/or R''' taken together may optionally be $\text{-(CH}_2\text{)}_k\text{-}$ where k is an integer from 2 to 6, to form a ring. Examples include, but are not limited to, methylamino, dimethylamino, ethylamino, diethylamino, diethylaminocarbonyl, methylethylamino, iso-propylamino, piperidino, trimethylamino, and propylamino.

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[0031] An *amino* group, as used herein, encompasses alkylamino, dialkylamino and trialkylamino groups (as defined above), and *aminoalkyl* likewise includes $-RNH_2$, $-RNHR'$, $-RNR''R'''$ and $-RNR''R'''R''''$. In preferred embodiments according to the invention, a substituted aminoalkyl group, such as a diethanolaminopropyl group, is substituted on the nitrogen of the β -amino ester moiety of the compound.

[0032] The term *aromatic*, as used herein, refers to a moiety having delocalized electrons due to conjugated double bonds, which may form a ring (as in an aryl moiety); *heteroaromatic* means an aromatic compound in which a carbon is replaced with one or more nitrogen, oxygen, phosphorus, silicon or sulfur atoms.

[0033] In general, the terms *aryl* and *heteroaryl*, as used herein, refer to mono- or polycyclic, heterocyclic, polycyclic, and polyheterocyclic unsaturated moieties having preferably 3-14 carbon atoms, each of which may be substituted or unsubstituted. Substituents include, but are not limited to, any of the previously mentioned substituents, *i.e.*, the substituents recited for aliphatic moieties, or for other moieties as disclosed herein, resulting in the formation of a stable compound. In certain embodiments of the present invention, *aryl* refers to a mono- or bicyclic carbocyclic ring system having one or two aromatic rings including, but not limited to, phenyl, naphthyl, tetrahydronaphthyl, indanyl, indenyl, and the like. In certain embodiments of the present invention, the term *heteroaryl*, as used herein, refers to a cyclic aromatic radical having from five to ten ring atoms of which one ring atom is selected from S, O, and N; zero, one, or two ring atoms are additional heteroatoms independently selected from S, O, and N; and the remaining ring atoms are carbon, the radical being joined to the rest of the molecule via any of the ring atoms, such as, for example, pyridyl, pyrazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, oxazolyl, isooxazolyl, thiadiazolyl, oxadiazolyl, thiophenyl, furanyl, quinoliny, isoquinoliny, and the like.

[0034] It will be appreciated that *aryl* and *heteroaryl* groups can be unsubstituted or substituted, wherein substitution includes replacement of one, two, three, or more of the hydrogen atoms thereon independently with any one or more of the following moieties including, but not limited to: aliphatic; heteroaliphatic; aryl;

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heteroaryl; arylalkyl; heteroarylalkyl; alkoxy; aryloxy; heteroalkoxy; heteroaryloxy; alkylthio; arylthio; heteroalkylthio; heteroarylthio; -F; -Cl; -Br; -I; -OH; -NO₂; -CN; -CF₃; -CH₂CF₃; -CHCl₂; -CH₂OH; -CH₂CH₂OH; -CH₂NH₂; -CH₂SO₂CH₃; -C(O)R_x; -CO₂(R_x); -CON(R_x)₂; -OC(O)R_x; -OCO₂R_x; -OCON(R_x)₂; -N(R_x)₂; -S(O)₂R_x; -NR_x(CO)R_x, wherein each occurrence of R_x independently includes, but is not limited to, aliphatic, heteroaliphatic, aryl, heteroaryl, arylalkyl, or heteroarylalkyl, wherein any of the aliphatic, heteroaliphatic, arylalkyl, or heteroarylalkyl substituents described above and herein may be substituted or unsubstituted, branched or unbranched, cyclic or acyclic, and wherein any of the aryl or heteroaryl substituents described above and herein may be substituted or unsubstituted. Additional examples of generally applicable substituents are illustrated by the specific embodiments shown in the Examples that are described herein.

[0035] The term *carboxylic acid* as used herein refers to a group of formula -CO₂H.

[0036] The terms *halo* and *halogen* as used herein refer to an atom selected from fluorine, chlorine, bromine, and iodine.

[0037] The term *heteroaliphatic*, as used herein, refers to aliphatic moieties that contain one or more oxygen, sulfur, nitrogen, phosphorus, or silicon atoms, *e.g.*, in place of carbon atoms. Heteroaliphatic moieties may be branched, unbranched, cyclic or acyclic and include saturated and unsaturated heterocycles such as morpholino, pyrrolidinyl, *etc.* In certain embodiments, heteroaliphatic moieties are substituted by independent replacement of one or more of the hydrogen atoms thereon with one or more moieties including, but not limited to aliphatic; heteroaliphatic; aryl; heteroaryl; arylalkyl; heteroarylalkyl; alkoxy; aryloxy; heteroalkoxy; heteroaryloxy; alkylthio; arylthio; heteroalkylthio; heteroarylthio; -F; -Cl; -Br; -I; -OH; -NO₂; -CN; -CF₃; -CH₂CF₃; -CHCl₂; -CH₂OH; -CH₂CH₂OH; -CH₂NH₂; -CH₂SO₂CH₃; -C(O)R_x; -CO₂(R_x); -CON(R_x)₂; -OC(O)R_x; -OCO₂R_x; -OCON(R_x)₂; -N(R_x)₂; -S(O)₂R_x; -NR_x(CO)R_x, wherein each occurrence of R_x independently includes, but is not limited to, aliphatic, heteroaliphatic, aryl, heteroaryl, arylalkyl, or heteroarylalkyl, wherein any of the aliphatic, heteroaliphatic, arylalkyl, or heteroarylalkyl

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substituents described above and herein may be substituted or unsubstituted, branched or unbranched, cyclic or acyclic, and wherein any of the aryl or heteroaryl substituents described above and herein may be substituted or unsubstituted. Additional examples of generally applicable substituents are illustrated by the specific embodiments shown in the Examples that are described herein.

[0038] The term *heterocyclic*, as used herein, refers to an aromatic or non-aromatic, partially unsaturated or fully saturated, 3- to 10-membered ring system, which includes single rings of 3 to 8 atoms in size and bi- and tri-cyclic ring systems which may include aromatic five- or six-membered aryl or aromatic heterocyclic groups fused to a non-aromatic ring. These heterocyclic rings include those having from one to three heteroatoms independently selected from oxygen, sulfur, and nitrogen, in which the nitrogen and sulfur heteroatoms may optionally be oxidized and the nitrogen heteroatom may optionally be quaternized. In certain embodiments, the term heterocyclic refers to a non-aromatic 5-, 6-, or 7-membered ring or a polycyclic group wherein at least one ring atom is a heteroatom selected from O, S, and N (wherein the nitrogen and sulfur heteroatoms may be optionally oxidized), including, but not limited to, a bi- or tri-cyclic group, comprising fused six-membered rings having between one and three heteroatoms independently selected from the oxygen, sulfur, and nitrogen, wherein (i) each 5-membered ring has 0 to 2 double bonds, each 6-membered ring has 0 to 2 double bonds, and each 7-membered ring has 0 to 3 double bonds, (ii) the nitrogen and sulfur heteroatoms may be optionally oxidized, (iii) the nitrogen heteroatom may optionally be quaternized, and (iv) any of the above heterocyclic rings may be fused to an aryl or heteroaryl ring.

[0039] The term *aromatic heterocyclic*, as used herein, refers to a cyclic aromatic radical having from five to ten ring atoms of which one ring atom is selected from sulfur, oxygen, and nitrogen; zero, one, or two ring atoms are additional heteroatoms independently selected from sulfur, oxygen, and nitrogen; and the remaining ring atoms are carbon, the radical being joined to the rest of the molecule via any of the ring atoms, such as, for example, pyridyl, pyrazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, oxazolyl, isooxazolyl,

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thiadiazolyl, oxadiazolyl, thiophenyl, furanyl, quinolinyl, isoquinolinyl, and the like. Aromatic heterocyclic groups can be unsubstituted or substituted with substituents selected from the group consisting of branched and unbranched alkyl, alkenyl, alkynyl, haloalkyl, alkoxy, thioalkoxy, amino, alkylamino, dialkylamino, trialkylamino, acylamino, cyano, hydroxy, halo, mercapto, nitro, carboxyaldehyde, carboxy, alkoxycarbonyl, and carboxamide.

[0040] The term *carbonyldioxy*, as used herein, refers to a carbonate group of the formula $-O-CO-OR$.

[0041] The term *carbamoyl*, as used herein, refers to an amide group of the formula $-CONH_2$.

[0042] The term *hydrocarbon*, as used herein, refers to any chemical group comprising hydrogen and carbon. The hydrocarbon may be substituted or unsubstituted. The hydrocarbon may be unsaturated, saturated, branched, unbranched, cyclic, polycyclic, or heterocyclic. Illustrative hydrocarbons include, for example, methyl, ethyl, n-propyl, iso-propyl, cyclopropyl, allyl, vinyl, n-butyl, tert-butyl, ethynyl, cyclohexyl, methoxy, diethylamino, and the like. As would be known to one skilled in this art, all valencies must be satisfied in making any substitutions.

[0043] The term *thiohydroxyl* or *thiol*, as used herein, refers to a group of the formula $-SH$.

[0044] The term *ureido*, as used herein, refers to a group of the formula $-NH-CO-NH_2$.

[0045] The following are more general terms used throughout the present application:

[0046] As used herein, the singular forms “a”, “an”, and “the” include the plural reference unless the context clearly indicates otherwise. Thus, for example, a reference to “a monomer” includes a plurality of such monomers.

