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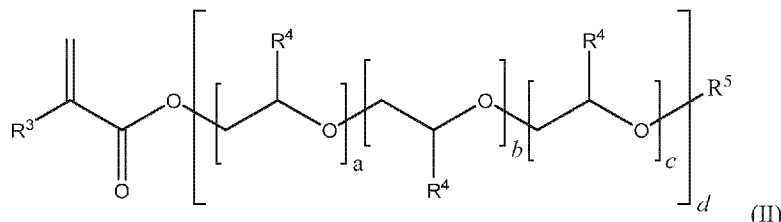
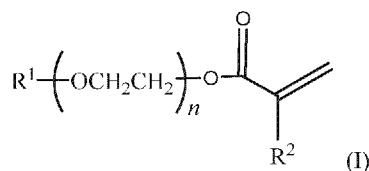
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(54) Title: PERSONAL CARE RINSE OFF FORMULATION



(57) **Abstract:** An aqueous personal care rinse off formulation is provided comprising: a dermatologically acceptable vehicle; a dermatologically acceptable cleaning surfactant; and a gradient polymer comprising: 5-35 wt% structural units (meth)acrylic acid; 35-65 wt% structural units C₁₋₈ alkyl (meth)acrylate; > 10-30 wt% structural units a specialized associative monomer having structure (I) wherein R¹ is linear saturated C₁₂₋₂₆ alkyl group; wherein R² is hydrogen or methyl group and wherein n is 10-30; 0.01-2 wt% structural units multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% structural units sulfonated monomer; wherein the polymer comprises < 0.02 wt% structural units monomer having structure (II) wherein R³ is -H or -CH₃; R⁴ is -H or C₁₋₄ alkyl group; R⁵ is -C₁₋₄ alkyl group; α is 0-50; b is 0-20; c is 0-50; α + c is 1-100 and d is 1-4; and wherein the gradient polymer has a gradient polymeric morphology.

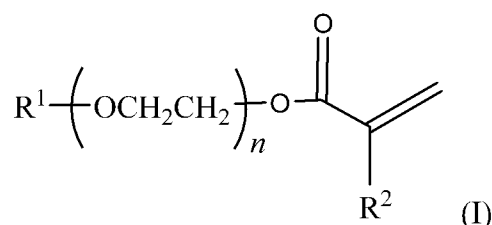


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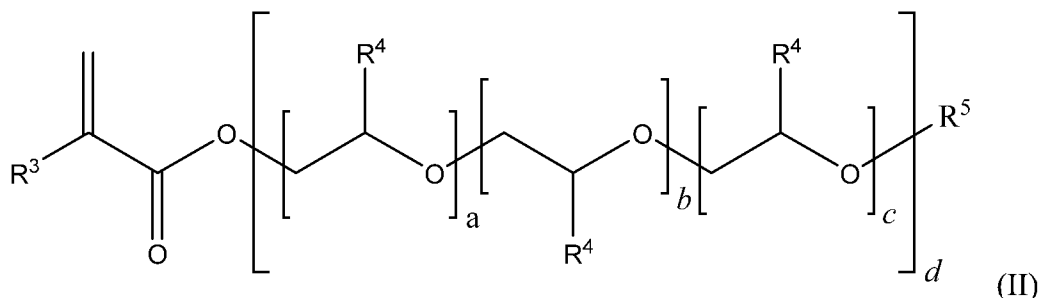
— *with international search report (Art. 21(3))*

PERSONAL CARE RINSE OFF FORMULATION

[0001] The present invention relates to an aqueous personal care rinse off formulation. In particular, the present invention relates to an aqueous personal care rinse off formulation, comprising: a dermatologically acceptable vehicle; a dermatologically acceptable cleaning surfactant; and a gradient polymer comprising: (a) 5 to 35 wt%, based on dry weight of the gradient polymer, of structural units of (meth)acrylic acid; (b) 35 to 65 wt%, based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate; (c) > 10 to 30 wt%, of structural units of a specialized associative monomer having structure I



wherein each R¹ is independently selected from a linear saturated C₁₂₋₂₆ alkyl group; wherein each R² is independently selected from a hydrogen and a methyl group and wherein *n* is 10 to 30; and (d) 0.01 to 2 wt%, based on dry weight of the gradient polymer, of structural units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt%, based on dry weight of the gradient polymer, of structural units of sulfonated monomer; wherein the polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, of structural units of monomer having structure II



wherein each R³ is independently selected from -H and -CH₃; wherein each R⁴ is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R⁵ is independently selected from a -C₁₋₄ alkyl group; wherein *a* is 0 to 50; wherein *b* is 0 to 20; wherein *c* is 0 to 50; wherein *a* + *c* is 1 to 100; and wherein *d* is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

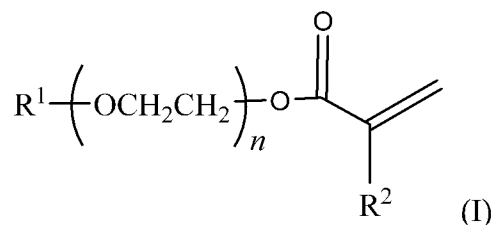
[0002] Amino acid based surfactants have an array of desirable properties for use in personal care rinse off formulations (e.g., shampoo, body wash). Such surfactants are often naturally derived and readily biodegradable. They are very mild and cause less irritation to skin and

hair compared to more traditional sulfate and sulfonate based surfactants like sodium lauryl sulfate and sodium lauryl ether sulfate. They tend to demonstrate lower toxicity and reduced negative impact on the environment than more traditional sulfate and sulfonate based surfactants. They have good cleaning and foaming properties.

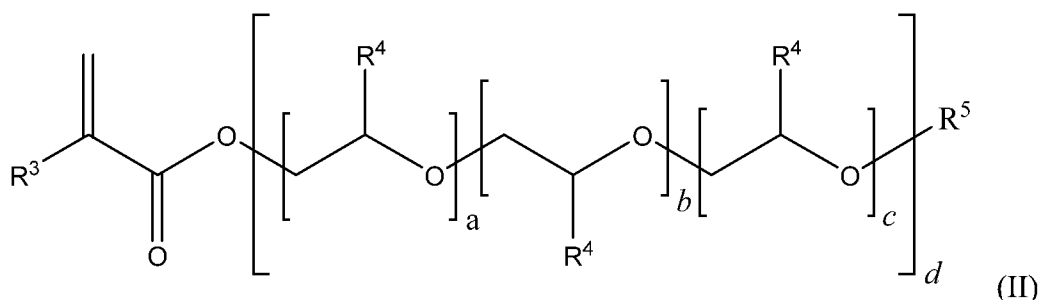
[0003] Notwithstanding, formulations comprising amino acid based surfactants are challenging to efficiently thicken. Some conventional thickeners achieve target viscosity at high usage levels which may negatively impact foaming performance. In other cases, conventional thickeners can provide adequate thickening, but the formulation viscosity is sensitive to changes in temperature; becoming watery at a high temperature and jelly like at low temperatures. Some conventional thickeners such as xanthan gum or cellulose esters exhibit potential compatibility issues resulting in phase separation.

[0004] Accordingly, there remains a continuing need for viscosity modifiers that facilitate formulation of aqueous personal care rinse off formulations, in particular amino acid surfactant containing aqueous personal care rinse off formulations (e.g., shampoo, body wash), with increased viscosity at low shear rates while maintaining desired flow properties at higher shear rates.

[0005] The present invention provides an aqueous personal care rinse off formulation comprising: a dermatologically acceptable vehicle; a dermatologically acceptable cleaning surfactant; and a gradient polymer comprising: (a) 5 to 35 wt%, based on dry weight of the gradient polymer, of structural units of (meth)acrylic acid; (b) 35 to 65 wt%, based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate; (c) > 10 to 30 wt%, of structural units of a specialized associative monomer having structure I

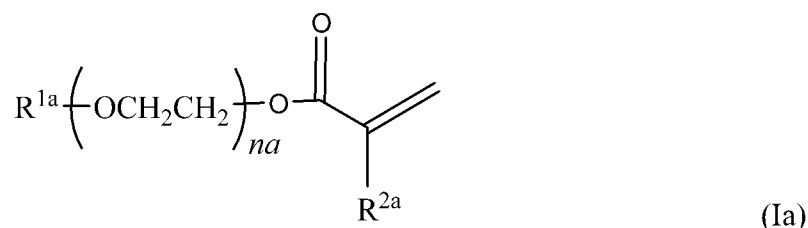


wherein each R¹ is independently selected from a linear saturated C₁₂₋₂₆ alkyl group; wherein each R² is independently selected from a hydrogen and a methyl group and wherein *n* is 10 to 30; and (d) 0.01 to 2 wt%, based on dry weight of the gradient polymer, of structural units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt%, based on dry weight of the gradient polymer, of structural units of sulfonated monomer; wherein the polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, of structural units of monomer having structure II

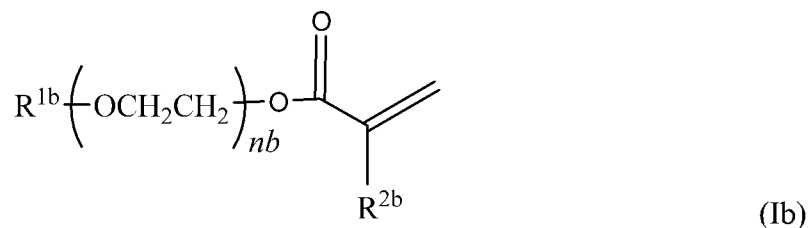


wherein each R^3 is independently selected from -H and -CH₃; wherein each R^4 is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R^5 is independently selected from a -C₁₋₄ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100; and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

[0006] The present invention provides an aqueous personal care rinse off formulation comprising: a dermatologically acceptable vehicle; a dermatologically acceptable cleaning surfactant; and a gradient polymer comprising: (a) 5 to 35 wt%, based on dry weight of the gradient polymer, of structural units of (meth)acrylic acid; (b) 35 to 65 wt%, based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate; (c) > 10 to 30 wt%, of structural units of a specialized associative monomer having structure I, wherein the structural monomer units of specialized associative monomer having structure I is a blend of a first specialized associative monomer having structure Ia

