The following statement is a full description of this invention, including the best method of performing it known to us:
The present invention relates to novel cationic, graft and cross-linked copolymers.

It has already been proposed to use in cosmetic compositions such as hair lacquers and wavesetting lotions a variety of different types of homo- and co-polymer. Amongst these one can mention polyvinyl pyrrolidone, copolymers such as vinyl pyrrolidone/vinyl acetate copolymer, copolymers obtained from vinyl acetate and an unsaturated carboxylic acid such as crotonic acid, copolymers obtained from vinyl acetate, crotonic acid and an acrylic or methacrylic ester or an alkyl vinyl ether, copolymers obtained from vinyl acetate, crotonic acid and a vinyl ester of a long-chain acid or an allyl or methallyl ester of a long-chain acid, copolymers derived from an ester of an unsaturated alcohol and a short-chain saturated carboxylic acid, from a short-chain unsaturated acid and from an ester of a long-chain saturated alcohol and a short-chain unsaturated acid, and copolymers obtained by polymerising at least one unsaturated ester and at least one unsaturated acid.

Some of these copolymers, which have been used to a very large extent, do possess good affinity for the keratin of the hair but, nevertheless, they do not possess the combination of properties which are required if excellent wavesetting lotions are to be obtained.
It has now been found, very surprisingly, according to the present invention, that it is possible to obtain excellent cosmetic compositions, in particular wavesetting lotions, using a certain type of copolymer which is, at the same time, cationic, grafted and cross-linked.

According to the present invention there is provided such a copolymer obtained by copolymerisation of the following:

(a) at least one cosmetic monomer selected from the consisting of a vinyl ester of an acid having 2 to 18 carbon atoms, an allyl or methallyl ester of an acid having 2 to 18 carbon atoms, an acrylate or methacrylate ester of a saturated alcohol having 1 to 18 carbon atoms, an alkyl vinyl ether in which the alkyl radical has 2 to 18 carbon atoms, an olefine having 4 to 18 carbon atoms, a vinyl heterocycle, a dialkyl or N,N-dialkylaminoalkyl maleate in which each alkyl radical has 1 to 3 carbon atoms, or an anhydride of an unsaturated acid.
Compositions containing these novel copolymers give rise to better results than those available hitherto. Wavesetting lotions containing such copolymers form films having a lacquerability which is noticeably better than that obtained with the known resins. The copolymers of the present invention also provide other advantages. In particular, the films obtained possess a higher gloss than those obtained with the known copolymers. Furthermore, they possess a very great affinity for the hair so that they adhere better to the hair which enables the hair to be combed without significant loss of the copolymer film on the hair.

It is, of course, well known that with the known
hair lacquers and the like when one combs the hair effectively all of the resin becomes detached from the hair and falls in the form of a white powder. In contrast, with the compositions of the present invention it is possible to comb the hair without significant loss of the copolymer although the copolymer can readily be removed by brushing or washing with the aid of a conventional shampoo.

By the expression "graft and cross-linked copolymer" is meant a copolymer which contains a principal polymer chain possessing branches or grafts which are attached one to another with the aid of a cross-linking agent. Thus, in effect, the graft and cross-linked copolymers possess a network of branches, the density of which depends on the degree of unsaturation of the cross-linking agent.

Graft copolymers are, of course, well known and they can be represented schematically in the following manner:

  C D C
  D D D C
  C C C D
  
Figure 1

The principal chain A - B - A - B - B .........
A - A - B - A - B ....... represents the "backbone" of the graft copolymer while the chains C - D ....... D - C -
constitute the grafts. A graft and cross-linked copolymer can be represented schematically in the following manner:

\[ \text{Figure 2} \]

The principal chain or the "backbone" \(-\text{A-B-B-B} \ldots \text{A-B-A-B}\) is identical to that in the graft copolymer as are the grafts. However, between these grafts and chains there are present the radicals \(-\text{E-X-E}\) which are attached to different grafts and/or to different "backbones" of the polymer.

The radicals \(-\text{E-X-E}\) are derived from the cross-linking agent which is doubly unsaturated as indicated in Figure 2 thus giving rise to two-dimensional cross-linking. It will be appreciated, however, that the cross-linking agent can have a higher degree of unsaturation which gives rise to three-dimensional structures.

The cross-linking agent used in the present invention is preferably ethylene glycol dimethacrylate, a diallyl phthalate, a divinyl benzene, tetraallyl-oxyethane or a polyallyl sucrose having 2 to 5 allyl
groups per mol of sucrose. The degree of unsaturation in the cross-linking agents is thus from 2 to 5 in the case of the polyallyl sucroses.