[0047] The term “keratin” as used herein refers any one of a class of fibrous structural proteins found in hair, wool, and nails. Keratin proteins contains a large quantity of cysteine residues. Human hair is a keratin that has approximately 15% cysteine residues cross-linked by disulfide bridges.

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[0048] As used herein, a “monomer” is a repeating structural unit appearing in a polymer or an oligomer. Thus, for example, the polymer polybutadiene is comprised of repeating units derived from butadiene.

[0049] The term “oligomer,” as used herein, refers to a chemical compound with less than 10 repeating structural units. In particular, a compound according to the invention containing less than 10 β -amino ester groups is considered an oligomer, notwithstanding the size of the block connecting the amino ester groups.

[0050] The term “polymer,” as used herein, refers to a chemical compound of repeating structural units (monomers) connected by covalent bonds. A polymer is typically of high molecular weight comprising 10s to 100s to 1000s or even more monomers. However, as used herein, the term “polymer” also includes “oligomers.”

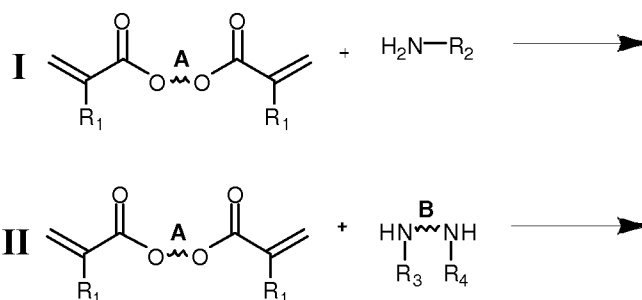
[0051] The term “rubber,” as used herein, means a compound containing repeating units of butadiene, isoprene, chloroprene, styrene-butadiene, or variations thereof, and also includes ethylene vinyl acetate (EVA) (such as sold under the tradename Elvax®), urethane rubber, silicone rubber or silicone elastomer. These units incorporated in a molecule constitute the “rubber moiety” of the molecule, as that term is used herein.

[0052] The symbol  in a chemical structure means that different atoms and/or bonds may be found at that position. Thus, in formula (I), A is designated with symbol  because a number of options exist for the configuration of A. In connection with the end groups, to form an acrylate or methacrylate end group, for example, Z  means that Z and the carbon to which it is attached form a $\text{CH}_2=$ terminus of the acrylate or methacrylate end group. Alternatively, in the same formula, the  symbol may represent a bond with the next monomer repeat group.

Preferred embodiments

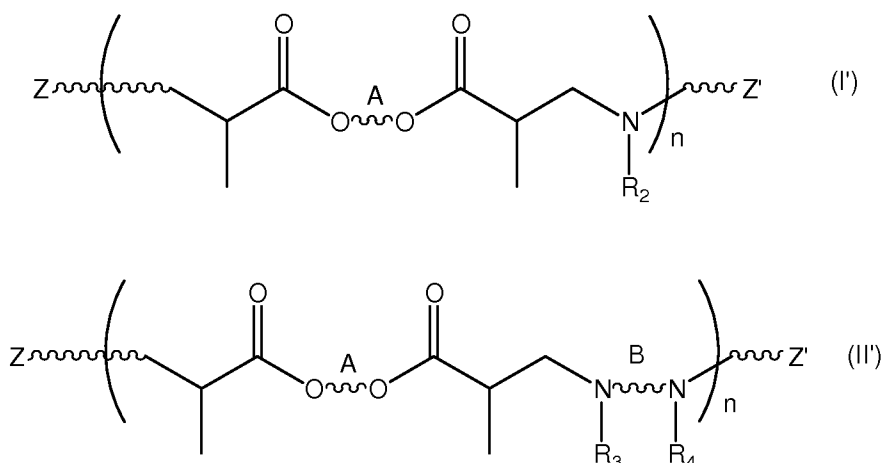
[0053] Hair treatment compositions according to the invention comprise a β -amino ester compound which may be formed by reacting a diacrylate or dimethacrylate with an amine according to one of the following general reaction schemes:

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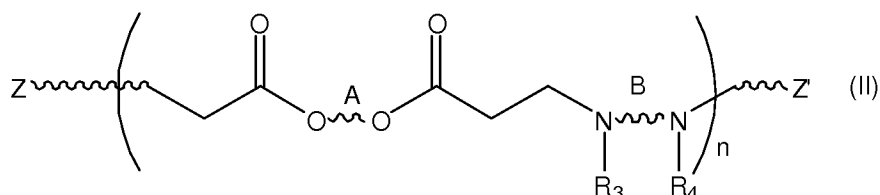
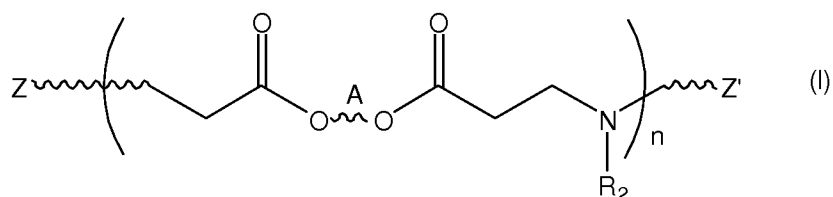
[0054] In these formulas R_1 is a hydrogen or methyl, which defines the starting material as a diacrylate or a dimethacrylate. R_2 , R_3 , and R_4 are selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxy, alkylthioether, siloxyl, and thiohydroxyl groups.

[0055] If the starting material is a dimethacrylate, the above reactions form compounds represented by the corresponding formulas (I') and (II'), wherein A, B, Z, Z' and n are as defined above for formulas (I) and (II):



[0056] Where the starting material is a diacrylate, the above reactions form compounds represented by the corresponding formulas (I) and (II):

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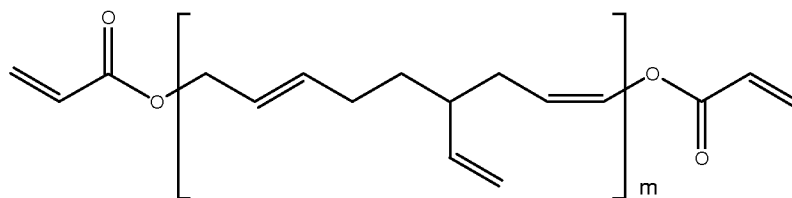


[0057] Such compounds include, without limitation, the compounds disclosed in the aforementioned patents and published applications incorporated by reference.

[0058] In an embodiment of the present invention, n is in the range of 1 to 10,000. In certain other embodiments of the present invention, n is in the range of 1 to 1,000, 1 to 100 or 3 to 10.

[0059] In preferred embodiments, the acrylate or methacrylate moieties in the compounds are linked by a relatively high molecular weight moiety A. In the presently preferred embodiments, A is a rubber moiety, including without limitation, a material comprising monomers selected from butadiene, styrene-butadiene, chloroprene, and isoprene monomers.

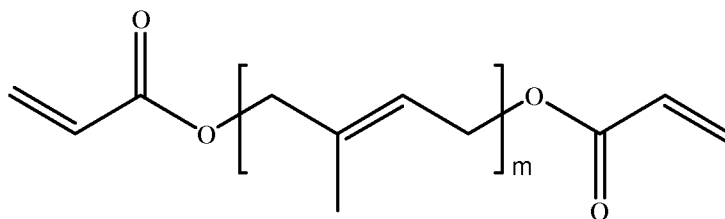
[0060] Rubber-containing materials that may be reacted to form a polymer according to the invention include, without limitation, polybutadiene diacrylate, which is represented by the formula



or its corresponding dimethacrylate.

[0061] Polyisoprene diacrylate may also be used, represented by the following formula,

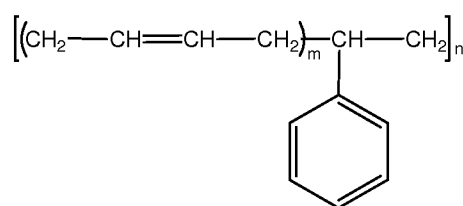
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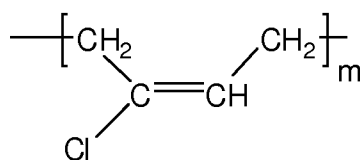
The corresponding dimethacrylate may also be used.

[0062] In these starting materials m may be 1 to 60, and in certain embodiments 1 to 40, 1 to 30 or 20 to 30.

[0063] Alternatively, polychloroprene or styrene-butadiene rubbers may be modified into diacrylates or dimethacrylates, which can then be reacted according to the general reaction schemes I and II above. Styrene/butadiene rubbers have the following general structure:



[0064] Poly-chloroprene has the general structure



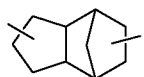
[0065] In presently preferred embodiments polybutadiene diacrylates (PBDs) are employed as a starting material. Although not limiting the invention, diacrylates and dimethacrylates having a number average molecular weight in the range of 1000 g/mol to 5,000 g/mol may be used. In the examples elaborated below, two different starting material were used, having a number average molecular weight of 1400 g/mol and 3000 g/mol, respectively.

[0066] In other embodiments, A is an optionally substituted carbon chain or heteroatom containing carbon chain containing 1 to 30 atoms in the chain. Thus, in some instances, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,2-ethanediol diacrylate, 1,6-hexanediol diacrylate, 2,5-hexanediol diacrylate, and

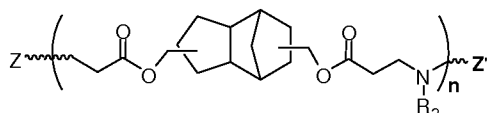
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1,3-propanediol diacrylate may be used as a diacrylate starting material, such that A comprises a carbon chain having less than 30 atoms.