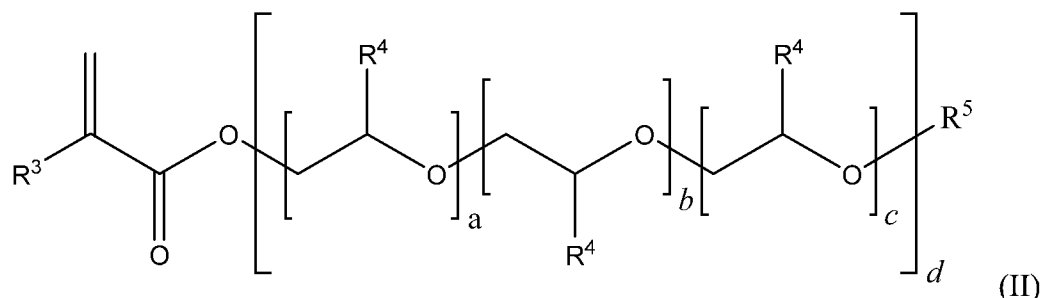


wherein each R^{1a} is independently selected from a linear saturated C₁₂₋₁₉ alkyl group; wherein each R^{2a} is independently selected from a hydrogen and a methyl group and wherein na is 10 to 30; and a second specialized associative monomer having structure Ib



wherein each R^{1b} is independently selected from a linear saturated C₂₀₋₂₆ alkyl group; wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group and wherein nb is 10 to 30; and (d) 0.01 to 2 wt%, based on dry weight of the gradient polymer,

of structural units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt%, based on dry weight of the gradient polymer, of structural units of sulfonated monomer; wherein the polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, of structural units of monomer having structure II



wherein each R^3 is independently selected from -H and -CH₃; wherein each R^4 is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R^5 is independently selected from a -C₁₋₄ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100; and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

[0007] The present invention provides a method of cleaning at least one of mammalian skin and hair, comprising: applying an aqueous personal care rinse off formulation of the present invention to the skin or hair of a mammal; and rinsing the aqueous personal care rinse off formulation from the skin or hair with a rinse water.

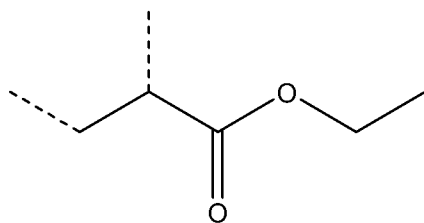
DETAILED DESCRIPTION

[0008] We have surprisingly found that gradient polymer, as described herein, facilitates the formulation of aqueous personal care rinse off cleaning products, in particular amino acid surfactant containing aqueous personal care rinse off cleaning products (e.g., shampoo, body wash), to increase viscosity at low shear rates while maintaining flow properties of the product at higher shear rates.

[0009] Unless otherwise indicated, ratios, percentages, parts, and the like are by weight.

[0010] Percentages of monomer units in a polymer are percentages of solids or neat monomer weight, i.e., excluding any water present in a polymer emulsion.

[0011] The term "structural monomer units" as used herein and in the appended claims refers to the remnant of the indicated monomer; thus a structural monomer unit of ethyl acrylate is illustrated:



where the dotted lines represent the points of attachment to the polymer backbone.

[0012] The term “(meth)acrylic acid” as used herein and in the appended claims is intended to serve as a generic expression embracing both acrylic acid and methacrylic acid.

[0013] The term “(meth)acrylate” as used herein and in the appended claims is intended to serve as a generic expression embracing both acrylate and methacrylate.

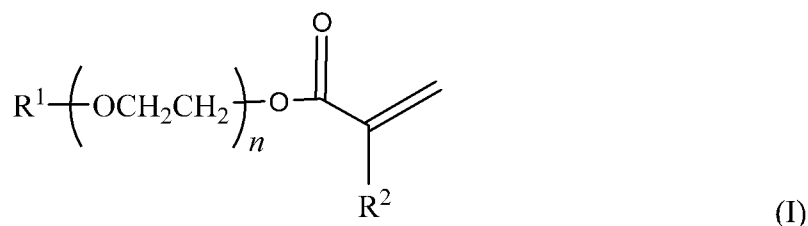
[0014] The term "gradient polymeric morphology" as used herein and in the appended claims refers to a polymer having a continually changing monomeric compositional content. The preparation of gradient polymers having a gradient polymeric morphology is well known in the art. U.S. Patent No. 3,804,881, hereby incorporated by reference in its entirety, discloses a process for preparing gradient polymers having a gradient polymeric morphology wherein the process comprises polymerizing at least one primary polymerizable monomer feed varying in compositional content by continuously adding at least one different secondary polymerizable monomer feed to the at least one primary polymerizable monomer feed.

[0015] The term "dermatologically acceptable" as used herein and in the appended refers to ingredients that are typically used for topical application to the skin, and is intended to underscore that materials that are toxic when present in the amounts typically found in skin care compositions are not contemplated as part of the present invention.

[0016] Preferably, the aqueous personal care rinse off formulation of the present invention is selected from the group consisting of a shampoo, a conditioning shampoo, a body wash, an exfoliating body wash, a facial wash, an exfoliating facial wash and a liquid hand soap. More preferably, the aqueous personal care rinse off formulation of the present invention is selected from the group consisting of a shampoo, a conditioning shampoo, body wash, a facial wash and a liquid hand soap. Most preferably, the aqueous personal care rinse off formulation of the present invention is selected from the group consisting of a shampoo and a conditioning shampoo.

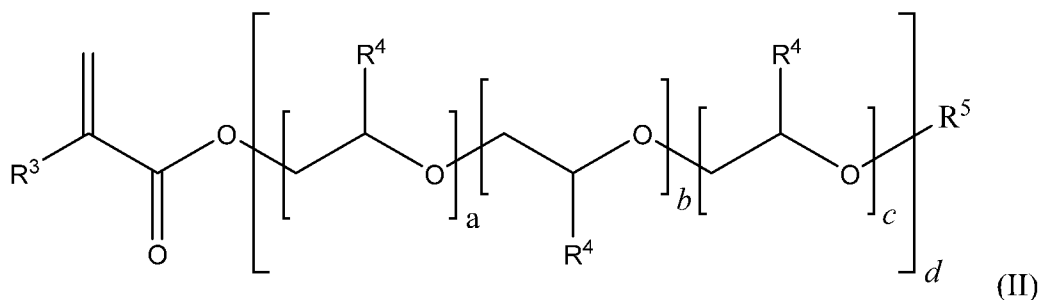
[0017] Preferably, the aqueous personal care rinse off formulation of the present invention, comprises: a dermatologically acceptable vehicle (preferably, wherein the aqueous personal care rinse off formulation comprises 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle); a

dermatologically acceptable cleaning surfactant (preferably, wherein the aqueous personal care rinse off formulation comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant)(preferably, wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant); and a gradient polymer (preferably, wherein the aqueous personal care rinse off formulation comprises 0.1 to 15 wt% (preferably, 0.5 to 10 wt%; more preferably, 0.75 to 5 wt%; most preferably, 1 to 2.5 wt%), based on weight of the aqueous personal care rinse off formulation, of the gradient polymer) comprising: (a) 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; (b) 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural monomer units of C₁₋₈ alkyl (meth)acrylate monomer; (c) > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I



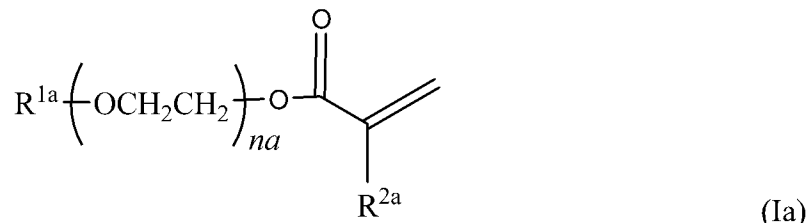
wherein each R¹ is independently selected from a linear saturated C₁₂₋₂₆ alkyl group (preferably, C₁₂₋₂₄ alkyl group; more preferably, C₁₄₋₂₄ alkyl group; most preferably, C₁₆₋₂₂ alkyl group); wherein each R² is independently selected from a hydrogen and a methyl group (preferably, wherein R² is a methyl group) and wherein *n* is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and (d) 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer (e.g., AMPS); wherein the gradient polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more

preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II

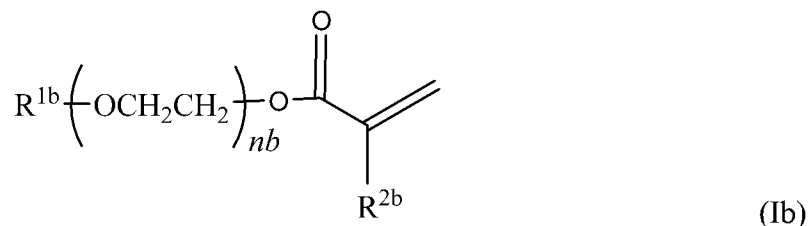


wherein each R^3 is independently selected from -H and -CH₃; wherein each R^4 is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R^5 is independently selected from a -C₁₋₄ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100 and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology. More preferably, the aqueous personal care rinse off formulation of the present invention, comprises: a dermatologically acceptable vehicle (preferably, wherein the aqueous personal care rinse off formulation comprises 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle); a dermatologically acceptable cleaning surfactant (preferably, wherein the aqueous personal care rinse off formulation comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant)(preferably, wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant); and a gradient polymer (preferably, wherein the aqueous personal care rinse off formulation comprises 0.1 to 15 wt% (preferably, 0.5 to 10 wt%; more preferably, 0.75 to 5 wt%; most preferably, 1 to 2.5 wt%), based on weight of the aqueous personal care rinse off formulation, of the gradient polymer) comprising: (a) 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; (b) 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural monomer units of C₁₋₈ alkyl (meth)acrylate monomer; (c) > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I; wherein the specialized associative monomer having

structure I is a blend of a first specialized associative monomer having structure Ia (preferably, 51 to 99 wt%; more preferably, 75 to 97 wt%; most preferably, 85 to 95 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ia)



wherein each R^{1a} is independently selected from a linear saturated C_{12-19} alkyl group (preferably, a linear saturated C_{12-18} alkyl group; more preferably, a linear saturated C_{14-18} alkyl group; most preferably, a linear saturated C_{16-18} alkyl group); wherein each R^{2a} is independently selected from a hydrogen and a methyl group (preferably, wherein R^{2a} is a methyl group) and wherein na is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and a second specialized associative monomer having structure Ib (preferably, 1 to 49 wt%; more preferably, 3 to 25 wt%; most preferably, 6 to 15 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ib)



wherein each R^{1b} is independently selected from a linear saturated C_{20-26} alkyl group (preferably, a linear saturated C_{20-24} alkyl group; more preferably, a linear saturated C_{21-23} alkyl group; most preferably, a linear saturated C_{22} alkyl group); wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group (preferably, a methyl group) and wherein nb is 10 to 30 (preferably, 15 to 30; more preferably, 18 to 28; most preferably, 20 to 28); and (d) 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer (e.g., AMPS); wherein the gradient polymer comprises < 0.02 wt%,

based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II, wherein each R³ is independently selected from -H and -CH₃; wherein each R⁴ is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R⁵ is independently selected from a -C₁₋₄ alkyl group; wherein *a* is 0 to 50; wherein *b* is 0 to 20; wherein *c* is 0 to 50; wherein *a* + *c* is 1 to 100 and wherein *d* is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

