

PATENT SPECIFICATION

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(54) TERPOLYMERS AND HIGHER POLYMERS OF N-ALKYL-
 OR N-ALKOXYALKYL-ACRYLAMIDES OR
 -METHACRYLAMIDES, PROCESS FOR THEIR PREPARATION,
 AND THEIR USE IN COSMETICS

(71) We, L'OREAL, a French Body Corporate, of 14 Rue Royale 75008, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to terpolymers and higher copolymers based on N-alkyl- or N-alkoxyalkyl-acrylamide or N-alkyl- or N-alkoxyalkyl methacrylamide and their use in cosmetics, especially in lacquers and wavesetting lotions.

The present invention also relates to a process for the preparation of these copolymers.

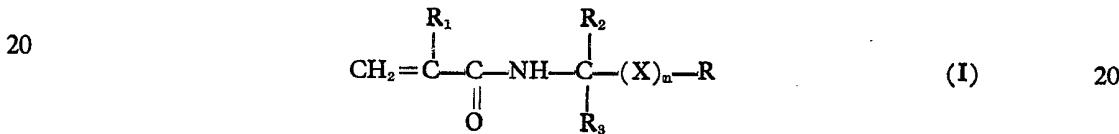
10 A large number of synthetic polymers have already been proposed for use in lacquers or wavesetting lotions.

It has now been found that it is possible to produce excellent lacquers and wavesetting lotions using the copolymers of this invention.

15 The copolymers according to the invention, contrary to those previously used, impart excellent properties to the lacquers and wavesetting lotions and in particular provide a good hold for a hairstyle.

Accordingly, the present invention provides copolymers, and especially terpolymers, containing units resulting from the copolymerisation of solely:

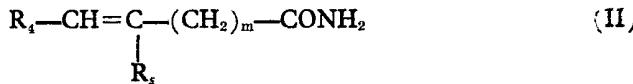
(a) 5 to 90% by weight of at least one monomer of the formula:



in which:

R represents a linear or branched alkyl radical having from 1 to 10 carbon atoms, R₁, R₂ and R₃ each represents a hydrogen atom or a methyl radical, n is 0 or 1, and, if n=1, X represents an oxygen atom;

25 (b) 5 to 90% by weight of at least one monomer of the formula:



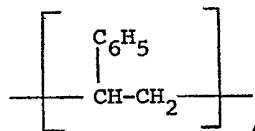
in which:

m is 0 or 1,
and, if m = 0, R₄ represents a hydrogen atom, —COOH or —COO (ammonium

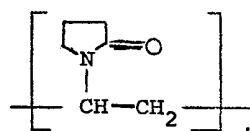
group) and R₅ represents a hydrogen atom or a methyl radical,
or, if m = 1, R₄ represents a hydrogen atom and R₅ represents —COOH or

—COO (ammonium group);

and (c) 5 to 60% by weight of at least one monomer which is styrene giving rise to
units of formula



N-vinylpyrrolidone giving rise to units of formula



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or a monomer of any one of the following formulae:



giving rise to units of formula



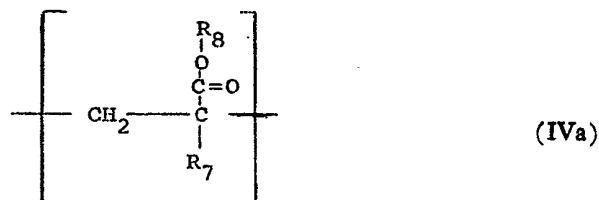
15 in which:

R₆ represents a hydrogen atom or a methyl radical:

15



giving rise to units of formula



20 in which:

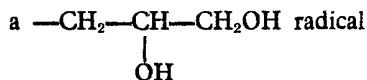
R₇ represents a hydrogen atom or a methyl radical and

R₈ represents a linear or branched alkyl radical having from 1 to 18 carbon atoms,
a quaternised or non-quaternised