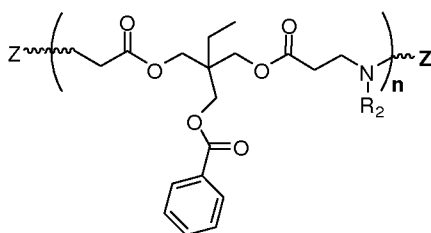
[0067] The linker A between the acrylate or methacrylate moieties of the compound may comprise a substituted carbon chain wherein the substituents join to form one or more rings. For example, such multicyclic moiety A may be represented by the formula



The corresponding compound useful in a hair treatment composition according to the invention has the following formula, wherein Z, Z' and R₂ are as described above.:



[0068] Alternatively, linker A may comprise a carbon chain or heteroatom-containing carbon chain having one or more aromatic substituents on the chain, resulting in compounds according to the following formula,



[0069] The diacrylate or dimethacrylate starting material may be reacted with amines having varying functional groups at varying ratios. For example, acceptable PBD:amine ratios may range from about 1: 2 to about 2: 1. In the examples elaborated below, PBD:amine ratios were varied between 1:1.8 and 1:1.2.

[0070] The compounds according to the invention, resulting from the above-described reaction, sometimes have small amounts of unreacted amine. In preferred embodiments, the compound used in the composition according to the

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invention contains less than 1 wt%, preferably less than 0.1 wt% percent, and more preferably less than 0.01 wt% unreacted amine.

[0071] A suitable diacrylate or dimethacrylate may be reacted with a primary amine having a formula NH_2R (where R_2 is as defined above) by Michael Addition. The R_2 group on the primary amine may be selected to impart desired properties to the composition. Thus, the amine may be selected to modify the properties imparted to the composition by the rubber moiety, to reduce a greasy, heavy feel while maintaining the frictional attributes obtained with the rubber, for example. Alternatively, hydrophilic groups may be incorporated into the compound via the amine to improve water solubility. Likewise, hydrophobic groups may be used to improve oil phase formulation and/or interaction with hair lipids. Aromatic moieties and styrene-containing moieties may be used to increase the stiffness of the finished compounds.

[0072] The following primary amines have been used to formulate compounds according to the invention: propylamine; butylamine; pentylamine; hexylamine; octylamine; 1-aminodecane; isopropylamine; sec-butylamine; isobutylamine; tert-butylamine; 2-aminopentane; isopentylamine; 2-amino-6-methylheptane; 3-(dimethylamino)-1-propylamine; 2-diethylaminoethylamine; 2-(diisopropylamino)ethylamine; 3-(diethylamino)propylamine; N,N-dimethylethylenediamine; ethanolamine; 3-amino-1-propanol; amino-2-propanol; 4-amino-1-butanol; 5-amino-1-pentanol; 6-amino-1-hexanol; n-(3-aminopropyl)diethanolamine; 2-(2-aminoethoxy)ethanol; 2-methoxyethylamine; 3-methoxypropylamine; 3-ethoxypropylamine; 3-butoxypropylamine; aminoacetaldehyde dimethyl acetal; 3-Isopropoxypropylamine; aminoacetaldehyde diethyl acetal; 4-aminobutyraldehyde diethyl acetal; 3-aminopropyltriethoxysilane; 2-methoxybenzylamine; 4-methoxybenzylamine; 2-phenoxyethylamine; 3,4-dimethoxyphenethylamine; 4-methoxyphenethylamine; 2-methoxyphenethylamine; tyramine; benzylamine; 4-methylbenzylamine; phenethylamine; 4-aminobenzylamine; 4-tert-butylbenzylamine; 4-phenylbenzylamine; 4-iodobenzylamine; 4-(aminomethyl)pyridine; 3-picolyamine; 2-fluorobenzylamine; 4-fluorobenzylamine; 4-fluorophenethylamine; 3-3-(trifluoromethyl)benzylamine;

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2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-heptafluorononylamine; cyclopropylamine; cyclopentylamine; N-(3-aminopropyl)-2-pyrrolidinone; cyclohexylamine; cyclohexanemethylamine; 2-(1-cyclohexenyl)ethylamine; 1-(2-aminoethyl)piperidine; 3-morpholinopropylamine; ($\pm$)-3-amino-1,2-propanediol; 2-amino-1,3-propanediol; 2-Amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; N,N-bis(2-hydroxyethyl)ethylenediamine; oxamic Acid; and 2-amino-2-(hydroxymethyl)propane-1,3-diol.

[0073] Suitable amines containing siloxyl substituents may be used as starting materials, including, without limitation, 3-aminopropyl(diethoxy)methylsilane; 3-(2-aminoethylamino) propyldimethoxymethylsilane; N-[3-(trimethoxysilyl)propyl]ethylenediamine; 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane; and 1-[3-(trimethoxysilyl)propyl]urea.

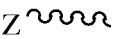
[0074] The amino acids, including Alanine, Leucine, Serine, Cysteine, Tyrosine, Glutamic Acid, Glutamine, Lysine, and Arginine are also suitable to form compounds according to the invention.

[0075] Alternatively, a bis (amine) starting material may be used. The amine groups in such bis (amine) starting materials are linked by a moiety B, as shown in reaction scheme II above. In general B is a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxy, alkylthioether, and thiol groups.

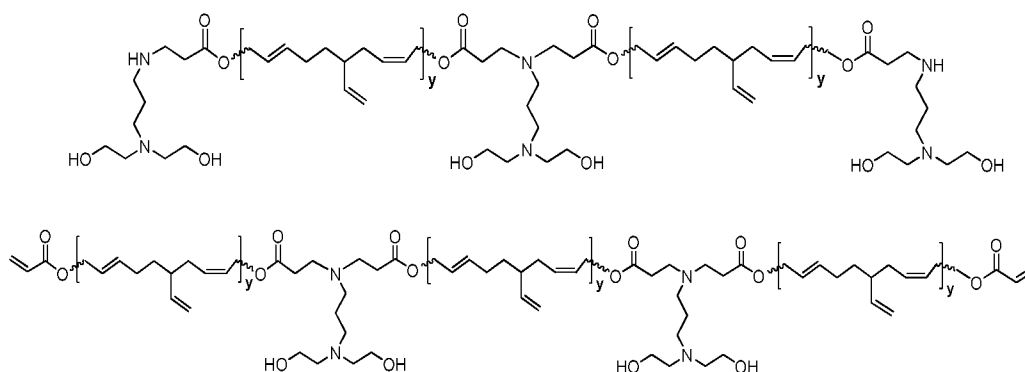
[0076] Bis(secondary amine) monomers that are useful in the present invention include, but are not limited to, N,N'-dimethylethylenediamine, piperazine, 2-methylpiperazine, 1,2-bis(N-ethylamino)ethylene, and 4,4'-trimethylenedipiperidine.

[0077] End groups Z and Z', together with the atoms to which they are attached, represent acrylate, methacrylate or amino end group. In embodiments, Z and Z' form an amino group or unsaturated acrylate or methacrylate group on both

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termini of the polymer. Thus, for example, in the case where Z and Z' form an amino moiety, Z' is hydrogen and Z is -NR₂-H. Where the end group is acrylate, Z  means that Z and the carbon to which it is attached form a CH₂= terminus of the acrylate or methacrylate end group while Z' forms a

[0078] Non-limiting examples of polymers with amine terminated end groups and acrylate terminated end groups are:



wherein y is 1 to 100.

[0079] In embodiments, n in formulas (I) to (IV) may range from 1 to 10,000. However, presently preferred compounds of the invention are oligomers, having 3 to 10 amino ester units. A composition according to the invention may contain a plurality of oligomers of different length.

[0080] The preferred compositions used in the invention include a cosmetically acceptable carrier such that the composition can be applied to the hair without irritation to the eyes or scalp. The compositions may be in the form of an oil-in-water emulsion, a water-in-oil emulsion, a dispersion, a suspension, a cream, a foam, a gel, a spray, a powder, a liquid or a pomade.

[0081] The β-amino ester compound is generally present in the composition in a range of about 0.01 percent by weight to about 20 percent by weight of the composition. In embodiments, the β-amino ester is present in a range of about 0.1 percent by weight to about 10.0 percent by weight of the composition; and in still other embodiments in a range of about 1.0 percent by weight to about 5.0 percent by weight.

[0082] The compositions according to the invention are preferably water or water-alcohol based, meaning that that they contain greater than 50 percent by

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weight water. Preferably water is present in the compositions according to the invention in a range of 60 to 99 percent by weight of the composition. In the presently preferred embodiments, water is present in a range of about 80 to about 95 percent by weight of the composition.

[0083] The cosmetically acceptable carrier for the compound contains ingredients conventionally used in hair treatment compositions. One or more emulsifiers may be included in a range of about 0.1 to about 10.0 percent by weight, in preferred embodiments, in a range of about 0.5 percent by weight to about 3.0 percent by weight. Suitable formulation amounts may be determined by those of ordinary skill in the art without undue experimentation, depending on how the composition is intended to be delivered. Suitable emulsifiers may be selected from those known in the art, including without limitation, Polysorbate 20, Polyacrylate-13, Polyisobutene, Oleth-10, and the like.