[0018] Preferably, the aqueous personal care rinse off formulation of the present invention, comprises 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle. More preferably, the aqueous personal care rinse off formulation of the present invention, comprises: 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle; wherein the dermatologically acceptable vehicle comprises water. Still more preferably, the aqueous personal care rinse off formulation of the present invention, comprises: 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle; wherein the dermatologically acceptable vehicle is selected from the group consisting of water and an aqueous C₁₋₄ alcohol mixture. Most preferably, the aqueous personal care rinse off formulation of the present invention, comprises: 25 to 98.9 wt% (preferably, 30 to 94.5 wt%; more preferably, 40 to 74.5 wt%; most preferably, 45 to 69 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable vehicle, wherein the dermatologically acceptable vehicle is water.

[0019] Preferably, the water used in the aqueous personal care rinse off formulation of the present invention is at least one of distilled water and deionized water. More preferably, the water used in the aqueous personal care rinse off formulation of the present invention is distilled and deionized.

[0020] Preferably, the aqueous personal care rinse off formulation of the present invention, comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant. More preferably, the aqueous personal care rinse off formulation of the present invention, comprises 1 to 60 wt%

(preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant; wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant. Still more preferably, the aqueous personal care rinse off formulation of the present invention, comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant; wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant selected from the group consisting of salts of alanine, arginine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, lysine, phenylalanine, serine, tyrosine, valine, sarcosine and mixture thereof. Yet more preferably, the aqueous personal care rinse off formulation of the present invention, comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant; wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant selected from the group consisting of dipotassium capryloyl glutamate, dipotassium undecylenoyl glutamate, disodium capryloyl glutamate, disodium cocoyl glutamate, disodium lauroyl glutamate, disodium stearyl glutamate, disodium undecylenoyl glutamate, potassium capryloyl glutamate, potassium cocoyl glutamate, potassium lauroyl glutamate, potassium myristoyl glutamate, potassium stearyl glutamate, potassium undecylenoyl glutamate, sodium capryloyl glutamate, sodium cocoyl glutamate, sodium lauroyl glutamate, sodium myristoyl glutamate, sodium olivoyl glutamate, sodium palmitoyl glutamate, sodium stearyl glutamate, sodium undecylenoyl glutamate, cocoyl methyl β -alaninate, lauroyl β -alaninate, lauroyl methyl β -alaninate, myristoyl β -alaninate, potassium lauroyl methyl β -alaninate, sodium cocoyl alaninate, sodium cocoyl methyl β -alaninate and sodium myristoyl methyl β -alaninate palmitoyl glycinate, sodium lauroyl glycinate, sodium cocoyl glycinate, sodium myristoyl glycinate, potassium lauroyl glycinate, potassium cocoyl glycinate, potassium lauroyl sarcosinate, potassium cocoyl sarcosinate, sodium cocoyl sarcosinate, sodium lauroyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate, sodium palmitoyl sarcosinate ammonium lauroyl sarcosinate, sodium lauroyl aspartate, sodium myristoyl aspartate, sodium cocoyl aspartate, sodium caproyl aspartate, disodium lauroyl aspartate, disodium myristoyl aspartate, disodium cocoyl aspartate, disodium caproyl aspartate, potassium lauroyl aspartate, potassium myristoyl aspartate, potassium cocoyl aspartate, potassium caproyl aspartate, dipotassium lauroyl aspartate,

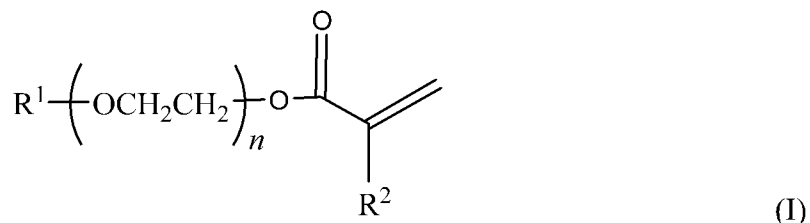
dipotassium myristoyl aspartate, dipotassium cocoyl aspartate, dipotassium caproyl aspartate and mixtures thereof. Most preferably, the aqueous personal care rinse off formulation of the present invention, comprises 1 to 60 wt% (preferably, 5 to 57.5 wt%; more preferably, 25 to 55 wt%; most preferably, 30 to 52.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a dermatologically acceptable cleaning surfactant; wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant selected from the group consisting of sodium cocoyl glutamate, sodium cocoyl alaninate, sodium cocoyl glycinate, sodium lauroyl sarcosinate and mixtures thereof.

[0021] Preferably, the dermatologically acceptable cleaning surfactant comprises a mixture of an amino acid surfactant and a non-amino acid surfactant. More preferably, the dermatologically acceptable cleaning surfactant comprises a mixture of an amino acid surfactant and a non-amino acid surfactant; wherein the amino acid surfactant is selected from the group consisting of salts of alanine, arginine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, lysine, phenylalanine, serine, tyrosine, valine, sarcosine and mixture thereof; and wherein the non-amino acid surfactant is selected from the group consisting of alkyl polyglycosides (e.g., coco glucoside, alkyl xyloside); amine-based surfactants (e.g., stearamidopropyl dimethylamine); amphoacetates (e.g., sodium cocoamphoacetate); betaines (e.g., alkyl betaines such as cetyl betaine and amido betaines such as cocamidopropyl betaine); carboxylates (e.g., sodium lauryl glucose carboxylate); fatty alcohols (e.g., cetearyl alcohol, stearyl alcohol, cetyl alcohol, lauryl alcohol); fatty alkanolamides (e.g., cocamide monoethanolamine, cocamide diethanolamine, soyamide diethanolamine, lauramide diethanolamine, oleamide monoisopropanolamine, stearamide monoethanolamine, myristamide monoethanolamine, lauramide monoethanolamine, capramide diethanolamine, ricinoleamide diethanolamine, myristamide diethanolamine, stearamide diethanolamine, oleylamide diethanolamine, tallowamide diethanolamine, lauramide monoisopropanolamine, tallowamide monoethanolamine, isostearamide diethanolamine, isostearamide monoethanolamine); isethionates (e.g., sodium cocoyl isethionate, sodium lauroyl methyl isethionate); quaternary ammonia compounds (e.g., behentrimonium chloride, cetrimonium chloride); succinates (e.g., disodium lauryl sulfosuccinate); sulfates (e.g., sodium lauryl ether sulfate (SLES)); sulfoacetates (e.g., sodium lauryl sulfoacetate); sulfonates (e.g., sodium C₁₄₋₁₆ olefin sulfonate); sultaines (e.g., cocamidopropyl hydroxysultaine); taurates (e.g., sodium methyl cocoyl taurate) and mixtures thereof. Still more preferably, the dermatologically acceptable cleaning surfactant comprises a mixture of an amino acid surfactant and a non-amino acid surfactant; wherein the amino acid surfactant is selected

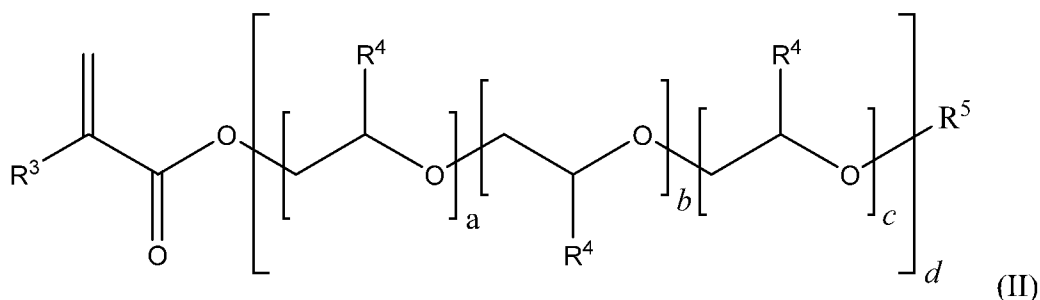
from the group consisting of dipotassium capryloyl glutamate, dipotassium undecylenoyl glutamate, disodium capryloyl glutamate, disodium cocoyl glutamate, disodium lauroyl glutamate, disodium stearoyl glutamate, disodium undecylenoyl glutamate, potassium capryloyl glutamate, potassium cocoyl glutamate, potassium lauroyl glutamate, potassium myristoyl glutamate, potassium stearoyl glutamate, potassium undecylenoyl glutamate, sodium capryloyl glutamate, sodium cocoyl glutamate, sodium lauroyl glutamate, sodium myristoyl glutamate, sodium olivoyl glutamate, sodium palmitoyl glutamate, sodium stearoyl glutamate, sodium undecylenoyl glutamate, cocoyl methyl β -alaninate, lauroyl β -alaninate, lauroyl methyl β -alaninate, myristoyl β -alaninate, potassium lauroyl methyl β -alaninate, sodium cocoyl alaninate, sodium cocoyl methyl β -alaninate and sodium myristoyl methyl β -alaninate palmitoyl glycinate, sodium lauroyl glycinate, sodium cocoyl glycinate, sodium myristoyl glycinate, potassium lauroyl glycinate, potassium cocoyl glycinate, potassium lauroyl sarcosinate, potassium cocoyl sarcosinate, sodium cocoyl sarcosinate, sodium lauroyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate, sodium palmitoyl sarcosinate ammonium lauroyl sarcosinate, sodium lauroyl aspartate, sodium myristoyl aspartate, sodium cocoyl aspartate, sodium caproyl aspartate, disodium lauroyl aspartate, disodium myristoyl aspartate, disodium cocoyl aspartate, disodium caproyl aspartate, potassium lauroyl aspartate, potassium myristoyl aspartate, potassium cocoyl aspartate, potassium caproyl aspartate, dipotassium lauroyl aspartate, dipotassium myristoyl aspartate, dipotassium cocoyl aspartate, dipotassium caproyl aspartate and mixtures thereof; and wherein the non-amino acid surfactant is selected from the group consisting of alkyl polyglycosides (e.g., coco glucoside, alkyl xyloside); betaines (e.g., alkyl betaines such as cetyl betaine and amido betaines such as cocamidopropyl betaine) and mixtures thereof. Most preferably, the dermatologically acceptable cleaning surfactant comprises a mixture of an amino acid surfactant and a non-amino acid surfactant; wherein the amino acid surfactant is selected from the group consisting of sodium cocoyl glutamate, sodium cocoyl alaninate, sodium cocoyl glycinate, sodium lauroyl sarcosinate and mixtures thereof; and wherein the non-amino acid surfactant is selected from the group consisting of coco glucoside, cocamidopropyl betaine and mixtures thereof.