The term "cosmetic monomer" refers to a monomer which has been used in the past to prepare a polymer having utility in the cosmetics field. A variety of different types of monomer can be used including, for example, a vinyl ester of an acid having 2 to 18 carbon atoms, an allyl or methallyl ester of an acid having 2 to 18 carbon atoms, an acrylate or methacrylate of a saturated alcohol having 1 to 18 carbon atoms, an alkyl vinyl ether in which the alkyl radical has 2 to 18 carbon atoms, an olefine having 4 to 18 carbon atoms, a vinyl heterocycle, di-alkyl or N,N'-dialkylaminoalkyl maleate in which each alkyl radical has 1 to 3 carbon atoms, or an anhydride of an unsaturated acid. Preferred such monomers include:

- vinyl acetate
- vinyl propionate
- methyl methacrylate
- stearyl methacrylate
- lauryl methacrylate
- ethyl vinyl ether
- cetyl vinyl ether
- stearyl vinyl ether
- hexene-1
- octadecene
N-vinyl pyrrolidone
N,N-diethylaminoethyl monomaleate
diethyl maleate and
maleic anhydride.
The polyethylene glycol onto which the grafting
takes place suitably has a molecular weight
between 200 and several million, preferably
between 300 and 30,000.
The copolymers of the present invention
are preferably derived from:
(a) 3 to 95% by weight of at least one
cosmetic monomer;
(b) 3 to 95% by weight of dimethylamino-
ethyl methacrylate;
(c) 2 to 50% by weight, preferably 5 to
30% by weight, of polyethylene glycol; and
(d) 0.01 to 8% by weight, based on the
total weight of (a) + (b) + (c), of the specified
cross-linking agent.
Thus if one copolymerises 123 grams (41%) of vinyl acetate, 147 grams (49%) of dimethylamino-
ethyl methacrylate and 30 grams (10%) of poly-
ethylene glycol the amount of cross-linking agent
required is between 0.03 grams (0.01%) and 24
grams (8%).
The graft and cross-linked copolymers of
the present invention can be in the form of their
quaternary salts. This is because the dimethylamino-
ethyl methacrylate can be quaternised. This can be carried out before or after the copolymer has been obtained. Suitable quaternising agents include dialkyl sulphates, for example diethyl sulphate and dimethyl sulphate, alkyl sulphonic acids such as methyl sulphonic acids, benzyl halides, for example benzyl chloride, bromide or iodide, and alkyl halides as well as the other known quaternising agents.

The copolymers of the present invention generally have a molecular weight of between 10,000 and one million, preferably between 15,000 and 500,000.

According to the present invention, the copolymers of the present invention can be obtained by polymerisation in a conventional manner, for example in bulk, in suspension, as an emulsion or in solution in a solvent. However, the polymerisation is preferably carried out in bulk or in suspension. The conventional free radical initiation polymerisation catalysts can be used, the particular one depending on the reactants involved. Typical such initiators include peroxides such as benzoyl peroxide, lauryl peroxide, acetyl peroxide and benzoyl hydroperoxide, catalysts which, on decomposition, produce an inert gas such as azo bis-isobutyronitrile and redox catalysts such as sodium persulphate, sodium sulphite and hydrogen.
peroxide. The concentration of initiator is generally between 0.2 and 15%, preferably 0.5 to 12%, by weight based on the total weight of the reactants i.e. cosmetic monomer, dimethylaminoethyl methacrylate, polyethylene glycol and cross-linking agent.

If the polymerisation is carried out in suspension, the various reactants should be immiscible with water or the inert liquid used as the continuous phase. In consequence, if one uses water as the continuous phase, it is necessary to saturate this with a mineral salt such as sodium chloride because polyethylene glycol is soluble in water. If one or more of the cosmetic monomers is also soluble in water the addition of sodium chloride also has the effect of putting this in suspension so that all the reactants are present in the form of droplets or globules.

Conventional suspending agents can be used to facilitate the reaction such as hydroxyethyl cellulose known under the trade name "CELLOSIZE", cross-linked polyacrylic acid known under the trade name "CARBOPOL" and the polyvinyl alcohols known under the trade name "RHODO VIOL".