20

—(CH₂)₂—N(CH₃)₂ radical,

a $-\text{CH}_2\text{CH}_2\text{OH}$ radical,



or a $-(\text{CH}_2-\text{CH}_2\text{O})_1\text{R}'$ radical,

in which R' represents a methyl or ethyl radical and 1 is 12;

5



5

giving rise to units of formula



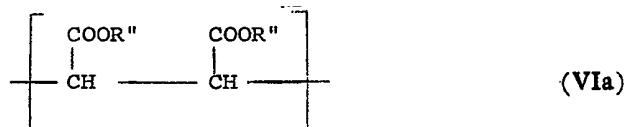
in which:

10 R_9 represents a linear or branched alkyl radical having from 1 to 16 carbon atoms;

10



giving rise to units of formula



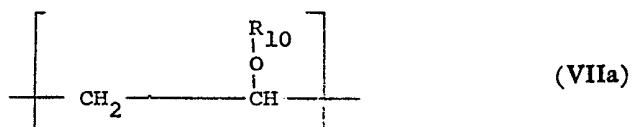
15 in which:

R'' represents an alkyl radical having from 1 to 3 carbon atoms;

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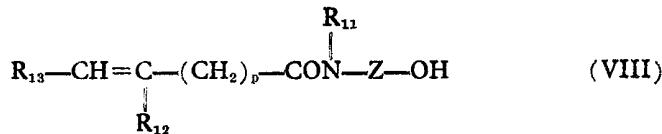
giving rise to units of formula



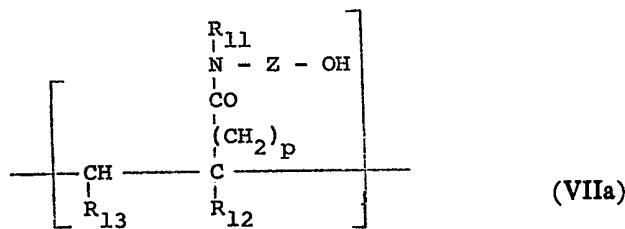
in which:

20 R_{10} represents a linear or branched alkyl radical having from 1 to 17 carbon atoms; and

20



giving rise to units of formula



in which:

R_{11} represents a hydrogen atom or a methyl radical,

Z represents a linear or branched alkylene radical having 1 to 6 carbon atoms,

which may or may not be substituted by one or two hydroxymethyl groups,

p is 0 or 1,

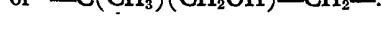
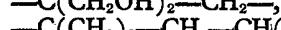
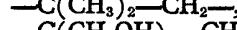
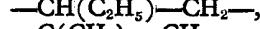
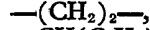
and, if $p=0$, R_{13} represents a hydrogen atom or $-COR_{14}$, in which R_{14} repre-

5 10 represents $-OH$, $-O$ (ammonium group) or $-NH-R_{15}$, in which R_{15} represents a hydrogen atom or $-Z-OH$, and R_{12} represents a hydrogen atom or the $-CH_3$ radical,

10 or, if $p=1$, R_{13} represents a hydrogen atom and R_{12} represents $-COR_{14}$, R_{14} having the same meaning as above.

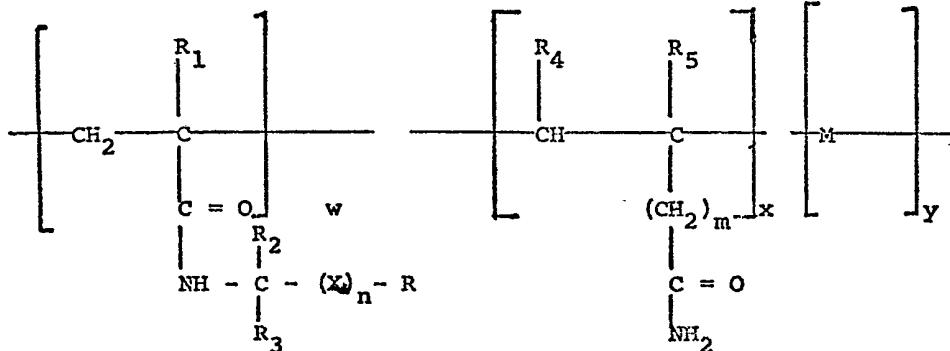
15 It will be appreciated that the expression "ammonium group" covers not only NH_4 but also substituted ammonium groups.