[0022] Preferably, the aqueous personal care rinse off formulation of the present invention comprises 0.1 to 15 wt% (preferably, 0.5 to 10 wt%; more preferably, 0.75 to 5 wt%; most preferably, 1 to 2.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a gradient polymer; wherein the gradient polymer comprises: (a) 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry

weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; (b) 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural monomer units of C₁₋₈ alkyl (meth)acrylate monomer; (c) > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I

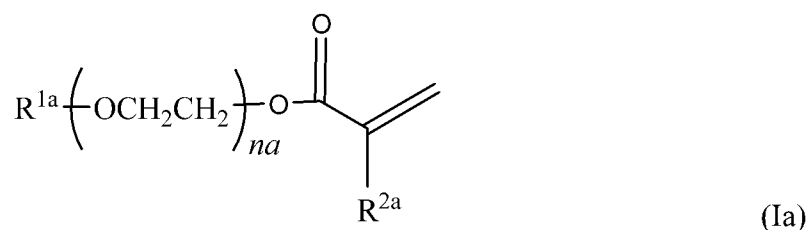


wherein each R¹ is independently selected from a linear saturated C₁₂₋₂₆ alkyl group (preferably, C₁₂₋₂₄ alkyl group; more preferably, C₁₄₋₂₄ alkyl group; most preferably, C₁₆₋₂₂ alkyl group); wherein each R² is independently selected from a hydrogen and a methyl group (preferably, wherein R² is a methyl group) and wherein *n* is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and (d) 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer (e.g., AMPS); wherein the gradient polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II

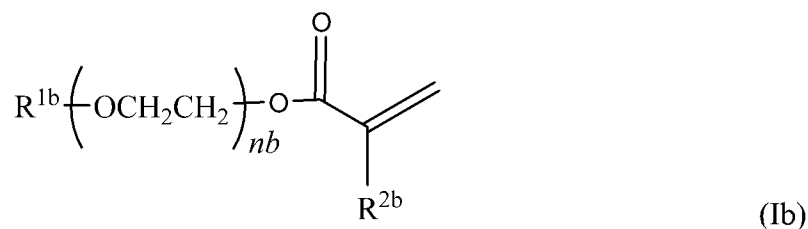


wherein each R³ is independently selected from -H and -CH₃; wherein each R⁴ is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R⁵ is independently

selected from a $-C_{1-4}$ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100 and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology. More preferably, the aqueous personal care rinse off formulation of the present invention comprises 0.1 to 15 wt% (preferably, 0.5 to 10 wt%; more preferably, 0.75 to 5 wt%; most preferably, 1 to 2.5 wt%), based on weight of the aqueous personal care rinse off formulation, of a gradient polymer; wherein the gradient polymer comprises: (a) 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; (b) 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural monomer units of C_{1-8} alkyl (meth)acrylate monomer; (c) > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I; wherein the specialized associative monomer having structure I is a blend of a first specialized associative monomer having structure Ia (preferably, 51 to 99 wt%; more preferably, 75 to 97 wt%; most preferably, 85 to 95 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ia)



wherein each R^{1a} is independently selected from a linear saturated C_{12-19} alkyl group (preferably, a linear saturated C_{12-18} alkyl group; more preferably, a linear saturated C_{14-18} alkyl group; most preferably, a linear saturated C_{16-18} alkyl group); wherein each R^{2a} is independently selected from a hydrogen and a methyl group (preferably, wherein R^2 is a methyl group) and wherein na is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and a second specialized associative monomer having structure Ib (preferably, 1 to 49 wt%; more preferably, 3 to 25 wt%; most preferably, 6 to 15 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ib)



wherein each R^{1b} is independently selected from a linear saturated C_{20-26} alkyl group (preferably, a linear saturated C_{20-24} alkyl group; more preferably, a linear saturated C_{21-23} alkyl group; most preferably, a linear saturated C_{22} alkyl group); wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group (preferably, a methyl group) and wherein nb is 10 to 30 (preferably, 15 to 30; more preferably, 18 to 28; most preferably, 20 to 28); and (d) 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer (e.g., AMPS); wherein the gradient polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II, wherein each R^3 is independently selected from -H and -CH₃; wherein each R^4 is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R^5 is independently selected from a -C₁₋₄ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100 and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

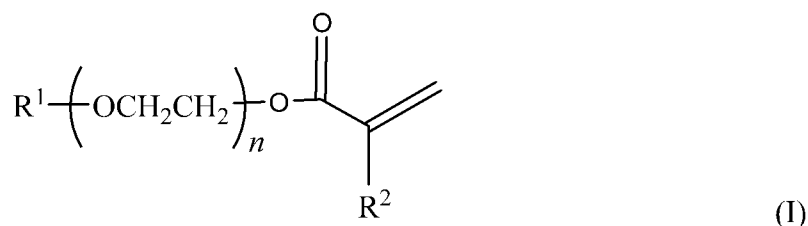
[0023] Preferably, the gradient polymer comprises 90 to 100 wt% (preferably, 95 to 100 wt%; more preferably, 98 to 100 wt%; still more preferably, 99 to 100 wt%; yet more preferably, 99.9 to 100 wt%; most preferably, 100 wt%) of the structural monomer units present in the gradient polymer are structural monomer units of (a)-(d). The structural monomer units of the gradient polymer do not include end groups on the gradient polymer derived from chain transfer agent or initiator (e.g., residues of chain transfer agent).

[0024] Preferably, the gradient polymer comprises 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; wherein the (meth)acrylic acid monomer is selected from the group consisting of methacrylic acid, acrylic

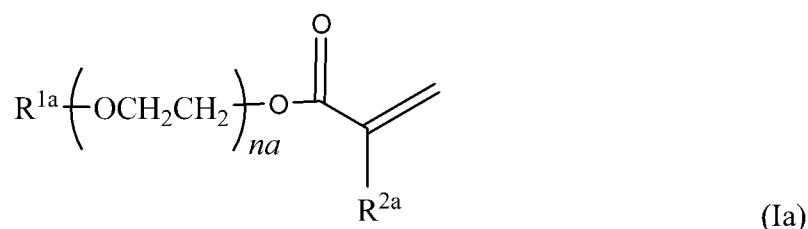
acid and mixtures thereof. More preferably, the gradient polymer comprises 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; wherein the (meth)acrylic acid monomer is a mixture of methacrylic acid and acrylic acid. Most preferably, the gradient polymer comprises 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; wherein the (meth)acrylic acid monomer is a mixture of 30 to 60 wt% (preferably, 32 to 58 wt%; more preferably, 33 to 55 wt%), based on weight of the mixture, of methacrylic acid and 40 to 70 wt% (preferably, 32 to 58 wt%; more preferably, 33 to 55 wt%), based on weight of the mixture, of acrylic acid.

[0025] Preferably, the gradient polymer comprises 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate monomer (preferably, C₁₋₆ alkyl (meth)acrylate monomer; more preferably, C₂₋₃ alkyl (meth)acrylate monomer; most preferably, C₂ alkyl acrylate monomer). More preferably, the gradient polymer comprises 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate monomer; wherein the C₁₋₈ alkyl (meth)acrylate monomer is selected from the group consisting of ethyl (meth)acrylate, propyl (meth)acrylate and mixtures thereof (preferably, ethyl acrylate, propyl acrylate and mixtures thereof). Most preferably, the gradient polymer comprises 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate monomer; wherein the C₁₋₈ alkyl (meth)acrylate monomer is ethyl acrylate.

