

WATER-SOLUBLE COPOLYMER
HAVING ALKYL-MODIFIED CARBOXYL GROUPS

Technical Field

5 [0001]

The present invention relates to a water-soluble copolymer having alkyl-modified carboxyl groups. More specifically, the present invention relates to a water-soluble copolymer having alkyl-modified carboxyl
10 groups, which may be preferably used as a thickening agent for cosmetics and the like.

Background

[0002]

15 A variety of copolymers are known as copolymers of (meth)acrylic acid and alkyl (meth)acrylate, which are used in thickening agents for cosmetics and the like; moisturizers for cataplasms and the like; emulsifiers; suspension stabilizers for suspensions; and the like. For
20 example, a copolymer obtained by reacting a specific amount of olefin-based unsaturated carboxylic acid monomers and a specific amount of alkyl (meth)acrylate (a carbon number of the alkyl group is 10-30) (See Patent Document 1), a copolymer obtained by reacting a specific amount of
25 olefin-based unsaturated carboxylic acid monomers and a specific amount of alkyl (meth)acrylate (a carbon number

of the alkyl group is 10-30) and a cross linking agent (See Patent Document 2), a copolymer obtained by reacting olefin-based unsaturated carboxylic acid monomers and alkyl (meth)acrylate (a carbon number of the alkyl group is 8-30) (See Patent Document 3) and the like are known.

These copolymers of (meth)acrylic acid and alkyl (meth)acrylate are used in the above applications usually after dissolving into water and the like and neutralize with alkali to form a neutralized viscous liquid at a concentration of about 0.1 to 1 weight %.

[0003]

This neutralized viscous liquid had a problem that their viscosity or transmittance reduces and a part of the copolymer precipitates when electrolytes used as various raw materials for products or additives coexist even at relatively low concentrations.

[0004]

In particular, recently, in a field of cosmetics and the like, cosmetics containing high amounts of minerals and the like in order to differentiate from other products as well as various properties, for example, good appearances such as transparency, non-sticky texture and the like are in the spotlight. Therefore, it is desired to invent a thickening agent which can form a neutralized viscous liquid having a high viscosity and a high transmittance even in the presence of a relatively high concentration of

electrolytes.

In addition, from a viewpoint of reducing manufacturing costs, it is desired to invent a thickening agent having properties leading to improvement in
5 manufacturing efficiencies in a variety of manufacturing processes.

[0005]

[Patent Document 1] JP 6190/1976A

[Patent Document 2] JP 232107/1984A

10 [Patent Document 3] US 5004598

Disclosure of the Invention

[0006]

The object of the present invention is to provide a
15 water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exist, the viscosity greatly increases when electrolytes are added, which has a high viscosity and a
20 high transmittance and which has moist textures without stickiness even in the presence of a relatively high concentration of electrolytes, and a thickening agent containing the same.

[0007]

25 The present invention relates to, as will be described, water-soluble copolymer having alkyl-modified carboxyl

groups.

[0008]

(1) A water-soluble copolymer having alkyl-modified carboxyl groups which is obtained by polymerizing 100 parts
5 by weight of (meth)acrylic acid, 0.5-5 parts by weight of alkyl (meth)acrylate comprising an alkyl group having a carbon number of 18-24, and 0-0.1 parts by weight of a compound having two or more of ethylenic unsaturated groups, wherein a 1 weight %-neutralized viscous liquid shows a
10 viscosity of 1500 mPa·s or lower and a transmittance of 90 % or higher, and when 0.25-5 parts by weight of sodium chloride is added to 100 parts by weight of the neutralized viscous liquid, the liquid shows a highest viscosity of 15000-40000 mPa·s and a transmittance of 90 % or higher.

15 [0009]

(2) The water-soluble copolymer having alkyl-modified carboxyl groups according to (1), wherein the compound having two or more of ethylenic unsaturated groups is at least one selected from a group consisting of
20 pentaerythritol allyl ether, diethylene glycol diallyl ether, polyethylene glycol diallyl ether and polyallyl saccharose.

[0010]

(3) A thickening agent comprising the water-soluble
25 copolymer having alkyl-modified carboxyl groups according to (1) or (2).

[0011]

The present invention will be explained in detail as below.

[0012] Additionally, in the present invention, acrylic acid and methacrylic acid are inclusively described as (meth)acrylic acid.

[0013]

Further, in the present invention, neutralization for the neutralized viscous liquid is to make the pH of the liquid 6.5-7.5.

[0014]

In the present invention, the water-soluble copolymer having alkyl-modified carboxyl groups is obtained by polymerizing (meth)acrylic acid and alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24 and optionally a compound having two or more of ethylenic unsaturated groups.