In the formula (VIII) above, the radical Z preferably represents:



25 As indicated above, the copolymers according to the invention are preferably terpolymers. However, the copolymers can be tetrapolymers or pentapolymers or higher copolymers. In the case of tetrapolymers or higher copolymers, the copolymers result from the copolymerisation of more than one monomer of the formula (I) and/or more than one monomer of the formula (II) and/or more than one of the monomers represented by the above formulae (III) to (VIII).

30 The terpolymers according to the invention can be represented by the following general formula:



35 in which: R , R_1 , R_2 , R_3 , R_4 , R_5 , n , m and X are as defined above for the formulae (I) and (II), w corresponds to 5 to 90% by weight, x corresponds to 5 to 90% by weight and y corresponds to 5 to 60% by weight, and M represents a unit derived from styrene, N-vinylpyrrolidone or a monomer of any one of the formulae (III) to (VIII) given above.

Examples of monomers of the formula (I), include particularly N-tertiary butyl-acrylamide, N-octylacrylamide, N-decylacrylamide, N-dodecylacrylamide, N-[(1,1-dimethyl) - propyl - 1] - acrylamide, N - [(1,1 - dimethyl) - butyl - 1] - acrylamide, N - [(1,1 - dimethyl) - pentyl - 1] - acrylamide, N isobutoxymethylacrylamide as well as the corresponding methacrylamides.

Examples of monomers of the formula (II), include particularly acrylamide, methacrylamide, maleamic acid and itaconamic acid.

Examples of monomers of the formula (III) to (VIII), include, particularly, acrylonitrile, methacrylonitrile, methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, hexyl, decyl, dodecyl, octadecyl, 2-hydroxyethyl and quaternised or non-quaternised 2-N,N-dimethylaminoethyl acrylate and methacrylate, and ω -methyl- or ω -ethyl-polyethylene glycol acrylate and methacrylate; vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl pivalate, vinyl neohexanoate, vinyl neooctanoate, vinyl neodecanoate, vinyl 2,2,4,4 - tetramethyl - valerate and vinyl 2 - isopropyl - 2,3 - dimethyl - butyrate; dimethyl maleate, diethyl maleate, dimethyl itaconate and diethyl itaconate; methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, isopropyl vinyl ether, octyl vinyl ether, dodecyl vinyl ether and octadecyl vinyl ether; N - hydroxymethylacrylamide, N - hydroxymethylmethacrylamide, N - (2 - hydroxyethyl) - acrylamide, N - (2 - hydroxyethyl) - methacrylamide, N - hydroxymethyl-maleamic acid, N - hydroxymethyl - maleamide, N,N' - dihydroxymethyl - maleamide, N - hydroxymethyl - itaconamic acid, N - hydroxymethyl - itaconamide, N,N - dihydroxymethyl - itaconamide, N - [(1 - hydroxymethyl) - propyl] - acrylamide, N - [(1 - hydroxymethyl) - propyl] - methacrylamide, N - [(1 - methyl - 1 - hydroxymethyl) - ethyl - 1] - acrylamide, N - [(1 - methyl - 1 - hydroxymethyl) - ethyl - 1] - methacrylamide, N - [1,1,1 - tris - (hydroxymethyl) - methyl] - acrylamide, N - [1,1,1 - tris - (hydroxymethyl) - methyl] - methacrylamide, N - [(3 - hydroxy - 1,1-dimethyl) - butyl] - acrylamide, N - [(3 - hydroxy - 1,1 - dimethyl) - butyl] - methacrylamide, N - (2 - hydroxyethyl) - N - methyl - acrylamide, N - (2 - hydroxyethyl) - N - methyl - methacrylamide, N - [1,1 - bis - (hydroxymethyl) - ethyl] - acrylamide and N - [1,1 - bis - (hydroxymethyl) - ethyl] - methacrylamide.