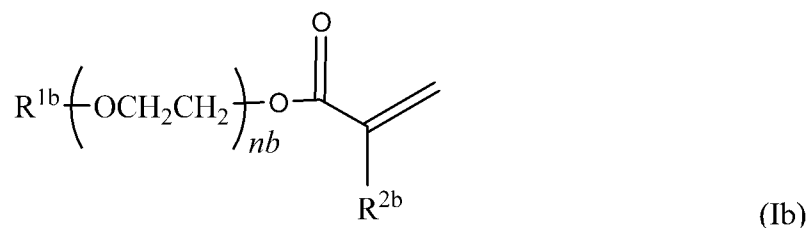
[0026] Preferably, the gradient polymer comprises > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I



wherein each R^1 is independently selected from a linear saturated C_{12-26} alkyl group (preferably, C_{12-24} alkyl group; more preferably, C_{14-24} alkyl group; most preferably, C_{16-22} alkyl group); wherein each R^2 is independently selected from a hydrogen and a methyl group (preferably, wherein R^2 is a methyl group) and wherein n is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26). More preferably, the gradient polymer comprises > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I; wherein the specialized associative monomer having structure I is a blend of a first specialized associative monomer having structure Ia (preferably, 51 to 99 wt%; more preferably, 75 to 97 wt%; most preferably, 85 to 95 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ia)



wherein each R^{1a} is independently selected from a linear saturated C_{12-19} alkyl group (preferably, a linear saturated C_{12-18} alkyl group; more preferably, a linear saturated C_{14-18} alkyl group; most preferably, a linear saturated C_{16-18} alkyl group); wherein each R^{2a} is independently selected from a hydrogen and a methyl group (preferably, wherein R^2 is a methyl group) and wherein na is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and a second specialized associative monomer having structure Ib (preferably, 1 to 49 wt%; more preferably, 3 to 25 wt%; most preferably, 6 to 15 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ib)



wherein each R^{1b} is independently selected from a linear saturated C_{20-26} alkyl group (preferably, a linear saturated C_{20-24} alkyl group; more preferably, a linear saturated C_{21-23} alkyl group; most preferably, a linear saturated C_{22} alkyl group); wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group (preferably, a

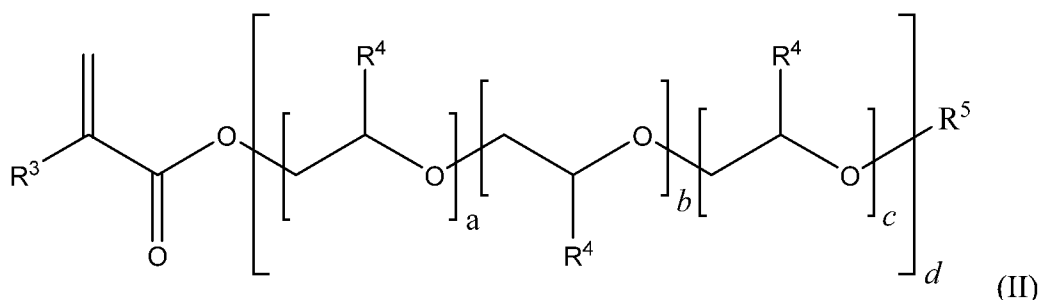
methyl group) ; and wherein nb is 10 to 30 (preferably, 15 to 30; more preferably, 18 to 28; most preferably, 20 to 28)(preferably, wherein R^{1a} and R^{1b} differ by less than 8 carbon atoms (more preferably, by less than 7 carbon atoms)).

[0027] Preferably, the gradient polymer comprises 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer. More preferably, the gradient polymer comprises 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the multiethylenically unsaturated monomer is selected from the group consisting of polyunsaturated aromatic monomers (e.g., divinyl benzene, divinyl naphthalene, trivinyl benzene); polyunsaturated alicyclic monomers (e.g., 1,2,4-trivinylcyclohexane); difunctional esters of phthalic acid (e.g., diallyl phthalate); polyunsaturated aliphatic monomers (e.g., isoprene, butadiene, 1,5-hexadiene, 1,5,9-decatriene, 1,9-decadiene, 1,5-heptadiene); polyalkenyl ethers (e.g., triallyl pentaerythritol, diallyl pentaerythritol, diallyl sucrose, octaallyl sucrose, trimethylolpropane diallyl ether); polyunsaturated esters of polyalcohols or polyacids (e.g., 1,6-hexanediol di(meth)acrylate, tetramethylene tri(meth)acrylate, allyl acrylate, diallyl itaconate, diallyl fumarate, diallyl maleate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, polyethylene glycol di(meth)acrylate); alkylene bisacrylamides (e.g., methylene bisacrylamide, propylene bisacrylamide); hydroxy and carboxy derivatives of methylene bis-acrylamide (e.g., N,N'-bismethylol methylene bisacrylamide); polyethyleneglycol di(meth)acrylates (e.g., ethyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate); polyunsaturated silanes (e.g., dimethyldivinylsilane, methyltrivinylsilane, allyldimethylvinylsilane, diallyldimethylsilane, tetravinylsilane); polyunsaturated stannanes (e.g., tetraallyl tin, diallyldimethyl tin) and mixtures thereof. Still more preferably, the gradient polymer comprises 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the multiethylenically unsaturated monomer is a polyalkenyl ether. Most preferably, the gradient polymer comprises 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the multiethylenically unsaturated monomer is trimethylolpropane diallyl ether.

[0028] Preferably, the gradient polymer further comprises 0.01 to 2 wt% (preferably, 0.02 to 1 wt%; more preferably, 0.04 to 0.5 wt%; most preferably, 0.06 to 0.1 wt%), based on dry weight of the gradient polymer, of residues of chain transfer agent. More preferably, the gradient polymer further comprises 0.01 to 2 wt% (preferably, 0.02 to 1 wt%; more preferably, 0.04 to 0.5 wt%; most preferably, 0.06 to 0.1 wt%), based on dry weight of the gradient polymer, of residues of chain transfer agent; wherein the chain transfer agent is selected from the group consisting of thio and disulfide containing compounds (e.g., C₁₋₁₈ alkyl mercaptans, mercaptocarboxylic acids, mercaptocarboxylic esters, thioesters, C₁₋₁₈ alkyl disulfides, aryl disulfides, polyfunctional thiols); phosphites and hypophosphites; haloalkyl compounds (e.g., carbon tetrachloride, bromotrichloromethane); unsaturated chain transfer agents (e.g., alpha-methylstyrene) and mixtures thereof. Still more preferably, the gradient polymer further comprises 0.01 to 2 wt% (preferably, 0.02 to 1 wt%; more preferably, 0.04 to 0.5 wt%; most preferably, 0.06 to 0.1 wt%), based on dry weight of the gradient polymer, of residues of chain transfer agent; wherein the chain transfer agent is a C₁₋₁₈ alkyl mercaptan. Most preferably, the gradient polymer further comprises 0.01 to 2 wt% (preferably, 0.02 to 1 wt%; more preferably, 0.04 to 0.5 wt%; most preferably, 0.06 to 0.1 wt%), based on dry weight of the gradient polymer, of residues of chain transfer agent; wherein the chain transfer agent is *n*-dodecyl mercaptan.

[0029] Preferably, the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer; wherein the sulfonated monomer is selected from the group consisting of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 2-methacrylamido-2-methylpropane sulfonic acid, 4-styrenesulfonic acid, vinyl sulfonic acid, 3-allyloxy sulfonic acid, 2-hydroxy-1-propane sulfonic acid (HAPS), 2-sulfoethyl(meth)acrylic acid, 2-sulfopropyl(meth)acrylic acid, 3-sulfopropyl(meth)acrylic acid, 4-sulfobutyl(meth)acrylic acid, salts thereof and mixtures thereof.

[0030] Preferably, the gradient polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II



wherein each R³ is independently selected from -H and -CH₃; wherein each R⁴ is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R⁵ is independently selected from a -C₁₋₄ alkyl group; wherein *a* is 0 to 50; wherein *b* is 0 to 20; wherein *c* is 0 to 50; wherein *a* + *c* is 1 to 100 and wherein *d* is 1 to 4.

[0031] Preferably, the gradient polymer comprises < 0.01 wt% (preferably, < 0.005 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of monomer selected from the group consisting of styrene, butyl acrylate, ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate and mixtures thereof.

[0032] Preferably, the gradient polymer comprises < 2 wt% (preferably, < 1 wt%; more preferably, < 0.5 wt%; still more preferably, < 0.1 wt%; yet more preferably, < 0.01 wt%; still yet more preferably, < 0.001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of monomer selected from the group consisting of C₆₋₁₈ alkyl (meth)acrylate, vinyl alkanoate having 6 to 18 carbon atoms, N-vinyl alkylamide having 6 to 18 carbon atoms, N-alkyl (meth)acrylamide having 6 to 18 carbon atoms and mixtures thereof.

[0033] Preferably, the gradient polymer comprises: (a) 5 to 35 wt% (preferably, 10 to 35 wt%; more preferably, 20 to 34 wt%; most preferably, 26 to 32 wt%), based on dry weight of the gradient polymer, of structural monomer units of (meth)acrylic acid monomer; (b) 35 to 65 wt% (preferably, 40 to 60 wt%; more preferably, 45 to 55 wt%; most preferably, 48 to 54 wt%), based on dry weight of the gradient polymer, of structural monomer units of C₁₋₈ alkyl (meth)acrylate monomer; (c) > 10 to 30 wt% (preferably, 12 to 30 wt%; more preferably, 15 to 25 wt%; most preferably, 16 to 20 wt%), based on dry weight of the gradient polymer, of structural monomer units of a specialized associative monomer having structure I; wherein the specialized associative monomer having structure I is a blend of a first specialized associative monomer having structure Ia (preferably, 51 to 99 wt%; more preferably, 75 to 97 wt%; most preferably, 85 to 95 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ia),

wherein each R^{1a} is independently selected from a linear saturated C_{12-19} alkyl group (preferably, a linear saturated C_{12-18} alkyl group; more preferably, a linear saturated C_{14-18} alkyl group; most preferably, a linear saturated C_{16-18} alkyl group); wherein each R^{2a} is independently selected from a hydrogen and a methyl group (preferably, wherein R^2 is a methyl group) and wherein na is 10 to 30 (preferably, 12 to 30; more preferably, 15 to 28; most preferably, 18 to 26); and a second specialized associative monomer having structure Ib (preferably, 1 to 49 wt%; more preferably, 3 to 25 wt%; most preferably, 6 to 15 wt%), based on weight of the specialized associative monomer having structure I, of the first specialized associative monomer having structure Ib), wherein each R^{1b} is independently selected from a linear saturated C_{20-26} alkyl group (preferably, a linear saturated C_{20-24} alkyl group; more preferably, a linear saturated C_{21-23} alkyl group; most preferably, a linear saturated C_{22} alkyl group); wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group (preferably, a methyl group) and wherein nb is 10 to 30 (preferably, 15 to 30; more preferably, 18 to 28; most preferably, 20 to 28); and (d) 0.01 to 2 wt% (preferably, 0.05 to 1 wt%; more preferably, 0.08 to 0.5 wt%; most preferably, 0.1 to 0.2 wt%), based on dry weight of the gradient polymer, of structural monomer units of multiethylenically unsaturated monomer; wherein the gradient polymer comprises < 0.05 wt% (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of sulfonated monomer (e.g., AMPS); wherein the gradient polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, (preferably, < 0.01 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit) of structural monomer units of monomer having structure II, wherein each R^3 is independently selected from -H and -CH₃; wherein each R^4 is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R^5 is independently selected from a -C₁₋₄ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100 and wherein d is 1 to 4; wherein the gradient polymer has a gradient polymeric morphology; and with any one or more of the following provisos (i)-(v): (i) wherein R^{1a} and R^{1b} differ by less than 8 carbon atoms (preferably, < 7 carbon atoms); (ii) wherein the structural monomer units of (meth)acrylic acid monomer include structural monomer units of both methacrylic acid and acrylic acid; (iii) wherein the gradient polymer comprises < 0.01 wt% (preferably, < 0.005 wt%; more preferably, < 0.001 wt%; still more preferably, < 0.0001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of monomer selected from the group consisting of styrene, butyl

acrylate, ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, butyl acrylate and mixtures thereof; (iv) wherein the gradient polymer comprises < 2 wt% (preferably, < 1 wt%; more preferably, < 0.5 wt%; still more preferably, < 0.1 wt%; yet more preferably, < 0.01 wt%; still yet more preferably, < 0.001 wt%; most preferably, less than detectable limit), based on dry weight of the gradient polymer, of structural monomer units of monomer selected from the group consisting of alkyl (meth)acrylate having 6 to 18 carbon, vinyl alkanoate having 6 to 18 carbon atoms, N-vinyl alkylamide having 6 to 18 carbon atoms, N-alkyl (meth)acrylamide having 6 to 18 carbon atoms and mixtures thereof; and/or (v) wherein the gradient polymer comprises 90 to 100 wt% (preferably, 95 to 100 wt%; more preferably, 98 to 100 wt%; still more preferably, 99 to 100 wt%; yet more preferably, 99.9 to 100 wt%; most preferably, 100 wt%) of the structural monomer units present in the gradient polymer are structural monomers units of (a)-(d).