If the polymerisation is carried out in an emulsion, an emulsifying agent such as potassium stearate, potassium palmitate, potassium laurate or laurylamine hydrochloride can be used.
The molecular weight of the graft and cross-linked copolymer can be regulated by introducing during the polymerisation small quantities (suitably from 0.05 to 0.4% by weight) of a chain regulator such as an aldehyde such as butyraldehyde, halogenated substances such as chloroform, bromoform and carbon tetrachloride and mercaptans such as lauryl mercaptan.

The present invention also provides a composition suitable for use in cosmetics which comprises at least one of the novel copolymers together with an appropriate vehicle. Such cosmetic compositions are suitably in the form of wave-setting lotions. Such lotions are generally aqueous or aqueous-alcoholic solutions containing 5 to 70% of alcohol, the concentration of the copolymer generally being between 0.4 and 5% by weight. The alcohols generally used in such lotions are preferably low molecular weight aliphatic alcohols (i.e. of 1 to 6, suitably of 1 to 4, carbon atoms) such as ethanol and isopropanol.

The aqueous solutions of the present invention can also be used to treat the hair so as to brighten it making it more lively and to facilitate disentangling. In this case, the aqueous solutions are preferably applied after rinsing and optionally after shampooing. The composition is allowed to act on the hair for several minutes, for example 5 to
10 minutes, and then the hair is rinsed with water.

It is to be understood that all the ingredients conventionally used in such cosmetic compositions can be present in the compositions of the present invention such as plasticising agents, perfumes and hair dyes.

The present invention also provides a process for wavesetting hair which comprises impregnating the hair with a lotion of the present invention, winding the hair on wavesetting rollers (generally having a diameter from 15 to 30 mm) and then drying the hair on the rollers.

The following Examples further illustrate the present invention.
EXAMPLE 1

200 grams of an aqueous solution containing 52 grams of sodium chloride and 0.3 grams of "Cellosize" are introduced into a 1 litre flask equipped with a mechanical stirrer, a nitrogen inlet tube, a thermometer and a condenser. Then a solution containing 41.8 grams of methyl methacrylate, 48.2 grams of dimethylaminoethyl methacrylate (MADAME), 10 grams of polyethylene glycol (molecular weight (MW) 20,000), 0.8 grams of ethylene glycol dimethacrylate and 2 grams of azo bis-isobutyronitrile is added. The mixture is then heated with agitation to 75°C. for three hours. After this time the polymerisation is terminated. Beads are obtained which are then washed and recovered in the usual manner. Yield: 90%.

Quaternisation of this polymer

20 grams of the graft and cross-linked polymer obtained are dissolved in 200 grams of absolute ethanol. The mixture is refluxed and then 7.7 grams of dimethyl sulphate added with agitation. After heating to 80°C., with stirring for 14 hours, the quaternised polymer has precipitated in the reaction mixture. By adding 50 grams of water a clear solution is obtained. The polymer is purified by precipitation in dioxane. Viscosity (as a 5% by weight solution in dimethyl formamide at 35°C): 40 centipoises.
EXAMPLE 2

Following the procedure of Example 1 the following materials are polymerised:

N-vinyl pyrrolidone 62 g
MADAME 28 g
Polyethylene glycol MW 20,000 10 g
Tetraallyloxyethane 0.02 g
Azo bis-isobutyronitrile 4 g
Sodium chloride 152 g
0.06% by weight solution of "Cellosize" in water 400 g

The polymer obtained is quaternised with 22.5 grams of dimethyl sulphate. This polymer has a viscosity (measured as before) of 7 centipoises.

EXAMPLE 3

25 grams of methyl methacrylate, 27 grams of stearyl methacrylate, 38 grams of N,N-dimethylaminoethyl methacrylate, 10 grams of polyethylene glycol of molecular weight 20,000, 0.1 gram of ethylene glycol dimethacrylate and 1.5 grams of azo bis-isobutyronitrile are introduced into a 1 litre flask equipped with a mechanical stirrer, a nitrogen inlet tube and a condenser. The mixture is heated at 80°C for 8 hours.