The copolymers according to the invention preferably have a molecular weight of 1,000 to 500,000 and more particularly a molecular weight of 2,000 to 200,000.

In a particular embodiment the copolymers according to the invention are cross-linked with a crosslinking agent used in a proportion of 0.01 to 2% by weight based on the total weight of the monomers employed for the reaction.

Examples of various crosslinking agents which can be used, include particularly diethylene glycol dimethacrylate, diallyl ether, tetraallyloxyethane, ethylene glycol dimethacrylate and ethylene glycol diacrylate.

According to a particular embodiment, if the radical R₄ represents a free carboxylic acid group, the latter can be neutralised with at least one organic base, such as monoethanolamine, diethanolamine, triethanolamine, the isopropanolamines such as triisopropanolamine, morpholine as well as certain amino-alcohols such as 2-amino-2-methyl-propanol and 2-amino-2-methyl-1,3-propanediol.

The carboxyl groups can suitably be neutralised with these organic bases in a proportion of 10 to 150%.

The present invention also relates to a process for the preparation of copolymer such as those described above.

These copolymers can be prepared by solution copolymerisation in an organic solvent such as an alcohol, an ester, a ketone or a hydrocarbon.

Examples of solvents include particularly methanol, isopropanol, ethanol, ethyl acetate, ethyl methyl ketone, and benzene.

The copolymerisation can also take place in suspension or in emulsion in an inert solvent such as water.

The copolymerisation can also take place in bulk.

These copolymerisations can be carried out in the presence of a polymerisation catalyst which generates free radicals, such as benzoyl peroxide, lauroyl peroxide, azo-bis-isobutyronitrile, hydrogen peroxide and various oxidation-reduction combinations such as (NH₄)₄S₂O₈ with FeCl₂.

The catalyst concentration is suitably 0.2 to 10% by weight based on the weight of the monomers used for the reaction and in accordance with the molecular weight of the copolymers which it is desired to obtain.

The present invention furthermore relates to the use of the copolymers of the invention in cosmetic compositions.

In particular, the present invention relates to cosmetic compositions which are in the form of lacquers or wavesetting lotions.

These cosmetic compositions contain at least one copolymer of this invention in solution in an appropriate cosmetic vehicle.

5 The cosmetic compositions according to the invention can be, for example, hair lacquers which may or may not be in the form of an aerosol, wavesetting lotions, hair treatment compositions, dyeing carriers, shampoos or compositions called "rinses" which are applied to the hair after washing the head of hair with a shampoo.

10 By way of example, a hair lacquer aerosol can be produced by packaging, in an aerosol container, 0.2 to 8% by weight of a copolymer according to the invention and 6 to 30%, preferably 8 to 25%, by weight of an alcohol, and a propellant gas liquefied under pressure, such as dichlorodifluoromethane, trichlorofluoromethane, nitrous oxide or carbon dioxide or mixtures of these.

15 Preferably, ethanol or isopropanol is used as the alcohol.

The wavesetting lotions according to the invention can be produced, for example, by introducing 0.3 to 6% by weight of a copolymer according to the invention into an aqueous-alcoholic solution, preferably having an alcohol content of 20 to 66%.

20 The cosmetic compositions according to the invention can also contain conventional cosmetic adjuvants such as perfumes, dyestuffs, preservatives, plasticisers, cationic products, non-ionic products, silicones for improving the gloss, or other cosmetic resins.