[0034] Preferably, the aqueous personal care rinse off formulation of the present invention, further comprises at least one ingredient selected from the group consisting of an absorbent; an aesthetic enhancer (e.g., starch); an alpha hydroxy acid; an antiaging agent; an antidandruff agent; an antifungal; an antimicrobial agent; an antioxidant (e.g., butylated hydroxytoluene); an antiseptic; an antistatic agent; a bioactive agent; a bleaching agent; a chelating agent; a colorant; a conditioning agent (e.g., silicone, polyquaternium, cationic guar); a dye; an emollient; an emulsifying agent; a film former (e.g., water proofing agent); a fixative polymer; a foaming agent; a fragrance; a hard particle; a humectant (e.g., glycerin, sorbitol, monoglycerides, lecithins, glycolipids, fatty alcohols, fatty acids, polysaccharides, sorbitan esters, polysorbates (e.g., Polysorbate 20, Polysorbate 40, Polysorbate 60, and Polysorbate 80), diols (e.g., propylene glycol), diol analogs, triols, triol analogs, cationic polymeric polyols); a lubricating agent; an opacifier; a pearlizing agent; a penetrant; a pH adjusting agent; a pigment; a plant extract; a preservative (e.g., benzoic acid, sorbic acid, phenoxyethanol); a protein/amino acid; a rheology modifier; a salt (e.g., NaCl); a sensory modifier; a slip agent; a soap; a soft particle; a sunscreen additive; a suspending agent; a UV light inhibitor; a vitamin and mixtures thereof.

[0035] Preferably, the aqueous personal care rinse off formulation of the present invention, further comprises 0 to 10 wt% (preferably, 0 to 3 wt%), based on weight of the aqueous personal care rinse off formulation, of a salt (e.g., NaCl).

[0036] Preferably, the aqueous personal care rinse off formulation of the present invention, further comprises an antimicrobial agent. More preferably, the aqueous personal care rinse off formulation of the present invention, further comprises an antimicrobial agent; wherein

the antimicrobial agent is selected from the group consisting of phenoxyethanol, benzoic acid, benzyl alcohol, sodium benzoate, DMDM hydantoin, 2-ethylhexyl glyceryl ether and isothiazolinone (e.g., methylchloroisothiazolinone, methylisothiazolinone). Still more preferably, the aqueous personal care rinse off formulation of the present invention, further comprises an antimicrobial agent; wherein the antimicrobial agent is an isothiazolinone (more preferably, wherein the antimicrobial is selected from the group consisting of methylisothiazolinone, methylchloroisothiazolinone and mixtures thereof; most preferably, wherein the biocide is methylisothiazolinone).

[0037] Preferably, the aqueous personal care rinse off formulation of the present invention, further comprises a pH adjusting agent. More preferably, the aqueous personal care rinse off formulation of the present invention, further comprises a pH adjusting agent. Most preferably, the aqueous personal care rinse off formulation of the present invention, further comprises a pH adjusting agent; wherein the aqueous personal care rinse off formulation has a pH of 4.5 to 9 (preferably, 5 to 8; most preferably, 5 to 7).

[0038] Preferably, the pH adjusting agent is selected from the group consisting of at least one of citric acid, lactic acid, hydrochloric acid, aminoethyl propanediol, triethanolamine, monoethanolamine, sodium hydroxide, potassium hydroxide, amino-2-methyl-1-propanol. More preferably, the pH adjusting agent is selected from the group consisting of at least one of citric acid, lactic acid, sodium hydroxide, potassium hydroxide, triethanolamine, amino-2-methyl-1-propanol. Still more preferably, the pH adjusting agent includes is triethanolamine. Most preferably, the pH adjusting agent is triethanolamine.

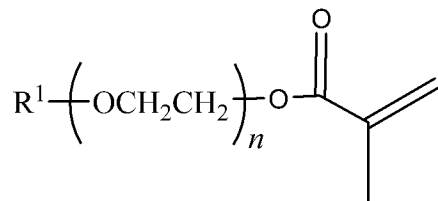
[0039] Preferably, the method of cleaning at least one of mammalian skin and hair (preferably, at least one of human skin and hair) of the present invention, comprises: applying an aqueous personal care rinse off formulation of the present invention to the skin or hair of a mammal (preferably, skin or hair of a human); and rinsing the aqueous personal care rinse off formulation from the skin or hair with a rinse water.

[0040] Some embodiments of the present invention will now be described in detail in the following **Examples**.

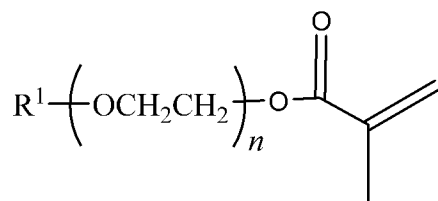
Synthesis S1: Gradient polymer

[0041] To a 3 L, 4 necked round bottom reactor equipped with a mechanical stirrer, thermocouple, condenser, and nitrogen sparge was added deionized water (350 g) and sodium lauryl sulfate (9.1 g). The reactor was purged with nitrogen and warmed to 85° C. Separately the following were prepared, namely: (1) a monomer emulsion A was prepared

from deionized water (450 g); sodium lauryl sulfate (16.4 g); ethyl acrylate (EA)(262 g); a lipophilically modified monomer (Lipo 1) (82.1 g) having the following structure



wherein R^1 was a linear saturated C_{16-18} alkyl group and n was an average of 18 to 26; a lipophilically modified monomer (Lipo 2) (9.6 g) having the following structure



wherein R^1 was a linear saturated C_{22} alkyl group and n was an average of 20 to 28; methacrylic acid (MAA_A)(45.68 g); acrylic acid (AA)(101.1 g) and n -dodecyl mercaptan (n -DDM)(0.4 g); (2) a monomer emulsion additive B was prepared by mixing deionized water (70 g); sodium lauryl sulfate (9.1 g); trimethylolpropane diallyl ether (x-link)(0.81 g) and methacrylic acid (MAA_B)(4.82 g); (3) an initiator solution (C1) was prepared by dissolving ammonium persulfate (0.35 g) in deionized water (15 g) and (4) an initiator solution (C2) was prepared by dissolving ammonium persulfate (0.55 g) in deionized water (84 g). At $\sim 85^\circ\text{C}$ reactor temperature, the reactor was charged with initiator solution (C1). Then monomer emulsion (A) was charged into the reactor while monomer emulsion additive (B) was charged simultaneously into monomer emulsion (A). The rate was controlled so that the feed of monomer emulsion (A) started at $\frac{1}{2} \times$ speed during the first 10 minutes and at $1 \times$ speed until finished at 120 min. and where feed of monomer emulsion additive (B) finished in 100 min. Simultaneously, initiator solution (C2) was feed into the reactor over 125 min. After these additions were completed, the monomer emulsion and initiator feed lines were rinsed with deionized water followed with monomer chasing with free radical catalyst and activator.

Syntheses S2-S4: Gradient polymer

[0042] The gradient polymers in **Syntheses S2-S4** were prepared according to the procedure described in **Synthesis S1** except with the composition changes as described in **TABLE 1**.

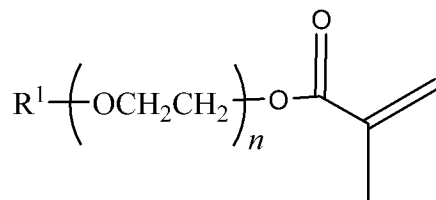
TABLE 1

Syn.	Reactant (g)							
	Emulsion A						Emulsion additive B	
	EA	Lipo 1	Lipo 2	MAA _A	AA	<i>n</i> -DDM	MAA _B	x-link
S1	262	82.1	9.6	45.68	101.1	0.4	4.82	0.81
S2	262	82.1	9.6	53.78	91	0.4	6.82	0.81
S3	262	82.1	9.6	61.88	80.9	0.4	8.82	0.81
S4	262	82.1	9.6	70.08	70.7	0.4	10.82	0.81

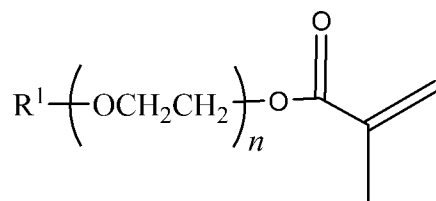
Synthesis S5: Non-gradient polymer

[0043] To a 3 L, 4 necked round bottom reactor equipped with a mechanical stirrer, thermocouple, condenser, and nitrogen sparge was added deionized water (275 g) and sodium lauryl sulfate (9.1 g). The reactor was purged with nitrogen and warmed to 85° C.