[0084] A fatty alcohol, or a mixture, may be provided in an amount of 0.1 to about 5.0 percent by weight of the composition to provide thickening and/or emollient properties. In embodiments, a fatty alcohol component such as cetearyl alcohol (a mixture of fatty alcohols), may be provided in a range of about 0.1 to 1.0 percent by weight of the composition.

[0085] One or more fatty acids may be provided in a range of about 0.1 percent by weight to 5.0 percent by weight of the composition. Fatty acids, include without limitation, palmitic acid, stearic acid, linoleic acid, myristic acid, and others known in the art to provide thickening and/or emollient properties in a hair treatment composition.

[0086] Compositions according to the invention may also include at least one additive conventionally used in hair treatment compositions. Non-limiting examples of suitable additives include emollients, processing aids, dyes, anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, fragrances, screening agents, preserving agents, proteins, vitamins, silicones, polymers such as thickening polymers, plant oils, mineral oils, synthetic oils and any other additive conventionally used in compositions for the care and/or treatment of keratinous fibers.

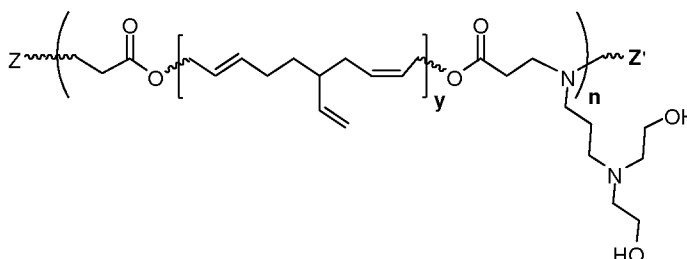
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General Synthetic Procedure

[0087] The synthesis of the compounds described below was performed in 30ml clear glass jars with phenolic caps lined with polyethylene core liners, and stirred with 15.9x9.5mm Teflon® coated spin bar. For each reaction, 5g of PBD was added to each vial. Amine was added by pipette for liquids or by mass for solids at desired ratios. Vials were stirred at 90°C for 48 hours. The spin bar was removed while the reaction material was still hot. Polymers were allowed to cool to room temperature before observing for color and viscosity as a rough monitor of reaction completeness. As the reactions went to completion, the viscosity dramatically increased and the mixtures turned more yellow/amber in color. Products were stored at 4°C.

[0088] Primary amines were obtained from Sigma-Aldrich, Inc. (St. Louis, Mo.) and VWR International, LCC (West Chester, Pa.). PBDs were obtained from Sartomer Company, Inc. (Exton, Pa.) (Sartomer product #CN307) and San Esters (New York, NY) (product # BAC-15 and BAC-45).

Example 1-1



[0089] The above polymer was synthesized following the procedure outlined above using 5.0 grams of polybutadiene diacrylate (99%) having a molecular weight of 3000Da (1 equivalent) and 325.11mg of N-(3-aminopropyl) diethanolamine (1.2 equivalents). The resulting material was characterized via ¹H NMR.

[0090] ¹H NMR (CDCl₃): δ (ppm) 1.0-1.3 (m), 1.3-1.5 (m), 1.6-1.7 (m), 1.8-2.2 (m), 2.4-2.5 (m), 2.5-2.7 (m), 2.7-2.8 (m), 3.6-3.7 (m), 4.8-5.1 (m), 5.2-5.4 (m), 5.4-5.7 (m).

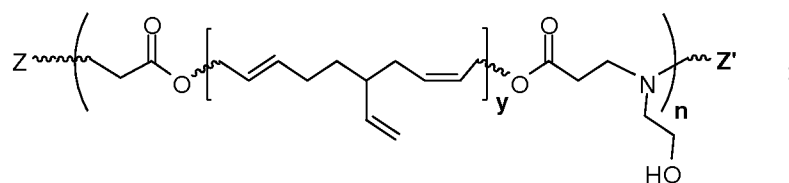
[0091] All NMR spectra were recorded on a Varian Mercury 300MHz spectrometer and taken in CDCl₃.

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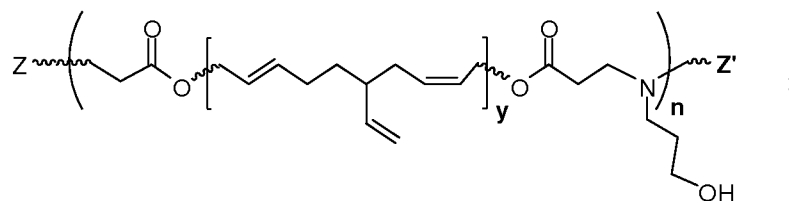
[0092] In like manner, Examples 1-2 through 1-11 below were formed from polybutadiene diacrylate polymer (molecular weight 1400Da or 3000Da) and suitable amines to form the β -amino ester compounds listed below.

Compositions were formulated and tested as set forth below.

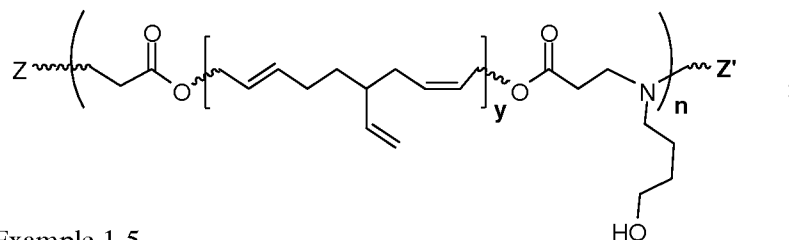
[0093] Example 1-2



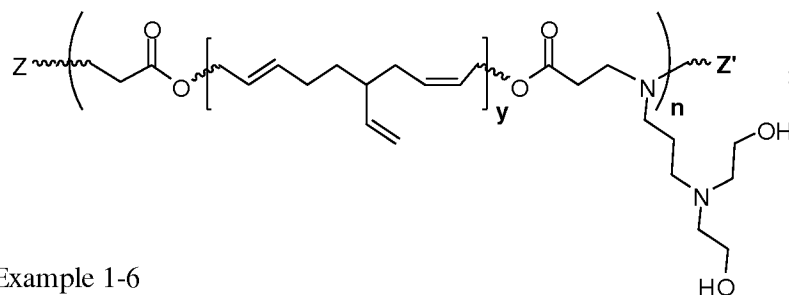
Example 1-3



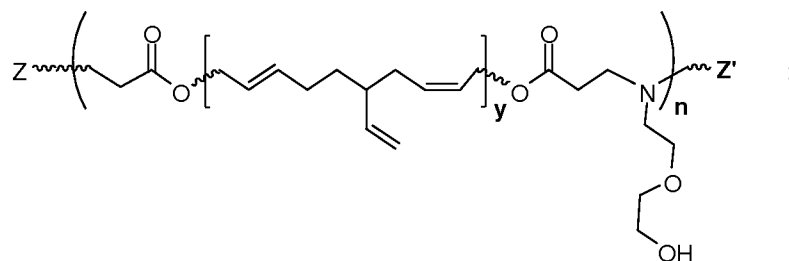
Example 1-4



Example 1-5

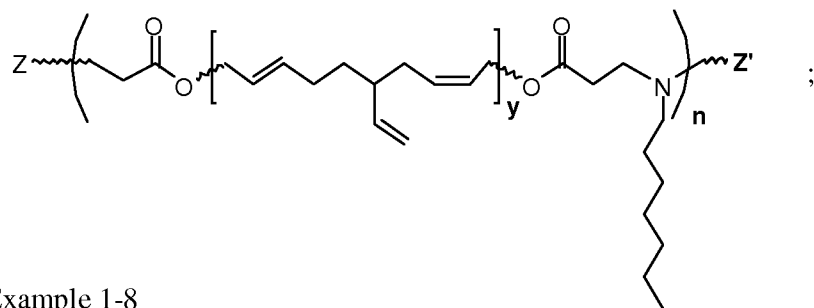


Example 1-6

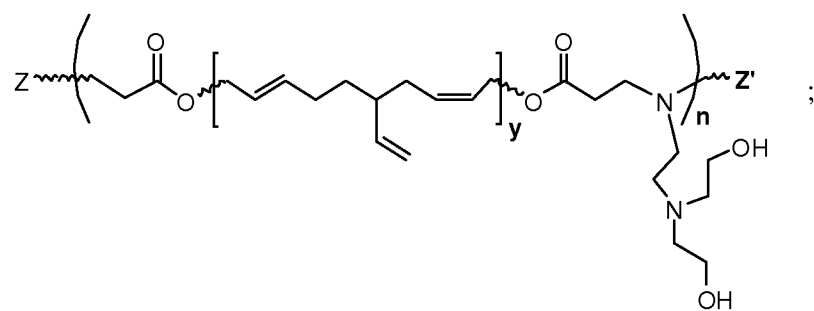


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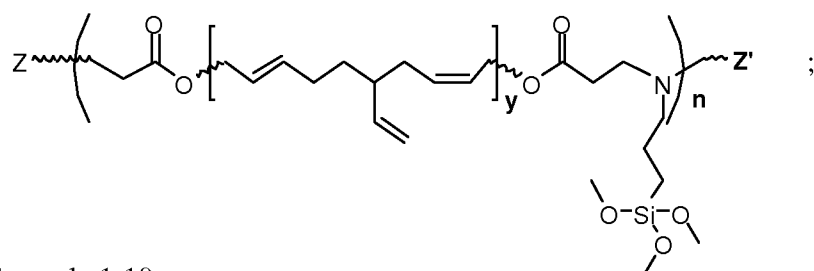
Example 1-7