The following Examples of the preparation of the copolymers and of compositions based on them serve to illustrate the invention.

Examples of the Preparation of Copolymers

25 EXAMPLE 1.

400 g of ethanol, 55 g of N-tertiary butylacrylamide, 27.5 g of acrylamide, 17.5 g of methylmethacrylate and 1 g of azo-bis-isobutyronitrile are introduced into a one litre flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet tube.

30 The reaction mixture is heated at 80°C for 8 hours by means of a thermostatically controlled apparatus and is then allowed to cool to ambient temperature.

35 The solution is then poured dropwise into a vessel containing ethyl acetate as a precipitant. The precipitated polymer is then filtered off and dried under reduced pressure.

Yield: 76%.

Viscosity: 2.95 cPo (as a 5% strength solution in DMF at 34.6°C).

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EXAMPLE 2.

65 g of N-tertiary butylacrylamide, 20 g of acrylamide, 15 g of N-hydroxymethylacrylamide and 1 g of azo-bis-isobutyronitrile are copolymerised using the method described in Example 1.

40 Viscosity: 2.61 cPo (5% strength solution in DMF at 34.6°C).

Other Examples of copolymers (Examples 3 to 17) are given in Table I, the quantities are expressed in grams. All these copolymers were prepared in accordance with Example 1, only the nature of the precipitant being different.

TABLE I

Examples	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
N-T-Butylacrylamide	50	40	50	60	60	50	35	40	40	40	40	40	30	20	35
Acrylamide	25	20	30	30	15	35	15	40	40	40	40	20	30	55	25
N-Vinylpyrrolidone	25	40													20
Acrylonitrile		20													
Styrene			10												
2-Hydroxyethyl Methacrylate				25											25
Methyl Methacrylate					15	10									
Stearyl Methacrylate						5									
Vinyl Acetate							20								
Diethyl Maleate								20							
Butyl Vinyl Ether									20						
Dimethylaminoethyl Methacrylate										35					
Polyethylene Glycol Monomethyl Ether Methacrylate											40				
N-[(1-Methyl-1-Hydroxymethyl)-Ethyl-1]-Acrylamide												40			
Precipitant	①	①	①	②	②	①	②	②	②	②	②	④	③	②	①
Viscosity (at 5% strength in DMF, 34.6°C in cP ₀)	2.22	2.32	2.00	2.10	2.18	2.54	2.31	1.85	1.60	2.15	2.05	2.90	2.35	2.18	2.18

Ref.: ① Petroleum ether ② Diethyl ether ③ Acetone ④ Heptane

*Examples of Compositions***EXAMPLE A.**

A wavesetting lotion is prepared, according to the invention, by mixing the following ingredients

5	Polymer prepared according to Example 1	2 g	5
	Perfume	0.1 g	
	Ethanol	45 g	
	Water, q.s.p.	100 g	

10 This wavesetting lotion, applied in the conventional manner, makes it possible to impart to the hair a glossy appearance, and excellent hold over a period of time.

In this Example, the copolymer prepared according to Example 1 can be replaced by an equal amount of the copolymer prepared according to Example 5, 10—12 or 15.

EXAMPLE B.

15 A hair lacquer is prepared, according to the invention, by mixing the following ingredients:

10

15

Polymer prepared according to Example 2	4 g
Perfume	0.3 g
Ethanol, q.s.p.	100 g

20 25 g of this solution are packaged in an aerosol container with 47 g of trichlorofluoromethane and 28 g of dichlorodifluoromethane.

20

By spraying this lacquer, an attractive glossy appearance of the head of hair, and a high lacquering power are achieved.

25 The hair is soft to the touch and the lacquer is easily removed by combing or brushing.

25

In this Example, the copolymer prepared according to Example 2 can be replaced by an equal amount of copolymer prepared according to Example 3, 4, 6—8 or 10.

EXAMPLE C.