After cooling 500 grams of absolute ethanol are introduced. The mixture is heated again until the polymer is completely dissolved in the
ethanol. The N,N-dimethylaminoethyl methacrylate is quaternised by introducing 30.5 grams of dimethyl sulphate and then heating for a further 4 hours at 80°C. The resulting copolymer has a viscosity of 3.8 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

**EXAMPLE 4**

Proceeding as in Example 3, the following materials are polymerised:

- Ethyl vinyl ethyl 20 g
- MADAME 35 g
- N-vinyl pyrrolidone 35 g
- Polyethylene glycol MW 20,000 10 g
- Azo bis-isobutyronitrile 3 g

This polymer is quaternised with 28 grams of dimethyl sulphate. The polymer obtained has a viscosity of 27 centipoises (as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

**EXAMPLE 5**

Following the procedure of Example 3, the following materials are polymerised:

- N-vinyl pyrrolidone 56 g
- MADAME 24 g
- N,N'-diethylaminoethyl mono-maleate 10 g
- Polyethylene glycol MW 20,000 10 g
Tetraallyloxyethane 0.1 g
Azo bis-isobutyronitrile 1.5 g

The polymer is then quaternised with 30 grams of dimethyl sulphate. The resulting copolymer has a viscosity of 2.40 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

EXAMPLE 6

Following the procedure of Example 3, the following materials are polymerised:

Methyl methacrylate 25 g
Lauryl methacrylate 27 g
MADAME 38 g
Polyethylene glycol MW 20,000 10 g
Ethylene glycol dimethacrylate 0.1 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 30.5 grams of dimethyl sulphate. The resulting polymer has a viscosity of 2.55 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

EXAMPLE 7

Following the procedure of Example 3, the following ingredients are polymerised:

Vinyl propionate 45 g
MADAME 45 g
Polyethylene glycol Mw 20,000 10 g
Tetraallyloxyethane 0.2 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 36 grams of dimethyl sulphate. It possesses a viscosity of 3 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C).

EXAMPLE 8

Following the procedure of Example 3, the following ingredients are polymerised:

Ethyl vinyl ether 20 g
MADAME 70 g
Polyethylene glycol Mw 20,000 10 g
Tetraallyloxyethane 0.2 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 56 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 7.7 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C).

EXAMPLE 9

Following the procedure of Example 3, the following are polymerised:

Octadecene-1 15 g
MADAME 75 g
Polyethylene glycol Mw 20,000 10 g
Ethylene glycol dimethacrylate 0.1 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 60 grams of dimethyl sulphate. The resulting polymer possesses a viscosity of 2.77 centipoises (measured as a 2% by weight solution in 50:50 aqueous ethanolic solution at 34.6°C).

EXAMPLE 10
Following the procedure of Example 3, the following ingredients are polymerised:
Vinyl acetate 41 g
MADAME 49 g
Polyethylene glycol MW 20,000 10 g
Tetraallyloxyethane 0.2 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 39 grams of dimethyl sulphate. Viscosity (measured as in Example 9) : 3.55 centipoises.

EXAMPLE 11
Following the procedure of Example 3, the following ingredients are polymerised:
Methyl methacrylate 30 g
MADAME 63 g
Polyethylene glycol MW 20,000 7 g
Ethylene glycol dimethacrylate 0.08 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 50.4 grams of dimethyl sulphate. The polymer obtained
possesses a viscosity of 3.6 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

EXAMPLE 12

Following the procedure of Example 3, the following ingredients are polymerised:

Vinyl acetate 10 g  
N-vinyl pyrrolidone 56 g  
MADAME 24 g  
Polyethylene glycol MW 20,000 10 g  
Tetraallyloxyethane 0.02 g  
Azo bis-isobutryonitrile 1.5 g  

This polymer is quaternised with 19.2 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 3.6 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C.).

EXAMPLE 13

Following the procedure of Example 3, the following ingredients are polymerised:

N-vinyl pyrrolidone 54 g  
Diethyl maleate 18 g  
MADAME 18 g  
Polyethylene glycol MW 20,000 10 g  
Tetraallyloxyethane 0.02 g  
Azo bis-isobutryonitrile 1.5 g
This polymer is quaternised with 144 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 3.2 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 31.6°C).

EXAMPLE 14
Following the procedure of Example 3, the following ingredients are polymerised:

- Vinyl acetate 20 g
- N-vinyl pyrrolidone 42 g
- Diethyl maleate 14 g
- MADAME 14 g
- Polyethylene glycol MW 20,000 10 g
- Tetraallyloxyethane 0.02 g
- Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 11.2 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 4.3 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C).

EXAMPLE 15
Following the procedure of Example 3, the following ingredients are polymerised:

- N-vinyl pyrrolidone 54 g
- Maleic anhydride 18 g
- MADAME quaternised with dimethyl sulphate 18 g
Polyethylene glycol MW 20,000 10 g
Tetraallyloxyethane 0.02 g
Azo bis-isobutyronitrile 1.5 g

The polymer obtained possesses a viscosity of 3.7 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C).