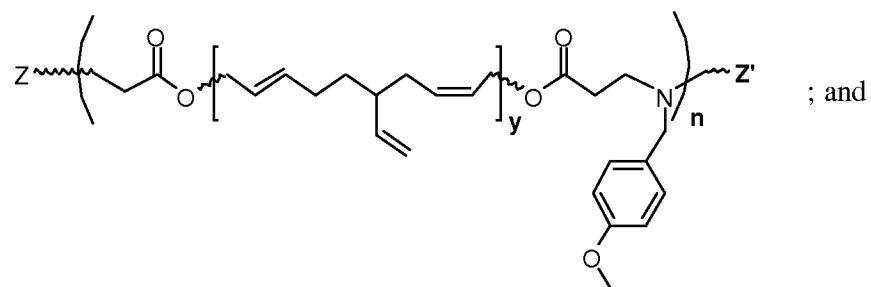
Example 1-8



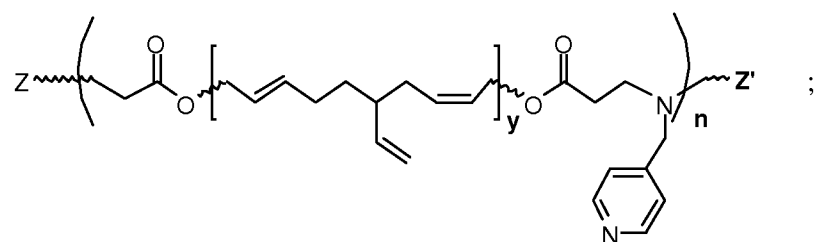
Example 1-9



Example 1-10



Example 1-11



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Example 2-1 Feel Test

[0094] The feel properties of preferred polymers on hair were assessed. 10g of a 1% (w/w) in THF solution was prepared. Solutions were applied to dry 1g x 2.5cm wide x 22cm long hair tresses of virgin straight medium brown hair (International Hair Importers). Tresses were curled with a ½ in. diameter curling iron (Hot Tools Model 1101) on the highest heat setting (approximately 200°C) for 30 seconds. Each tress was evaluated with clean hands for the following attributes: tack, grease, friction, and the presence of a coating. Each attribute was rated against the following scale: 0=none, 1=slight, 2=moderate, 3=excessive.

[0095] The desired feel properties are no grease, no tackiness, very little coating or none at all, and slight friction. The results obtained in Table 1 were exemplary of preferred compositions, based on the feel properties obtained.

TABLE 1

Compound	Tack	Grease	Coating	Friction
PBD:amine 1:1.2				
14PBD:octylamine	0	0	1	0
14PBD:amino 2-propanol	0	0	1	0
14PBD:n-(3-aminopropyl) diethanolamine	0	0	0	2
14PBD:4-methoxybenzylamine	0	0	1	0
14PBD:4-(Aminomethyl)pyridine	0	0	1	0
30PBD:3-amino-1-propanol	0	0	1	0
30PBD:4-amino-1-butanol	1	0	0	0
30PBD:2-(2-Aminoethoxy)ethanol	1	0	0	0
PBD:amine 1:1.8				
14PBD:3-aminopropyltriethoxysilane	0	0	2	0
14PBD:4-Methoxybenzylamine	1	0	1	0
14PBD:4-(Aminomethyl)pyridine	0	0	1	0
30PBD:ethanolamine	1	0	0	0
30PBD:n-(3-aminopropyl) diethanolamine	0	0	0	1

14PBD means polybutadiene diacrylate having a molecular weight of 1400Da.

30PBD means polybutadiene diacrylate having a molecular weight of 3000Da.

Example 3-1 Snap and Movement Test

[0096] The movement of hair treated with each polymer in Table 1 was assessed.

A 1% (w/w) solution of 10g of each polymer in THF was prepared. Solutions

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were applied to dry 1g x 2.5cm wide x 22cm long hair tresses of virgin straight medium brown hair (International Hair Importers). Tresses were curled with a ½ inch diameter curling iron (Hot Tools Model 1101) on the highest heat setting (approximately 200°C) for 30 seconds. Once cool, the ends of the tress were extended to full length and released. Snap is defined as the initial recoil of the tress, while movement is defined as the length of time after the initial recoil that the tress was in motion, as well as the intensity of motion. Both attributes were rated against the following scale: 0=poor, 1=ok, 2=good, 3=great, 4= excellent. Scores of 4 for both snap and movement were desired.

[0097] The results for snap and movement for thirteen compounds tested are given in Table 2.

TABLE 2

Compound	Snap	Movement
PBD:amine (1:1.2)		
14PBD:octylamine	3	3
14PBD:amino 2-propanol	2	2
14PBD:n-(3-aminopropyl) diethanolamine	3	3
14PBD:4-methoxybenzylamine	3	3
14PBD:4-methoxybenzylamine	3	3
30PBD:4-(Aminomethyl)pyridine	2	2
30PBD:3-amino-1-propanol	0	0
30PBD:4-amino-1-butanol	2	2
PBD:amine 1:1.8		
14PBD:3-aminopropyltriethoxysilane	3	3
14PBD:4-Methoxybenzylamine	3	3
14PBD:4-(Aminomethyl)pyridine	3	3
30PBD:Ethanolamine	3	3
30PBD:n-(3-aminopropyl) diethanolamine	2	2

[0098] The polymers on Table 3 were chosen as exhibiting better properties based on the overall results obtained in the feel and the snap/movement tests. Feel scores were given more weight than snap/movement scores as feel is a more desirable property.

TABLE 3

Compound	Tack	Grease	Coating	Friction	Snap	Movement
PBD:amine1:1.2						
14PBD:octylamine	0	0	1	0	3	3
14PBD:amino 2-propanol	0	0	1	0	2	2
14PBD:n-(3-aminopropyl) diethanolamine	0	0	0	2	3	3
14PBD:4-methoxybenzylamine	0	0	1	0	3	3
14PBD:4-methoxybenzylamine	0	0	1	0	3	3

Example 4-1 Consumer Use Test

[0099] β -amino ester compound according to Example 1-1 was formulated into a cream according to Formulation Example 5-1 below and a cream according to Formulation Example 5-2. These two formulations were given to 20 women. The women in the study were blinded to the ingredients and the potential performance benefits of the formulations. The women were asked to use each product for one week. Typically, the formulations were applied to wet hair and blown dry to a desired style. After using the two formulations, the women were interviewed and asked to fill out a product performance survey. The needs of the 20 women compared to how the two formulations delivered against those needs are shown in Table 4.

TABLE 4

Desired Benefit	Priority	Benefit Delivered From Cream	Benefit Delivered From Spray
Volume and body	High	High	Med
Thickening	High	High	Med
Weightlessness	High	High	Med
Lasting Effect	High	High	Low
Ease of Achieving Effect	High	Med	Low
Lack of Residue	Med	Med	Low
Softness	Low	Med	Low
Shine/Conditioning	Med	Med	Low

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Smoothness	Med	Med	Low
Hold/Control/Texture	Med	Med	Low
Ease of Use	Med	Med	High
Pleasant Smell	Med	Low	Low

Formulation Example 5-1

[00100] A styling cream containing β -amino ester compound according to the invention may include the following:

<u>Ingredients</u>	<u>%w/w</u>
Water	q.s.
β -amino ester compound	0.50-6.00
Polysorbate 20 (and) Polyacrylate-13 (and) Polyisobutene (Emulsifier)	0.50-4.00
Fragrance	0.20-3.00
Phenoxyethanol (and) Methylisothiazolinone (Preservative)	0.50-1.50
PPG-2 Myristyl Ether Propionate (Emollient)	0.10-5.00
Oleth-10 (Emulsifier)	0.10-2.00

Formulation Example 5-2

[00101] A styling cream containing β -amino ester compound was prepared with the following ingredients:

<u>Ingredients</u>	<u>%w/w</u>
Water	93.00
β -amino ester compound	3.00
Polysorbate 20 (and) Polyacrylate-13 (and) Polyisobutene	1.45
Fragrance	1.00
Phenoxyethanol (and) Methylisothiazolinone	0.50
PPG-2 Myristyl Ether Propionate	0.50
Oleth-10	0.50

[00102] The above composition was manufactured using the process described below.

[00103] A vessel was charged with water (Phase A) and heated to 75 °C. Phase B consisting of polysorbate 20, polyacrylate-13, and polyisobutene was added to Phase A using high agitation and allowed to mix for 30 minutes or until homogeneous. The β -amino ester compound, oleth-10, and PPG-2 myristyl ether propionate were mixed in a separate vessel at 75 °C until homogeneous to form Phase C. Phase C was added to the above mixture of Phase A and Phase B and the contents were mixed until homogeneous. The mixture was cooled to 40 °C.

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Thereafter, Phase D, consisting of phenoxyethanol, and methylisothiazolinone, was added to the above mixture and the contents were mixed until homogeneous. The mixture was cooled to 30°C. Phase E, consisting of fragrance, was added to the above mixture and the contents were mixed until homogeneous. Water (q.s.) was added to the mixture and homogenized to obtain the above composition.