An aerosol hair lacquer is prepared, according to the invention, by mixing the following ingredients:

30	Polymer prepared according to Example 11	5 g	30
	Perfume	0.07 g	
	Ethanol, q.s.p.	100 g	

35 93 g of this solution are then packaged in an aerosol container and carbon dioxide is introduced so as to bring the internal pressure to about 8 bars.

35

In this Example the polymer prepared according to Example 11 can advantageously be replaced by the same amount of one of the polymers prepared according to Example 12, 14 or 16.

EXAMPLE D.

40 A wavesetting lotion is prepared, according to the invention, by mixing the following ingredients:

40

45	Polymer prepared according to Example 9 (quaternised with dimethyl sulphate)	2 g	45
	Perfume	0.1 g	
	Isopropanol	45 g	
	Water, q.s.p.	100 g	

This wavesetting lotion, applied in the conventional manner, makes it possible to impart to the hair a glossy appearance, and excellent hold over a period of time. The polymer according to Example 9 can advantageously be replaced by the same amount of the polymer according to Example 13, which has also been quaternised.

EXAMPLE E.

A hair lacquer is prepared, according to the invention, by mixing the following ingredients:

5	Polymer prepared according to Example 2	4 g	5
	Perfume	0.3 g	
	Ethanol	100 g	

25 g of this solution are packaged in an aerosol container with 47 g of trichloro-
fluoromethane and 28 g of dichlorodifluoromethane.

By spraying this lacquer, an attractive glossy appearance of the head of hair, and
10 a high lacquering power are achieved.

The hair is soft to the touch and the lacquer is easily removed by combing or
brushing.

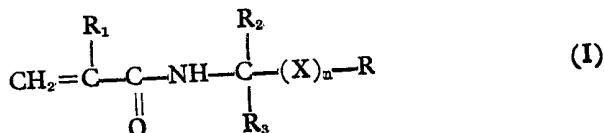
In this Example, the polymer according to Example 2 can advantageously be
replaced by the same amount of the polymer according to Example 17.

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WHAT WE CLAIM IS:—

15 1. A copolymer containing units derived solely from:
(a) 5 to 90% by weight of at least one monomer of formula:

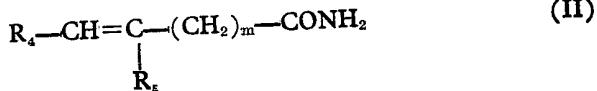


in which:

20 R represents a linear or branched alkyl radical having up to 10 carbon atoms,
 R_1 , R_2 and R_3 each independently represents a hydrogen atom or a methyl radical,
 n is 0 or 1
and X represents an oxygen atom;

20

(b) 5 to 90% by weight of at least one monomer of formula:



25

25

in which

m is 0 or 1, such that
if $m = 0$, R_4 represents a hydrogen atom, $-\text{COOH}$ or $-\text{COO}$ (ammonium

30 group) and R_5 represents a hydrogen atom or a methyl radical,
or, if $m = 1$, R_4 represents a hydrogen atom and R_5 represents $-\text{COOH}$ or
 $-\text{COO}$ (ammonium group);

and (c) 5 to 60% by weight of at least one of styrene, N-vinylpyrrolidone and a
monomer of any one of the formulae:



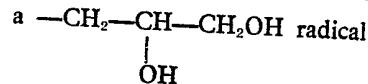
35 35 in which:
 R_6 represents a hydrogen atom or a methyl radical:



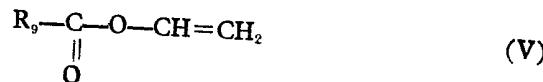
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in which:
 R_7 represents a hydrogen atom or a methyl radical and
40 R_8 represents a linear or branched alkyl radical having up to 18 carbon atoms,
a $-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_2$ radical which may be quaternised, a $-\text{CH}_2\text{CH}_2\text{OH}$ radical,