Separately the following were prepared, namely: (1) a monomer emulsion A was prepared from deionized water (570 g); sodium lauryl sulfate (25.5 g); ethyl acrylate (EA)(262 g); a lipophilically modified monomer (Lipo 1) (82.1 g) having the following structure



wherein R¹ was a linear saturated C₁₆₋₁₈ alkyl group and *n* was an average of 18 to 26; a lipophilically modified monomer (Lipo 2) (9.6 g) having the following structure



wherein R¹ was a linear saturated C₂₂ alkyl group and *n* was an average of 20 to 28; methacrylic acid (MAA)(50.5 g); acrylic acid (AA)(101.1 g); *n*-dodecyl mercaptan (*n*-DDM)(0.4 g) and trimethylolpropane diallyl ether (x-link)(0.81 g); (2) an initiator solution (C1) was prepared by dissolving ammonium persulfate (0.35 g) in deionized water (15 g) and (3) an initiator solution (C2) was prepared by dissolving ammonium persulfate (0.55 g) in deionized water (84 g). At ~85 °C reactor temperature, the reactor was charged with initiator solution (C1). Then monomer emulsion (A) was charged into the reactor. The rate was controlled so that the feed of monomer emulsion (A) started at ½ x speed during the first 10 minutes and at 1x speed until finished at 120 min. Separately, initiator solution (C1) was started simultaneously with the feed of monomer emulsion (A) and was fed into the reactor over 125 min. After these additions were completed, the monomer and initiator feed lines

were rinsed with deionized water followed with monomer chasing with free radical catalyst and activator.

Syntheses S6-S8: Non-gradient polymer

[0044] The non-gradient polymers in **Syntheses S6-S8** were prepared according to the procedure described in **Synthesis S5** except with the composition changes as described in **TABLE 2**.

TABLE 2

<u>Syn.</u>	<u>Reactant (g)</u>						
	<u>EA</u>	<u>Lipo 1</u>	<u>Lipo 2</u>	<u>MAA_A</u>	<u>AA</u>	<u>n-DDM</u>	<u>x-link</u>
S5	262	82.1	9.6	50.5	101.1	0.4	0.81
S6	262	82.1	9.6	60.6	91	0.4	0.81
S7	262	82.1	9.6	70.7	80.9	0.4	0.81
S8	262	82.1	9.6	80.9	70.7	0.4	0.81

Viscosity and Turbidity Measurements

[0045] Solubilized viscosity and turbidity of solution containing 0.75% polymer active was determined for each of the polymers prepared according to **Syntheses S1-S8** as reported in **TABLE 3** using the following procedure:

1. Weighed out sufficient polymer to provide 0.75% polymer in final formulation.
2. Prediluted with deionized water to make 169 g solution.
3. Added 11.0 g of 20% w/w sodium hydroxide solution in water and stirred efficiently with overhead stirrer until homogenous.
4. Equilibrated in a war water bath for 10-15 min. so the internal temperature of the solution was 20 °C.
5. Measured pH between 7.8 to 10. Adjusted with 20% sodium hydroxide as necessary.
6. Measured viscosity at 20 °C and 0.3, 3, 6, 12, 20, 30 and 60 rpm using Brookfield viscometer with corresponding spindles to obtain measurements with at least 10% of scale.
7. Transferred sample into 1 oz vial for turbidity measurement.
8. Spun 1 oz vials on centrifuge at 3,500 rpm for 20 min.
9. Measured turbidity in Nephelometric Turbidity Units (NTU) on turbidity meter at 20 °C.

Results of viscosity and turbidity measurements are reported in **TABLE 3**.

TABLE 3

Syn.	Viscosity (mPa·s)						NTU
	3 rpm	6 rpm	12 rpm	20 rpm	30 rpm	60 rpm	
S1	26,200	13,600	7,550	4,590	3,440	1,950	17.0
S2	25,400	13,200	7,150	4,350	3,100	1,810	14.3
S3	31,800	17,800	9,430	5,850	4,200	2,340	9.0
S4	41,000	20,800	11,200	6,870	5,000	2,700	9.7
S5	4,600	2,680	1,570	1,068	840	512	69.1
S6	5,080	2,980	1,710	1,116	852	528	79.0
S7	10,080	5,520	3,130	2,070	1,504	888	63.8
S8	11,160	6,280	3,450	2,190	1,660	980	60.5

Comparative Examples CF1-CF6 and Examples F1-F6: Cleansing Formulations

[0046] Aqueous personal care cleansing formulations were prepared in each of **Comparative Examples CF1-CF6** and **Examples F1-F6** having the formulations noted in **TABLE 4**.

[0047] The Phase A components, if any, for each of **Comparative Examples CF1-CF6** and **Examples F1-F6** were mixed with mild agitation until dissolved. The Phase B components were mixed together in a separate container. The mixed Phase B components were then slowly added into the mixed Phase A components, if any. The Phase C components were then added into the mixed Phase A, if any, and Phase B components. The appropriate Phase D component was then mixed in as need to adjust to the pH noted in **TABLE 4**. The viscosity of the resulting aqueous personal care cleaning formulation was then measured at 20 °C using Brookfield viscometer with correspondent spindles as listed in **TABLE 5**.

TABLE 4

Phase	Ingredient	Example (wt%)											
		CF1	CF2	CF3	CF4	CF5	CF6	F1	F2	F3	F4	F5	F6
A	Water	40.0	40	40	40	40	--	40.0	40	40	40	40	--
	Polyquaternium-10 ¹	0.2	0.2	0.2	0.2	0.2	--	0.2	0.2	0.2	0.2	0.2	--
B	Sodium cocoyl glutamate ²	36.0	--	--	--	--	36.0	36.0	--	--	--	--	36.0
	Sodium lauroyl sarcosinate ³	--	--	--	--	30	--	--	--	--	--	30	--
	Sodium cocoyl alaninate ⁴	--	30	--	--	--	--	--	30	--	--	--	--
	Sodium cocoyl glycinate ⁵	--	--	30	30	--	--	--	--	30	30	--	--
	Cocamidopropyl betaine ⁶	8.57	8.57	8.57	8.57	8.57	4.29	8.57	8.57	8.57	8.57	8.57	4.29
	Coco Glucoside ⁷	6.0	6.0	6.0	6.0	6.0	--	6.0	6.0	6.0	6.0	6.0	--
C	Disodium cocoamphodiacetate ⁸	--	--	--	--	--	4.62	--	--	--	--	--	4.62
	Synthesis S4	--	--	--	--	--	--	2.0	2.0	1.8	1.5	2.0	2.0
	Synthesis S8	2.0	2.0	1.8	1.5	2.0	2.0	--	--	--	--	--	--
	Water	qs 100											
D	20% aq NaOH or 25% aq. Citric acid	6.5	7.0	7.5	7.5	6.5	6.5	6.5	7.0	7.5	7.5	6.5	6.5
E	Phenoxyethanol (and) ethylhexylglycerin ⁹	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
¹ UCARE™ JR-30M polymer from The Dow Chemical Company ² Puji AS02-25 (25%) from Changsha PUJI Biotechnology Co., Ltd. ³ Puji AS02-30 (30%) from Changsha PUJI Biotechnology Co., Ltd. ⁴ Puji YB2-30 (30%) from Changsha PUJI Biotechnology Co., Ltd. ⁵ Puji YC02-30 (30%) from Changsha PUJI Biotechnology Co., Ltd. ⁶ TC-CAB 35 (35%) from Guangzhou Tinci Materials Technology Co., Ltd. ⁷ ECOSENSE 919 (50%) from The Dow Chemical Company ⁸ Dehyton DC (39%) from BASF ⁹ Euxyl PE 9010 from Ashland													

TABLE 5

<u>Example</u>	<u>Additive</u>	<u>Viscosity (cP)</u>
CF1	Synthesis S8	11,717
CF2	Synthesis S8	13,537
CF3	Synthesis S8	34,893
CF4	Synthesis S8	4,459
CF5	Synthesis S8	5,799
CF6	Synthesis S8	6,119
F1	Synthesis S4	58,188
F2	Synthesis S4	39,292
F3	Synthesis S4	92,680
F4	Synthesis S4	16,436
F5	Synthesis S4	12,737
F6	Synthesis S4	12,237

Comparative Examples CF7-CF10 and Examples F7-F10: Cleansing Formulations

[0048] Aqueous personal care cleansing formulations were prepared in each of **Comparative Examples CF7-CF10** and **Examples F7-F10** having the formulations noted in **TABLE 6**.

The Phase A components were mixed together. The mixed Phase B components were then slowly added into the mixed Phase A components. The appropriate Phase C component was mixed into the mixed Phase A and Phase B components as needed to adjust the pH. The viscosity of the resulting aqueous personal care cleaning formulation was then measured at 20 °C using Brookfield viscometer with correspondent spindles at 20 rpm as listed in **TABLE 7**. The turbidity of each formulation was measured using a Micro 100 Turbidimeter (HF Scientific, Inc.) as listed in **TABLE 7**.

TABLE 6

Phase	Ingredient	Example (wt%)									
		CF7	CF8	CF9	CF10	F7	F8	F9	F10		
A	Water	59.0	51.84	52.02	52.54	59.0	51.84	52.02	52.54		
	Sodium cocoyl glutamate ¹	40.0	--	--	--	40.0	--	--	--		
	Sodium lauroyl sarcosinate ²	--	33.33	--	--	--	33.33	--	--		
	Sodium cocoyl alaninate ³	--	--	33.33	--	--	--	33.33	--		
	Sodium cocoyl glycinate ⁴	--	--	--	33.33	--	--	--	33.33		
B	Synthesis S4	--	--	--	--	2.0	2.0	2.0	2.0		
	Synthesis S8	2.0	2.0	2.0	2.0	--	--	--	--		
C	20% aq NaOH or 25% aq. Citric acid soln.	6.6	6.9	6.8	6.1	6.5	6.6	6.6	6.6		
D	Phenoxyethanol (and) ethylhexylglycerin ⁵	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0		
	Water	qs 100									
	Puji AS02-25 (25%) from Changsha PUJI Biotechnology Co., Ltd.										
	Puji AS02-30 (30%) from Changsha PUJI Biotechnology Co., Ltd.										
	Puji YB2-30 (30%) from Changsha PUJI Biotechnology Co., Ltd.										
	Puji YC02-30 (30%) from Changsha PUJI Biotechnology Co., Ltd.										
	Euxyl PE 9010 from Ashland										

TABLE 7

Example	Additive	Viscosity (cP)	Turbidity (NTU)
CF7	Synthesis S8	1,460	41.5
CF8	Synthesis S8	17,730	42.8
CF9	Synthesis S8	13,760	18.8
CF10	Synthesis S8	225	21.8
F7	Synthesis S4	11,890	12.1
F8	Synthesis S4	49,350	3.0
F9	Synthesis S4	30,150	4.3
F10	Synthesis S4	3,150	6.1

Rheological Data

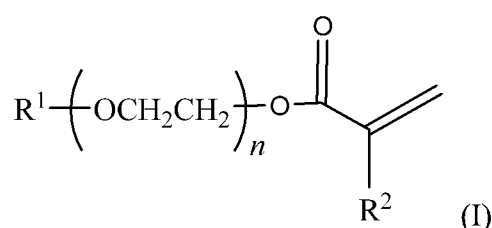
[0049] The rheology of the aqueous personal care cleansing formulations prepared according to **Comparative Examples CF7-CF10** and **Examples F7-F10** were characterized using a Discovery HR-3 Hybrid Rheometer (TA Instruments) with 40 mm parallel plate geometry. All testing was done at 25 °C. The tests included amplitude sweep with oscillation displacement from 0.0002 to 0.15 rad at 1 rad/s, and a flow sweep at shear rate of 0.01 to 500 s⁻¹. The G', G'' and tan δ values were obtained from the amplitude in the linear viscoelastic region, and the viscosity values were obtained from the shear rate sweep as listed in **TABLE 8**.