[0015]

The alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24 used in the present invention is an ester of (meth)acrylic acid and higher alcohol which comprises an alkyl group having a carbon number of 18-24, for example, an ester of (meth)acrylic acid and stearyl alcohol, an ester of (meth)acrylic acid and eicosanol, an ester of (meth)acrylic acid and behenyl alcohol, an ester of (meth)acrylic acid and tetracosanol

and the like. Among them, stearyl methacrylate, eicosanyl methacrylate, behenyl methacrylate and tetracosanyl methacrylate are preferably used because viscosity properties and textures are excellent regarding

5 neutralized viscous liquids of the water-soluble copolymer having alkyl-modified carboxyl groups obtained therefrom and the liquids in the presence of electrolytes.

Additionally, as an alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24, commercial
10 products, for example, a product BLEMMEER VMA70 manufactured by NOF Corporation and the like may be used.

[0016]

When (meth)acrylic acid and alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24
15 are combined in the present invention, either or both of (meth)acrylic acid and alkyl (meth)acrylate may be used alone or in a combination of two or more, respectively.

[0017]

The amount of alkyl (meth)acrylate which comprises an
20 alkyl groups having a carbon number of 18-24 used in the present invention is 0.5-5 parts by weight, more preferably 1-3 parts by weight with respect to 100 parts by weight of (meth)acrylic acid. When the amount of alkyl
(meth)acrylate which comprises an alkyl groups having a
25 carbon number of 18-24 is less than 0.5 parts by weight with respect to 100 parts by weight of (meth)acrylic acid, it

is possible that a transmittance in the presence of electrolyte of a neutralized viscous liquid of the obtained water-soluble copolymer having alkyl-modified carboxyl groups is insufficient, while when the amount is more than 5 parts by weight, it is possible that water-solubility of the obtained water-soluble copolymer having alkyl-modified carboxyl groups deteriorates.

[0018]

The compounds having two or more of ethylenic unsaturated groups optionally used in the present invention are not especially limited but compounds in which the ethylenic unsaturated groups are allyl groups are preferable. Among them, pentaerythritol allyl ether such as pentaerythritol diallyl ether, pentaerythritol triallyl ether and pentaerythritol tetraallyl ether and the like, diethylene glycol diallyl ether, polyethylene glycol diallyl ether and polyallyl succharose are more preferable. These compounds having two or more of ethylenic unsaturated groups may be used alone or in combination of two or more of them.

[0019]

The amount of the compound having two or more of ethylenic unsaturated groups used in the present invention is 0.001-0.1 parts by weight, more preferably 0.001-0.044 parts by weight with respect to 100 parts by weight of (meth)acrylic acid. When the amount of the compound having

two or more of ethylenic unsaturated groups is more than 0.1 parts by weight, it is possible that a transmittance in the presence of electrolyte of a neutralized viscous liquid of the obtained water-soluble copolymer having
5 alkyl-modified carboxyl groups deteriorates or the liquid becomes clouded.

[0020]

In the present invention, a method for obtaining the water-soluble copolymer having alkyl-modified carboxyl
10 groups by polymerizing (meth)acrylic acid and 0.5-5 parts by weight of alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24 with respect to 100 parts by weight of (meth)acrylic acid and, optionally 0-0.1 parts by weight of a compound having two or more of ethylenic
15 unsaturated groups with respect to 100 parts by weight of (meth)acrylic acid is not especially limited but ordinary methods such as a method for polymerizing these materials by stirring them in a solvent under an inactive gas atmosphere in the presence of a polymerization initiator
20 and the like may be used.

[0021]

Inactive gases for producing an inactive gas atmosphere include, for example, a nitrogen gas, an argon gas and the like.

25 The aforementioned solvent is not especially limited insofar as they dissolve (meth)acrylic acid, alkyl

(meth)acrylate which comprises an alkyl group having a carbon number of 18-24 and a compound having two or more of ethylenic unsaturated groups but not the obtained water-soluble copolymer having alkyl-modified carboxyl groups and do not inhibit a polymerization reaction.

Examples of such a solvent include, for example, normal pentane, normal hexane, normal heptane, cyclopentane, cyclohexane and the like. Among them, normal hexane and normal heptane are preferably used.

10 [0022]

The amount of the solvent to be used is preferably 300-5000 parts by weight with respect to 100 parts by weight of (meth)acrylic acid from viewpoints of improving stirring workability and economy.

15 [0023]

The aforementioned polymerization initiator is preferably a radical polymerization initiator for example, α, α' -azoisobutyronitrile,

2,2'-azobis-2,4-dimethylvarelonitrile,

20 2,2'-azobismethylisobutylate and the like. Among them, 2,2'-azobismethylisobutylate is preferably used from a viewpoint that a high molecular weight of water-soluble copolymer having alkyl-modified carboxyl groups can be obtained.

25 [0024]

The amount of the polymerization initiator to be used

is desirably 0.00003-0.002 moles with respect to 1 mole of (meth)acrylic acid. When the amount of the polymerization initiator is less than 0.00003 moles, it is possible that polymerization reaction rate is slow to be not economic.

5 When the amount of the polymerization initiator is more than 0.002 moles, it is possible that polymerization progresses rapidly to make reaction control difficult.