40



or a $-(\text{CH}_2 - \text{CH}_2\text{O})_1\text{R}'$ radical, in which R' represents a methyl or ethyl radical and 1 is 12;



5 in which:

R_9 represents a linear or branched alkyl radical having up to 16 carbon atoms;

in which:

R'' represents an alkyl radical having from 1 to 3 carbon atoms;



10

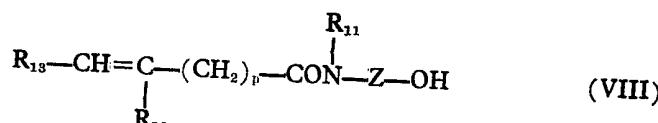
in which:

R_{10} represents a linear or branched alkyl radical having up to 17 carbon atoms;



5

and



15 in which:

R_{11} represents a hydrogen atom or a methyl radical,

15

Z represents a linear or branched alkylene radical having up to 6 carbon atoms,

which is unsubstituted or substituted by one or two hydroxymethyl groups,

20 p is 0 or 1 such that if $\text{p}=0$, R_{13} represents a hydrogen atom or $-\text{COR}_{14}$ in which R_{14} represents

20

$-\text{OH}$, $-\text{O}$ (ammonium group) or $-\text{NH}-\text{R}_{15}$, in which R_{15} represents a

hydrogen atom or $-\text{Z}-\text{OH}$, and R_{12} represents a hydrogen atom or a methyl

or, if $\text{p}=1$, R_{13} is a hydrogen atom and R_{12} is COR_{14} in which R_{14} is as defined

25 above.

25

2. A copolymer according to claim 1 which has a molecular weight of 1,000 to 500,000.

3. A copolymer according to claim 2 which has a molecular weight of 2,000 to 200,000.

30 4. A copolymer according to any one of the preceding claims which is a terpolymer.

30

5. A copolymer according to any one of claims 1 to 3 which is crosslinked with a crosslinking agent used in a proportion of 0.01 to 2% by weight based on the total weight of the monomers.

35 6. A copolymer according to claim 5 in which the crosslinking agent is diethylene glycol dimethacrylate, diallyl ether, tetraallyloxyethane, ethylene glycol dimethacrylate or ethylene glycol diacrylate.

35

40 7. A copolymer according to any one of the preceding claims in which the monomer of formula (I) is N-tertiary butylacrylamide, N-octylacrylamide, N-decylacrylamide, N-dodecylacrylamide, N - [(1,1 - dimethyl) - propyl - 1] - acrylamide, N - [(1,1 - dimethyl) - butyl - 1] - acrylamide, N - [(1,1 - dimethyl) - pentyl - 1] - acrylamide or a corresponding methacrylamide.

40

45 8. A copolymer according to any one of the preceding claims in which the monomer of formula (II) is acrylamide, methacrylamide, maleamic acid or itaconamic acid.

45

9. A copolymer according to any one of the preceding claims in which the monomer of any one of the formulae (III) to (VIII) is acrylonitrile, methacrylonitrile, methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, hexyl, decyl, dodecyl, octadecyl,