Table 8

Ex	Additive	G' (Pa)	G'' (Pa)	Tan(delta) (Radians)	Viscosity (Pa·s) @				
					Zero	0.1 s⁻¹	1 s⁻¹	10 s⁻¹	100 s⁻¹
CF7	Syn. S8	1.9	1.5	0.8	10.6	3.4	1.2	1.5	0.3
CF8	Syn. S8	16.0	11.5	0.7	133.5	48.8	30.4	10.9	1.6
CF9	Syn. S8	11.3	7.0	0.6	94.0	30.0	16.6	8.6	1.8
CF10	Syn. S8	0.3	0.5	1.4	2.8	1.3	0.4	0.2	0.2
F7	Syn. S4	17.6	8.9	0.5	139.3	32.7	13.1	7.7	1.3
F8	Syn. S4	48.5	50.7	1.0	440.8	149.2	65.5	26.7	4.1
F9	Syn. S4	33.6	28.5	0.9	308.3	88.5	36.4	16.3	5.2
F10	Syn. S4	10.6	4.8	0.5	93.0	18.3	4.6	1.9	1.2

We claim:

1. An aqueous personal care rinse off formulation, comprising:
 - a dermatologically acceptable vehicle;
 - a dermatologically acceptable cleaning surfactant; and
 - a gradient polymer comprising:
 - (a) 5 to 35 wt%, based on dry weight of the gradient polymer, of structural units of (meth)acrylic acid;
 - (b) 35 to 65 wt%, based on dry weight of the gradient polymer, of structural units of C₁₋₈ alkyl (meth)acrylate;
 - (c) > 10 to 30 wt%, of structural units of a specialized associative monomer having structure I

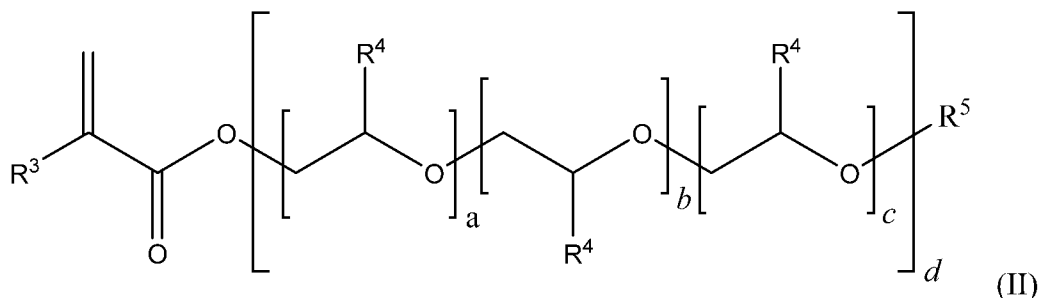


wherein each R¹ is independently selected from a linear saturated C₁₂₋₂₆ alkyl group; wherein each R² is independently selected from a hydrogen and a methyl group and wherein *n* is 10 to 30; and

- (d) 0.01 to 2 wt%, based on dry weight of the gradient polymer, of structural units of multiethylenically unsaturated monomer;

wherein the gradient polymer comprises < 0.05 wt%, based on dry weight of the gradient polymer, of structural units of sulfonated monomer;

wherein the polymer comprises < 0.02 wt%, based on dry weight of the gradient polymer, of structural units of monomer having structure II

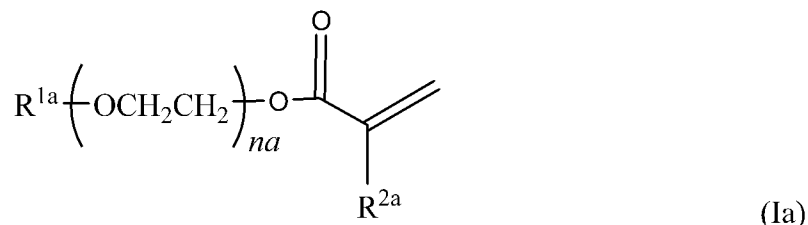


wherein each R³ is independently selected from -H and -CH₃; wherein each R⁴ is independently selected from -H and a -C₁₋₄ alkyl group; wherein each R⁵ is

independently selected from a $-C_{1-4}$ alkyl group; wherein a is 0 to 50; wherein b is 0 to 20; wherein c is 0 to 50; wherein $a + c$ is 1 to 100; and wherein d is 1 to 4; and wherein the gradient polymer has a gradient polymeric morphology.

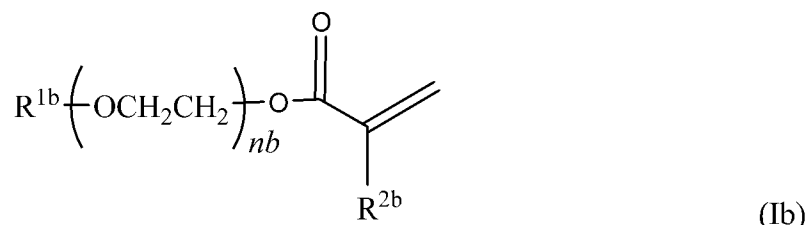
2. The aqueous personal care rinse off formulation of claim 1, wherein the structural monomer units of specialized associative monomer having structure I is a blend of

a first specialized associative monomer having structure Ia



wherein each R^{1a} is independently selected from a linear saturated C_{12-19} alkyl group; wherein each R^{2a} is independently selected from a hydrogen and a methyl group and wherein na is 10 to 30; and

a second specialized associative monomer having structure Ib



wherein each R^{1b} is independently selected from a linear saturated C_{20-26} alkyl group; wherein each R^{2b} is independently selected from a linear saturated hydrogen and a methyl group; and wherein nb is 10 to 30.

3. The aqueous personal care rinse off formulation of claim 1, wherein the structural units of (meth)acrylic acid include structural units of both methacrylic acid and acrylic acid.

4. The aqueous personal care rinse off formulation of claim 1, wherein the single stage gradient polymer comprises < 0.01 wt%, based on dry weight of the gradient polymer, of structural units of monomer selected from the group consisting of styrene, butyl acrylate, ethylhexyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, butyl acrylate and mixtures thereof.

5. The aqueous personal care rinse off formulation of claim 1, wherein the polymer comprises < 2 wt%, based on dry weight of the gradient polymer, of monomer selected from the group consisting of alkyl (meth)acrylate having 6 to 18 carbon, vinyl

alkanoate having 6 to 18 carbon atoms, N-vinyl alkylamide having 6 to 18 carbon atoms, N-alkyl (meth)acrylamide having 6 to 18 carbon atoms and mixtures thereof.

6. The aqueous personal care rinse off formulation of claim 1, wherein the dermatologically acceptable vehicle comprises water.

7. The aqueous personal care rinse off formulation of claim 1, wherein the dermatologically acceptable cleaning surfactant comprises an amino acid surfactant.

8. The aqueous personal care rinse off formulation of claim 1, wherein the amino acid surfactant is selected from the group consisting of sodium cocoyl glutamate, sodium cocoyl alaninate, sodium cocoyl glycinate, sodium lauroyl sarcosinate and mixtures thereof.

9. The aqueous personal care rinse off formulation of claim 1, wherein the aqueous personal care rinse off formulation further comprises a thickening salt.

10. A method of cleaning at least one of mammalian skin and hair, comprising:

(a) applying an aqueous personal care rinse off formulation of claim 1 to the skin or hair; and

(b) rinsing the aqueous personal care rinse off formulation from the skin or hair with a rinse water.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/106020

A. CLASSIFICATION OF SUBJECT MATTER

A61K8/06(2006.01)i; A61K8/81(2006.01)i; A61Q5/02(2006.01)i; C08F220/18(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)

IPC: A61K A61Q 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; ENTXT; DWPI; STNext Registry; STNext Caplus; CNKI: gradient polymer; specialized associative monomer; ethyl acrylate; methacrylic acid; multiethylenically unsaturated monomer; DOW GLOBAL TECHNOLOGIES; ROHM AND HAAS COMPANY; ZENG Fanwen

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 111295177 A (UNILEVER PLC) 16 June 2020 (2020-06-16) claim 1, Table 1 polymer J, example 2, paragraphs 0057-0058, 0088	1-10
X	CN 111356708 A (DOW GLOBAL TECHNOLOGIES LLC et al.) 30 June 2020 (2020-06-30) claims 1-10, Table 1	1-10
X	CN 111315343 A (UNILEVER PLC) 19 June 2020 (2020-06-19) claims 1-15, example 1	1-10
X	WO 2019086276 A1 (UNILEVER PLC et al.) 09 May 2019 (2019-05-09) claims 1-15, examples 1-2, Table 1	1-10



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

“D” document cited by the applicant in the international application

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

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“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

18 December 2023

Date of mailing of the international search report

22 December 2023

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/106020

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WO	2019086276	A1	09 May 2019	EP	3703646	A1	09 September 2020
				None			