**EXAMPLE 16**

Following the procedure of Example 3, the following ingredients are polymerised:

N-vinyl pyrrolidone 55 g
MADAME 35 g
Polyethylene glycol MW 4,000 10 g
Tetraallyloxyethane 0.02 g
Azo bis-isobutyronitrile 1.5 g

This polymer is quaternised with 28 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 6.4 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution at 34.6°C).

**EXAMPLE 17**

Following the procedure of Example 3, the following ingredients are polymerised:
N-vinyl pyrrolidone 66 g
MADAME 24 g
Polyethylene glycol MW 1,500 10 g
Tetraallyloxyethane 0.02 g
Azo bis-isobutynitrile 1.5 g

This polymer is quaternised with 19.2 grams of dimethyl sulphate. The polymer obtained possesses a viscosity of 5.1 centipoises (measured as a 2% by weight solution in a 50:50 aqueous ethanolic solution ± 34.6°C.).
EXAMPLE A

A wavesetting lotion is prepared by mixing the following ingredients:

Polymer prepared according to Example 1 2 g
Perfume 0.1 g
Ethyl alcohol 45 g
Water q.s.p. 100 g

This wavesetting lotion is applied in a conventional manner to the hair to which it gives a brilliant appearance; it adheres well to the hair.

The polymer of Example 1 can be replaced by the same quantity of the polymer prepared in any one of Examples 2, 6, 8 and 12, with similar results.

EXAMPLE B

A wavesetting lotion is prepared by mixing the following ingredients:

Polymer prepared according to Example 5 3.5 g
Perfume 0.1 g
Dyestuff sufficient to colour the lotion 0.2 g
Isopropyl alcohol 40 g
Water q.s.p. 100 g

In this Example, the polymer of Example 5 can be replaced by the same quantity of the polymer prepared in any one of Examples 3, 7, 10 and 13 with similar results.
After impregnation of hair with one of these lotions, the hair is rolled on wavesetting rollers having a diameter of 15 to 30 mm and then dried on the rollers with the application of heat. After removing the rollers, an excellent set with a good hold is obtained.

EXAMPLE C

A wavesetting lotion is prepared by mixing
the following ingredients:
Polymer prepared according to Example 4  1.5 g
Perfume  0.1 g
Ethyl alcohol  45 g
Water q.s.p.  100 g

In this Example the polymer of Example 4 can be replaced by the same quantity of the polymer prepared according to any one of Examples 8, 12 and 15, with similar results.

EXAMPLE D

A wavesetting lotion is prepared by mixing
the following ingredients:
Polymer prepared according to Example 6  2 g
2-Amino-2-methyl-propanol q.s.p. pH = 7
Isopropyl alcohol  40 g
Water q.s.p.  100 g

In this Example the polymer of Example 6 can be replaced by the same quantity of one of the
polymers prepared in any one of Examples 8 to 11, with similar results.

**EXAMPLE E**

A wavesetting lotion is prepared by mixing the following ingredients:

- Polymer prepared according to Example 5 3 g
- 2-Amino-2-methyl-propan-1,3-diol q.s.p. pH = 7.2
- Perfume 0.1 g
- Ethyl alcohol 45 g
- Water q.s.p. 100 g

This wavesetting lotion is applied in a conventional manner to the hair. It gives to the hair an excellent hold with a glossy appearance without making it at all sticky.

In this Example the polymers of Example 5 can be replaced by the same quantity of one of the polymers prepared in Examples 16 and 17, with similar results.

**EXAMPLE F**

A hair treatment composition is prepared by mixing the following ingredients:

- Polymer prepared according to Example 2 1 g
- Perfume 0.1 g
- Water q.s.p. 100 g

This composition is applied for several minutes to hair which has previously been shampooed.
and rinsed with water. After further rinsing with water, brilliant and supple hair is obtained which disentangles very easily.

Similar results are obtained when the copolymer of Example 2 is replaced by the same quantity of one of the polymers prepared in any one of Examples 5, 12, 13, 16 and 17.

**EXAMPLE G**

A treatment composition for the hair is prepared by mixing the following ingredients:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer prepared according to Example 4</td>
<td>2.5 g</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Water q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

By proceeding as in Example F brilliant and supple hair which disentangles very easily is obtained.