2-hydroxyethyl or quaternised or non-quaternised 2-N,N-dimethylaminoethyl acrylate or methacrylate, or ω -methyl or ω -ethyl-polyethylene glycol acrylate or methacrylate; vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl pivalate, vinyl neoheptanoate, vinyl neoctanoate, vinyl neodecanoate, vinyl 2,2,4,4-tetramethyl-valerate or vinyl 2-isopropyl-2,3-dimethyl-butyrate; dimethyl maleate, diethyl maleate, dimethyl itaconate or diethyl itaconate; methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, isopropyl vinyl ether, octyl vinyl ether, dodecyl vinyl ether or octadecyl vinyl ether; N - hydroxy - methylacrylamide, N - hydroxymethylmethacrylamide, N - (2 - hydroxyethyl) - acrylamide, N - (2 - hydroxyethyl) - methacrylamide, N - hydroxymethyl - maleamic acid, N - hydroxymethyl - maleamide, N,N' - dihydroxymethyl - maleamide, N - hydroxymethyl - itaconamic acid, N - hydroxymethyl-itaconamide, N,N - dihydroxymethyl - itaconamide, N - [(1 - hydroxymethyl)-propyl] - acrylamide, N - [(1 - hydroxymethyl) - propyl] - methacrylamide, N - [(1-methyl - 1 - hydroxymethyl) - ethyl - 1] - acrylamide, N - [(1 - methyl - 1 - hydroxymethyl) - ethyl - 1] - methacrylamide, N - [1,1,1 - tris - (hydroxymethyl) - methyl] - acrylamide, N - [1,1,1 - tris - (hydroxymethyl) - methyl] - methacrylamide, N - [(3-hydroxy - 1,1 - dimethyl) - butyl] - acrylamide, N - [3 - hydroxy - 1,1 - dimethyl) - butyl] - methacrylamide, N - (2 - hydroxyethyl) - N - methyl - acrylamide, N - (2-hydroxyethyl) - N - methyl - methacrylamide, N - [1,1 - bis - (hydroxymethyl) - ethyl] - acrylamide or N - [1,1 - bis - (hydroxymethyl) - ethyl] - methacrylamide.

10 10. A copolymer according to any one of the preceding claims in which n is 0.

11. A copolymer according to claim 10 in which R_4 and R_5 do not represent a $-COO$ (ammonium group), component (c) is of formula (III) to (VII) and if of formula (IV) R_8 represents a linear or branched alkyl radical having up to 18 carbon atoms, a $-(CH_2)_2N(CH_3)_2$ radical or a $-CH_2CH_2OH$ radical.

15 15. 12. A copolymer according to claim 10 in which R_4 and R_5 do not represent a $-COO$ (ammonium group) and if component (c) is of formula (IV) R_8 represents a linear or branched alkyl radical having up to 18 carbon atoms, a $-(CH_2)_2N(CH_3)_2$ radical or a $-CH_2CH_2OH$ radical and if component (c) is of formula (VIII) R_{11} does not represent a $-O$ (ammonium group).

20 20. 13. A copolymer according to claim 1 substantially as described in any one of Examples 1 to 17.

25 25. 14. A process for the preparation of a copolymer as claimed in any one of the preceding claims which comprises reacting the monomers in bulk or in solution in the presence of a polymerisation catalyst which generates free radicals.

30 30. 15. A process according to claim 14 in which the catalyst concentration is 0.2 to 10% by weight based on the weight of the monomers.

35 35. 16. A process according to claim 14 substantially as described in any one of Examples 1 to 17.

40 40. 17. A copolymer as claimed in any one of claims 1 to 13 whenever prepared by a process as claimed in claim 14 to 16.

45 45. 18. A composition suitable for use in cosmetics which comprises at least one copolymer as claimed in any one of claims 1 to 13 and 17 and a cosmetic vehicle.

50 50. 19. A composition according to claim 18 which is packaged in an aerosol-producing container and comprises 0.2 to 8% by weight of copolymer and 6 to 30% by weight of an alcohol, and a propellant gas liquefied under pressure.

55 55. 20. A composition according to claim 19 which comprises 8 to 25% by weight of an alcohol.

21. A composition according to claim 18 which is a wave-setting lotion in the form of an aqueous-alcoholic solution containing 0.3 to 6% by weight of copolymer.

22. A composition according to any one of claims 18 to 20 which contains, as cosmetic adjuvant, a perfume, dyestuff, preservative, plasticiser, cationic product, non-ionic product, silicone or other cosmetic resin.

23. A composition according to any one of claims 18 to 22 in which the copolymer is one claimed in claim 12.

24. A composition according to any one of claims 18 to 22 in which the copolymer is one claimed in claim 13.

25. A composition according to claim 18 substantially as described in any one of Examples A to E.

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