Formulation Example 5-3

[00104] A styling spray containing β -amino ester compound according to the invention may include the following:

Ingredients	%w/w
Water	q.s.
β -amino ester compound	0.50-6.00
Oleth-10 (Emulsifier)	0.10-10.00
Ethoxydiglycol Oleate (Emollient)	0.10-5.00
Fragrance	0.20-3.00
Phenoxyethanol (and) Methylisothiazolinone (Preservative)	0.50-1.50
Sodium Chloride	0.10-1.50
Xanthan Gum (Rheology modifier)	0.10-1.50

Formulation Example 5-4

[00105] A styling spray containing β -amino ester compound was prepared with the following ingredients:

Ingredients	%w/w
Water	92.70
β -amino ester compound	3.00
Oleth-10	1.10
Ethoxydiglycol Oleate	1.00
Fragrance	1.00
Phenoxyethanol (and) Methylisothiazolinone	0.50
Sodium Chloride	0.40
Xanthan Gum	0.30

[00106] The above composition may be manufactured using the process described below.

[00107] A vessel was charged with water and xanthan gum was added to form Phase A. Xanthan gum was allowed to hydrate for 20 minutes. Phase A was then heated to 75°C. In a separate vessel, the β -amino ester compound, oleth-10 and ethoxydiglycol oleate were heated to 75°C and mixed to form a

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homogeneous Phase B. Phase B was added to Phase A and mixed until homogeneous. The mixture was cooled to 40 °C. Thereafter, Phase C, consisting of phenoxyethanol and methylisothiazolinone, was added to the above mixture and the contents mixed until homogeneous. The mixture was cooled to 30 °C. Then, Phase D consisting of sodium chloride and fragrance was added to the above mixture and the contents were mixed until homogeneous. Water (q.s.) was added to the mixture and homogenized to obtain the above composition.

Formulation Example 5-5

[00108] A styling non-aerosol mousse containing β -amino ester compound according to the invention may include the following:

<u>Ingredients</u>	<u>%w/w</u>
Water	q.s.
β -amino ester compound	0.50-6.00
Cocamidopropylamine Oxide (Surfactant)	0.10-10.00
Oleth-10 (Emulsifier)	0.10-10.00
Ethoxydiglycol Oleate (Emollient)	0.10-5.00
Fragrance	0.20-3.00
Phenoxyethanol (and) Methylisothiazolinone (Preservative)	0.50-1.50
Sodium Chloride	0.10-1.50
Xanthan Gum (Rheology modifier)	0.10-1.50

Formulation Example 5-6

[00109] A styling non-aerosol mousse containing β -amino ester compound was prepared with the following ingredients:

<u>Ingredients</u>	<u>%w/w</u>
Water	89.70
β -amino ester compound	3.00
Cocamidopropylamine Oxide	3.00
Oleth-10	1.10
Ethoxydiglycol Oleate	1.00
Fragrance	1.00
Phenoxyethanol (and) Methylisothiazolinone	0.50
Sodium Chloride	0.40
Xanthan Gum	0.30

[00110] The above composition was manufactured using the process described below.

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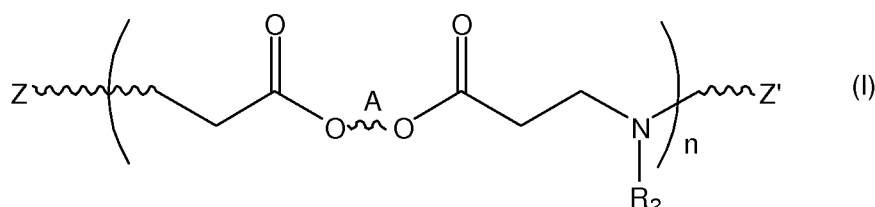
[00111] To form Phase A, a vessel was charged with water and xanthan gum. Xanthan gum was allowed to hydrate for 20 minutes. Phase A was then heated to 75°C. To obtain Phase B, β -amino ester compound, oleth-10 and ethoxydiglycol oleate were heated to 75°C in a separate vessel. The contents were mixed until homogeneous. Phase B was added to Phase A and mixed until homogeneous. The mixture was cooled to 40 °C. Thereafter, Phase C, consisting of phenoxyethanol and methylisothiazolinone, was added to the above mixture and the contents were mixed until homogeneous. The mixture was cooled to 30°C. Thereafter, Phase D, consisting of Cocamidopropylamine oxide, sodium chloride and fragrance was added to the above mixture of Phases A, B, and C until a homogeneous composition above was obtained. Water (q.s.) was added to the mixture and mixed until homogeneous.

[00112] Notwithstanding anything herein to the contrary, the foregoing embodiments are exemplary only and not to be considered as limiting the invention, which is defined by the appended claims.

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WHAT IS CLAIMED IS:

1. A hair treatment composition comprising a compound according to formula (I) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000; and Z and Z' , together with the atoms to which they are attached, represent acrylate, methacrylate or amino end groups;

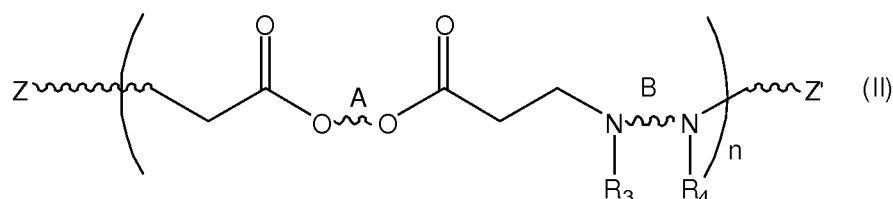
R_2 is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxy, alkylthioether, siloxyl, and thiohydroxyl groups; and

A comprises a rubber moiety.

2. A hair treatment composition according to claim 1, wherein A comprises 1-100 monomer units selected from the group consisting of butadiene, chloroprene, isoprene, and styrene-butadiene units.
3. A hair treatment composition according to claim 1, wherein A has a molecular weight in a range of about 1000 g/mol to about 10,000 g/mol.
4. A hair treatment composition according to claim 1, wherein A consists of polybutadiene monomer units.

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5. The hair treatment composition according to claim 1, wherein n is 1 to 100.
6. The hair treatment composition according to claim 1, wherein the composition is a hair styling product, shampoo or conditioner.
7. A hair treatment composition comprising a compound according to formula (II) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

Z and Z', together with the atoms to which they are attached, represent acrylate methacrylate or an amino end groups;

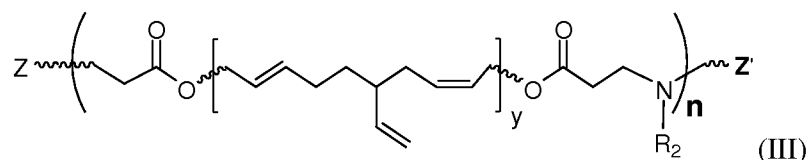
R₂ is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups;

B is a chain of 1 to 30 carbon atoms or heteroatoms which atoms or heteroatoms are unsaturated, saturated with hydrogen, or are substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, heteroaryl, alkoxy, alkoxyalkyl carbamoyl, carboxyl ester, carbonyldioxyl, amido, thiohydroxyl, alkylthioether, cyano, ureido, cyclic aliphatic, aromatic, and heteroaromatic groups, which substituents may be substituted or unsubstituted, or alternatively may bond with each other or with an atom on the chain to form a ring; and

A comprises a rubber moiety.

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8. A hair treatment composition according to claim 7, wherein A comprises 2 to 60 monomer units selected from the group consisting of polybutadiene, chloroprene, isoprene, and styrene-butadiene units.
9. A hair treatment composition according to claim 7, wherein A has a molecular weight in a range of about 1000 g/mol to about 10,000 g/mol.
10. A hair treatment composition according to claim 7, wherein A consists of polybutadiene monomer units.
11. The hair treatment composition according to claim 7, wherein n is 1 to 100.
12. The hair treatment composition according to claim 7, wherein the composition is a hair styling product, shampoo or conditioner.
13. A hair treatment composition comprising a compound of formula (III) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

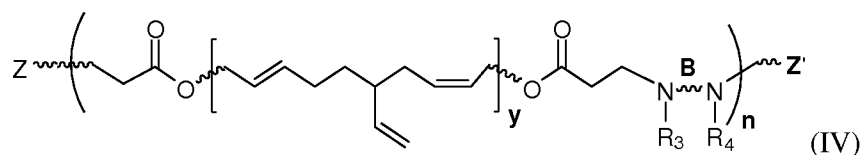
y is an integer between 1 and 1,000;

R_2 is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

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Z and Z', together with the atoms to which they are attached, represent acrylate, methacrylate or amino end groups.

14. The hair treatment composition according to claim 13, wherein n is 1 to 100.
15. The hair treatment composition according to claim 13, wherein y is 1 to 100.
16. The hair treatment composition according to claim 13, wherein the composition is a hair styling product, shampoo or conditioner.
17. The hair treatment composition according to claim 16, wherein the composition is a spray, cream, mousse or pomade.
18. The hair treatment composition according to claim 13, wherein R₂ is a C₁₋₁₀ straight-chain hydroxylalkyl radical.
19. The hair treatment composition according to claim 13, wherein R₂ is diethanolaminopropyl radical.
20. The hair treatment composition according to claim 13, wherein y is in a range of 1 to 25.
21. A hair treatment composition comprising a compound of formula (IV) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

y is an integer between 1 and 1,000;

R₃ and R₄ are independently selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl,

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amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

Z and Z', together with the atoms to which they are attached, represent an acrylate, methacrylate or amino end group; and

B is a chain of 1 to 30 carbon atoms or heteroatoms which atoms or heteroatoms are unsaturated, saturated with hydrogen, or are substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, heteroaryl, alkoxy, alkoxyalkyl carbamoyl, carboxyl ester, carbonyldioxyl, amido, thiohydroxyl, alkylthioether, cyano, ureido, cyclic aliphatic, aromatic, and heteroaromatic groups, which substituents may be substituted or unsubstituted, or alternatively may bond with each other or with an atom on the chain to form a ring.