In this Example, the polymer of Example 4 can be replaced by the same quantity of the polymer prepared according to Example 1 or 3, with similar results.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A graft cross-linked cationic copolymer obtained by copolymerisation of the following:
   
   (a) at least one cosmetic monomer selected from the group consisting of a vinyl ester of an acid having 2 to 18 carbon atoms, an allyl or methallyl ester of an acid having 2 to 18 carbon atoms, an acrylate or methacrylate ester of a saturated alcohol having 1 to 18 carbon atoms, an alkyl vinyl ether in which the alkyl radical has 2 to 18 carbon atoms, an olefine having 4 to 18 carbon atoms, a vinyl heterocycle, a dialkyl or N,N-dialkylamino-alkyl maleate in which each alkyl radical has 1 to 3 carbon atoms, or an anhydride of an unsaturated acid;
   
   (b) dimethylaminoethyl methacrylate;
   
   (c) polyethylene glycol; and
   
   (d) a poly unsaturated cross-linking agent.

2. A copolymer according to claim 1 in which the cosmetic monomer is vinyl acetate, vinyl propionate, methyl methacrylate, stearyl methacrylate, lauryl methacrylate, ethyl vinyl ether, cetyl vinyl ether, stearyl vinyl ether, hexene-1, octadecene, N-vinyl pyrrolidone, N,N-diethylaminoethyl mono-
maleate, diethyl maleate or maleic anhydride.

3. A copolymer according to any one of claims 1 to 2 in which the polyethylene glycol has a molecular weight of at least 200.

4. A copolymer according to claim 3 in which the polyethylene glycol has a molecular weight between 300 and 30,000.

5. A copolymer according to any one of the preceding claims in which the cross-linking agent is ethylene glycol dimethacrylate, a diallyl phthalate, a divinyl benzene, tetraallyloxyethane or a polyallyl sucrose having 2 to 5 allyl groups per mol of sucrose.

6. A copolymer according to any one of the preceding claims which is obtained by copolymerization of:

   (a) 3 to 95% by weight of at least one cosmetic monomer;

   (b) 3 to 95% by weight of dimethylaminoethyl methacrylate;

   (c) 2 to 50% by weight of polyethylene glycol; and

   (d) 0.01 to 8% by weight based on the total weight of (a) + (b) + (c), of cross-linking agent.
A copolymer according to any one of the preceding claims which has a molecular weight between 10,000 and 1,000,000.

A copolymer according to claim 7 which has a molecular weight between 15,000 and 500,000.

A copolymer according to any one of the preceding claims which is quaternised.

A copolymer according to claim 9 which is quaternised by dimethyl sulphate, diethyl sulphate, methyl sulphonie acid or benzyl chloride, bromide or iodide.

A copolymer according to claim 1 substantially as hereinbefore described.

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

A process for preparing a copolymer as claimed in any one of the preceding claims which comprises copolymerising at least one cosmetic monomer, dimethylaminoethyl methacrylate, polyethylene glycol and the cross-linking agent either in bulk or in suspension in a solvent in the presence
of 0.2 to 15% by weight based on the total weight of the reactant, of a polymerisation catalyst.

14. A process according to claim 13 in which the copolymerisation is carried out in the presence of 0.5 to 12% by weight, based on the total weight of the reactants, of a polymerisation catalyst.

15. Process according to claim 13 or 14 in which the copolymerisation is carried out in the presence of a chain regulator which is butyraldehyde, chloroform, bromoform, carbon tetrachloride or lauryl mercaptan.

16. Process according to claim 13 substantially as hereinbefore described.

17. Process according to claim 13 substantially as described in any one of Examples 1 to 17.

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

19. A cosmetic composition for the treatment of hair which comprises at least one cationic graft cross-linked copolymer as claimed in any one of claims 1 to 12 and 18 and an appropriate vehicle.

20. A composition according to claim 19 which contains 0.4 to 5% by weight of the copolymer in an aqueous or aqueous-alcoholic solution.

21. A composition according to claim 20 which is in the form of an aqueous-alcoholic solution containing 5 to 70% by weight of an aliphatic alcohol.

22. A composition according to claim 21 in which the aliphatic alcohol is ethanol or isopropanol.
23. A composition according to any one of claims 19 to 22 which also contains at least one perfume, hair dye or plasticizing agent.

24. A composition according to claim 19 substantially as hereinbefore described.

25. A method of setting hair which comprises applying to the hair a composition as claimed in any one of claims 20 to 24 which is in the form of an aqueous-alcoholic solution, winding the hair on wavesetting rollers and drying the hair.

DATED this 18th day of JUNE, 1973

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