22. The hair treatment composition according to claim 21, wherein n is 1 to 100.

23. The hair treatment composition according to claim 21, wherein y is 1 to 100.

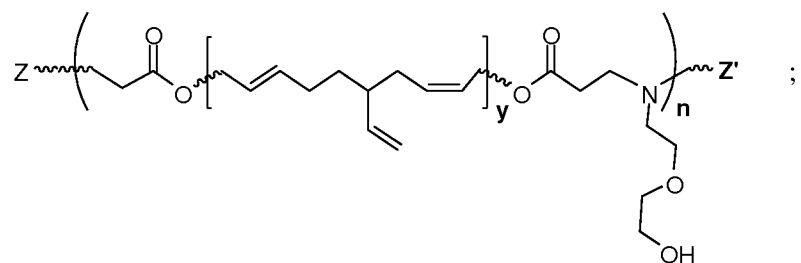
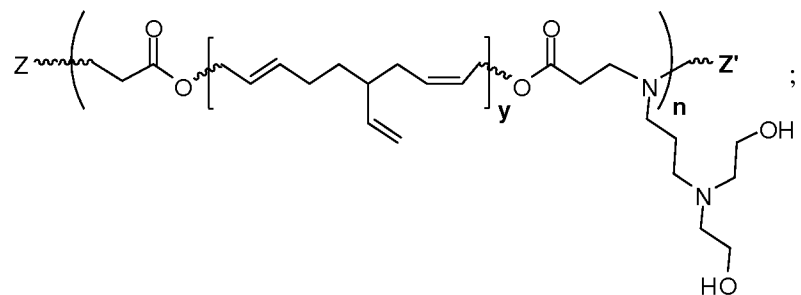
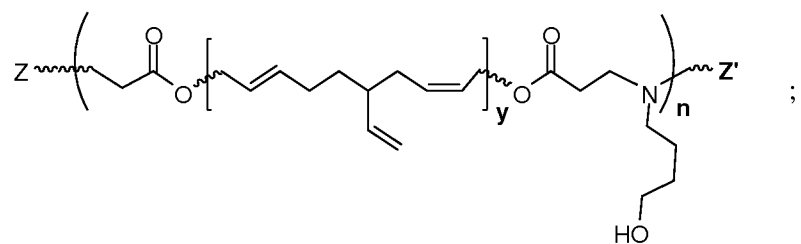
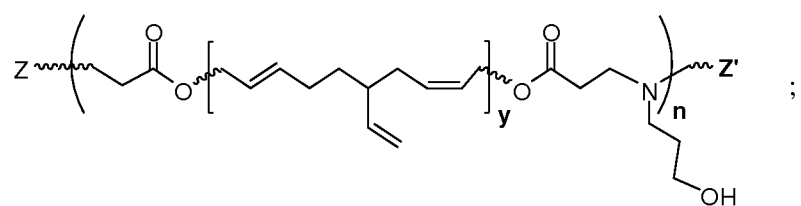
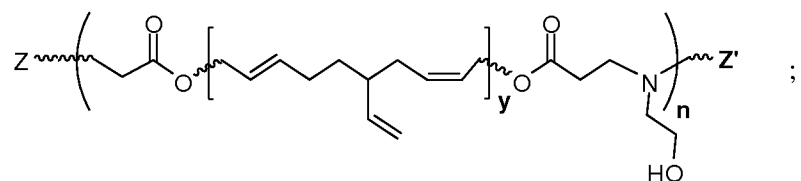
24. The hair treatment composition according to claim 21, wherein the composition is a hair styling product, shampoo, or conditioner.

25. The hair treatment composition according to claim 24, wherein the composition is a spray, cream, mousse or pomade.

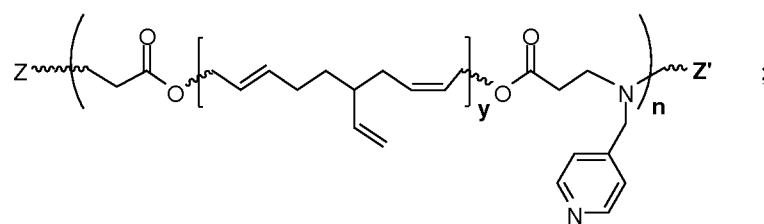
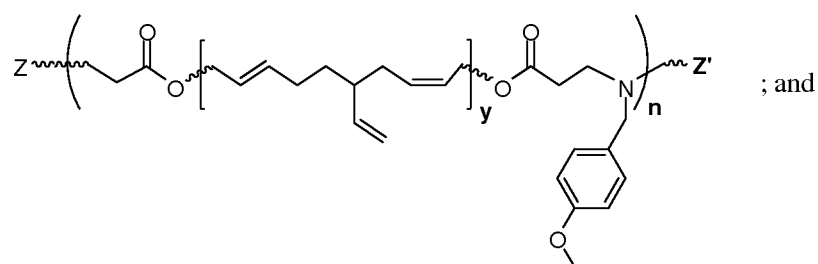
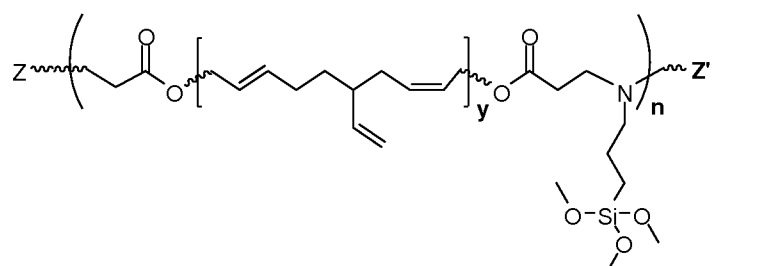
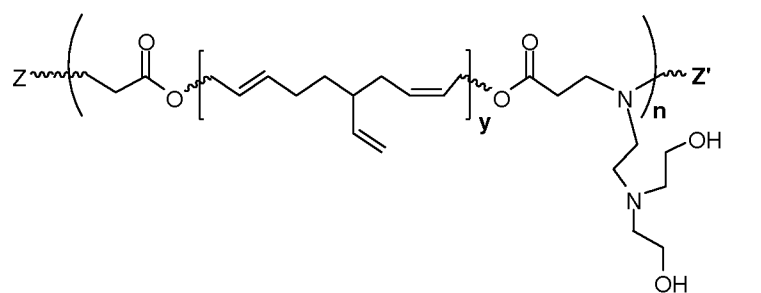
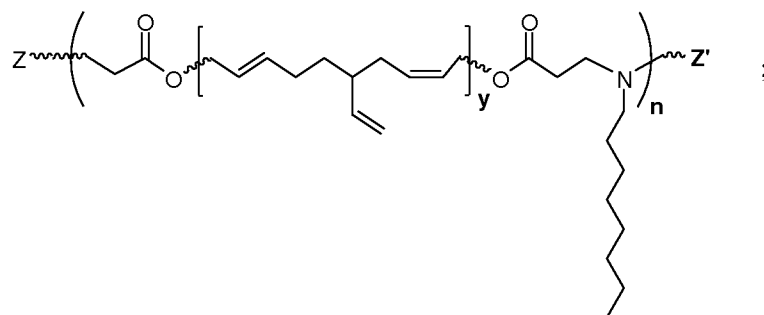
26. The hair treatment composition according to claim 21, wherein y is in a range of 1 to 25.

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27. A hair treatment composition comprising a compound selected from the group consisting of:

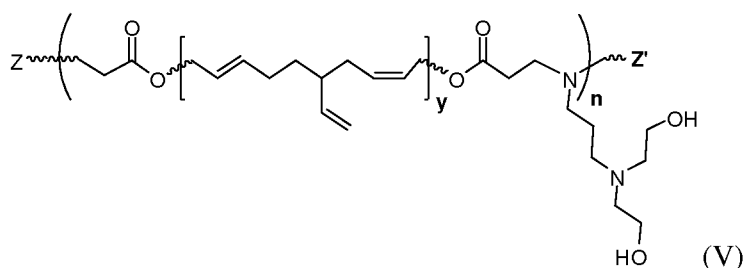


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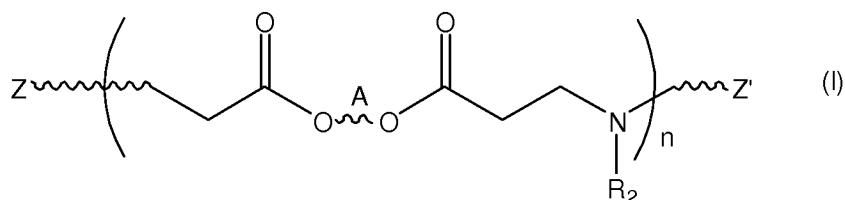
in a cosmetically acceptable carrier, wherein y is an integer between 1 and 100; n is an integer between 1 and 100; and Z and Z', together with the atoms to which they are attached, form an acrylate, methacrylate, or amino end group.

28. A hair treatment composition comprising a compound according to formula (V) in a cosmetically acceptable carrier



wherein y is in a range of 1 to 100, and n is in a range of 1 to 100.

29. A method of treating scalp hair comprising applying to the hair a composition comprising a compound of formula (I) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

Z and Z', together with the atoms to which they are attached, represent acrylate, methacrylate or amino end group;

R₂ is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano,

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carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

A is a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxyl, alkylthioether, and thiol groups; wherein said substituents may join to form one or more rings.

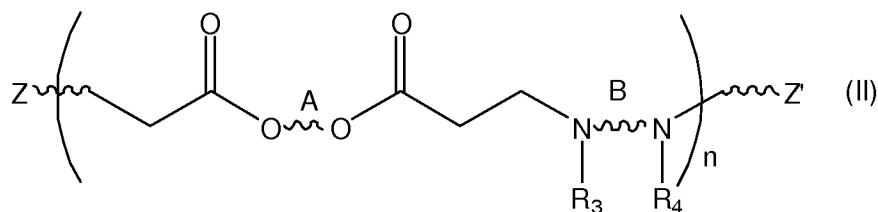
30. The method according to claim 29, wherein n is 1 to 100.

31. The method according to claim 29, wherein A is a substituted carbon chain forming 2 to 60 repeating monomer units of at least five carbon atoms.

32. The method according to claim 29, wherein said optionally substituted carbon chain or heteroatom-containing carbon chain contains 1 to 30 atoms in the chain.

33. The method according to claim 29, wherein the composition is a hair styling product, shampoo or conditioner.

34. A method of treating scalp hair comprising applying to the hair a composition comprising a compound of formula (II) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

Z, together with the atoms to which it is attached, forms an acrylate group, a methacrylate group or an amino group;

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R₃ and R₄ are independently selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

A and B are independently a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic, halogen, hydroxyl, cyano, and ureido groups; wherein said substituents may join to form one or more rings.

35. The method according to claim 34, wherein n is 1 to 100.

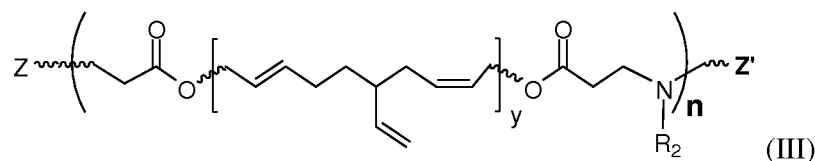
36. The method according to claim 34, wherein A comprises 1 to 100 monomer units selected from the group consisting of butadiene, chloroprene, isoprene and styrene-butadiene units.

37. The method according to claim 34, wherein A and B independently represent an optionally substituted carbon chain or heteroatom-containing carbon chain containing 1 to 30 atoms in the chain.

38. The method according to claim 34, wherein the composition is a hair styling product, shampoo or conditioner.

39. A method of treating scalp hair comprising applying to the hair a composition comprising a compound of formula (III) in a cosmetically acceptable carrier:

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wherein n is an integer between 1 and 10,000;

y is an integer between 1 and 1,000;

R₂ is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

Z and Z', together with the atoms to which they are attached, form acrylate methacrylate or amino end groups.

40. The method according to claim 39, wherein the composition is a hair styling product, shampoo or conditioner.

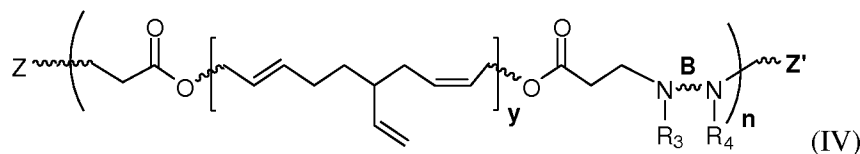
41. The method according to claim 39, wherein R₂ is a C₁₋₁₀ straight-chain hydroxyalkyl radical.

42. The method according to claim 39, wherein R₂ is a diethanolaminopropyl radical.

43. A method according to claim 39, wherein y is in a range of 1 to 25.

44. A method of treating scalp hair comprising applying to the hair a composition comprising a compound of formula (IV) in a cosmetically acceptable carrier:

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wherein n is an integer between 1 and 10,000;

y is an integer between 1 and 10,000;

R₃ and R₄ are independently selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxy, alkylthioether, siloxyl, and thiohydroxyl groups; and

Z and Z', together with the atoms to which they are attached, represent an acrylate, methacrylate or amino end group; and

B is a chain of 1 to 30 carbon atoms or heteroatoms which atoms or heteroatoms are saturated with hydrogen, unsaturated, or are substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, heteroaryl, alkoxy, alkoxyalkyl carbamoyl, carboxyl ester, carbonyldioxy, amide, thiohydroxyl, alkylthioether, cyano, ureido, , cyclic aliphatic, heterocyclic, aromatic, and heteroaromatic groups, which substituents may be substituted or unsubstituted, or alternatively may bond with each other or with an atom on the chain to form a ring.

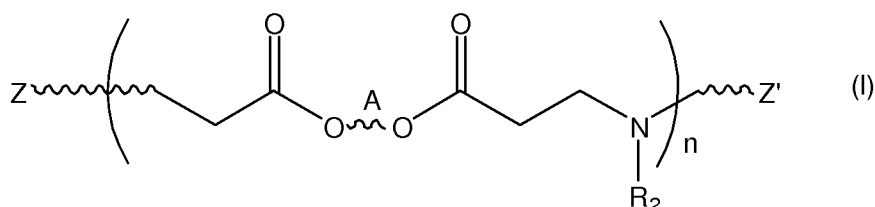
45. A method according to claim 44, wherein the composition is a hair styling product, shampoo, or conditioner.

46. The method according to claim 44, wherein the composition is a hair styling product in the form of a spray, cream or mousse or pomade.

47. A method according to claim 44, wherein y is in a range of 1 to 25.

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48. A compound according to formula (I):

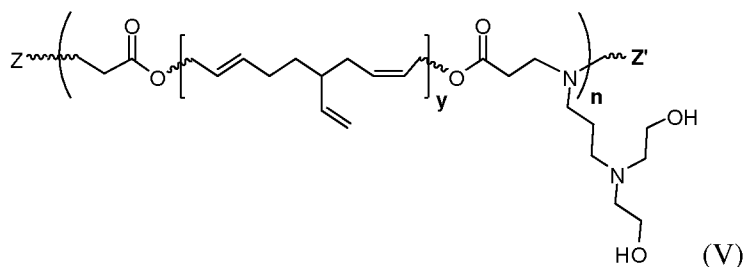


wherein n is an integer between 1 and 10,000; and Z and Z' , together with the atoms to which they are attached, represent acrylate methacrylate or amino end groups;

R_2 is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxy, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxy, alkylthioether, siloxyl, and thiohydroxyl groups; and

A comprises a rubber moiety having 2 to 100 monomer units selected from the group consisting of butadiene, chloroprene, isoprene, and styrene-butadiene units.

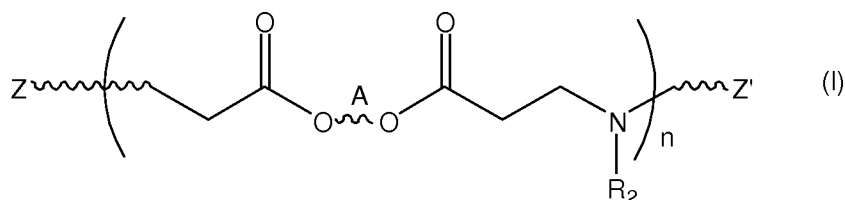
49. A compound according to claim 48, represented by formula (V)



wherein y is in a range of 2 to 100, and n is in a range of 1 to 100.

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50. A hair treatment composition comprising a compound according to formula (I) in a cosmetically acceptable carrier:



wherein n is an integer between 1 and 10,000;

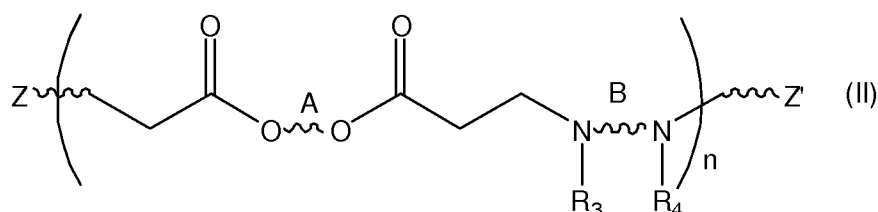
Z and Z', together with the atoms to which they are attached, represent acrylate, methacrylate or amino end group;

R₂ is selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

A is a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxyl, alkylthioether, and thiol groups; wherein said substituents may join to form one or more rings.

51. A hair treatment composition comprising a compound according to formula (II) in a cosmetically acceptable carrier:

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wherein n is an integer between 1 and 10,000;

Z , together with the atoms to which it is attached, forms an acrylate group, a methacrylate group or an amino group;

R_3 and R_4 are independently selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, alkylthioether, carbamoyl, carbonyldioxyl, carboxyl ester, cyclic aliphatic, cyclic heteroaliphatic, aromatic, heteroaromatic and ureido groups, each of which groups may be substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, acyl, alkoxy, alkoxyalkyl, amino, aminoalkyl, aryl, heteroaryl, amido, cyclic aliphatic, heterocyclic aliphatic, halogen, hydroxyl, cyano, carbamoyl, carboxylic acid, carbonyldioxyl, alkylthioether, siloxyl, and thiohydroxyl groups; and

A and B are independently a carbon chain or a heteroatom-containing carbon chain, optionally substituted with at least one substituent selected from the group consisting of alkyl, alkenyl, alkynyl, amino, alkylamino, dialkylamino, trialkylamino, aminoalkyl aryl, ureido, heterocyclic, aromatic heterocyclic, cyclic, aromatic cyclic, halogen, hydroxyl, alkoxy, cyano, amido, carbamoyl, carboxylic acid, ester, carbonyl, carbonyldioxyl, alkylthioether, and thiol groups; wherein said substituents may join to form one or more rings.