[0025]

The reaction temperature is preferably 50-90 °C, more
10 preferably 55-75 °C. When the reaction temperature is lower than 50 °C, it is possible that the viscosity of the reaction solution increases to make uniformly-stirring difficult. When the reaction temperature is above 90 °C, it is possible that polymerization progresses rapidly to
15 make reaction control difficult.

The reaction time, which depends on the reaction temperature, is usually 0.5-5 hours.

[0026]

The water-soluble copolymer having alkyl-modified
20 carboxyl groups of the present invention may be obtained by heating the reaction solution for example at 80-130 °C after completion of the reaction to evaporate the solvent. When the heating temperature is lower than 80 °C, it is possible that it takes long time to evaporate the solvent.
25 When the heating temperature is above 130 °C, it is possible that water-solubility of the obtained water-soluble

copolymer having alkyl-modified carboxyl groups deteriorates.

[0027]

The water-soluble copolymer having alkyl-modified
5 carboxyl groups thus obtained is characterized in that a
1 weight %-neutralized viscous liquid obtained from the
copolymer shows a viscosity of 1500 mPa·s or lower and a
transmittance of 90 % or higher, and when 0.25-5 parts by
weight of sodium chloride is added to 100 parts by weight
10 of the neutralized viscous liquid, the liquid shows a
highest viscosity of 15000-40000 mPa·s and a transmittance
of 90 % or higher. Usually, a liquid is considered to be
transparent when a transmittance is 90 % or higher.

[0028]

15 In viscosity measurements, 1 weight %-neutralized
viscous liquids having with a pH of 6.5-7.5, which is formed
by dissolving a predetermined amount of the water-soluble
copolymers to an appropriate amount of pure water with
stirring and adding a predetermined concentration of sodium
20 hydroxide or, if required, electrolyte-added solutions
prepared by adding a predetermined amount of sodium
chloride and stirring are used as evaluation samples after
standing for one hour.

Viscosity is measured at 25 °C after one minute
25 rotating at a rotational speed of 20 rpm by using a BH type
rotational viscometer with a spindle rotor No. 6.

[0029]

In the present invention, a transmittance is measured at a wavelength of 425 nm in a cell with a light path length of 1 cm after degassed a sample by centrifuging.

5 [0030]

For example, neutralized viscous liquids which has a pH of 6.5-7.5 and contains the water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention at about 1 weight % may be used as a
10 thickening agent for cosmetics and the like, wherein the neutralized viscous liquids are formed by dissolving the copolymer to pure water such as deionized water and neutralizing with alkali.

Alkalies used to neutralize the copolymer solution are
15 not particularly limited but include alkali metal hydroxides such as sodium hydroxide, amines such as triethanolamine, diisopropanolamine, and the like. Among them, sodium hydroxide is preferably used.

[0031]

20 The neutralized viscous liquids obtained from the water-soluble copolymer having alkyl-modified carboxyl groups according to the present invention have a very low viscosity when no electrolyte exists and have a greatly increased viscosity when electrolytes are added. Further,
25 the neutralized viscous liquids have a high viscosity and a high transmittance and have moist textures without

stickiness even in the presence of a relatively high concentration of electrolytes.

[0032]

It is not clearly understood why the water-soluble
5 copolymer having alkyl-modified carboxyl groups according
to the present invention shows the above property. However,
it is presumed that by using a specific amount of alkyl
(meth)acrylate which comprises an alkyl group having a
carbon number of 18-24, the alkyl groups having a carbon
10 number of 18-24 introduced into the water-soluble copolymer
having alkyl-modified carboxyl groups associate with each
other in an aqueous solution via hydrophobic interaction
to increase viscosity and thereby effects of electrolytes
change.

15 [0033]

Accordingly, use of the water-soluble copolymer having
alkyl-modified carboxyl groups according to the present
invention allows manufacturing cosmetics excellent in
transparency and having moist texture without stickiness
20 regardless of a relatively high concentration of various
electrolytes as additives.

Such cosmetics include, for example, lotion, emulsion,
serum, cream, cream pack, massage cream, cleansing cream,
cleansing gel, cleansing foam, sunscreen, styling gel,
25 eyeliner, mascara, lipstick, foundation and the like.

[0034]

In addition, due to a low viscosity in the absence of electrolytes, those thickening agents are very useful from a viewpoint of manufacturing efficiency for cosmetics and the like. That is, since a viscosity of a solution may be maintained to low in a variety of manufacturing processes before adding electrolytes, working efficiencies in a reaction process, a transfer process, a heating process, a compounding process and the like before adding electrolytes may be greatly improved by leaving a process for adding electrolytes later.

Effect of the Invention

[0035]

The present invention provides a water-soluble copolymer having alkyl-modified carboxyl groups which is able to produce a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a high viscosity and a high transmittance and which has moist textures without stickiness even in the presence of a relatively high concentration of electrolytes.

Best mode for carrying out the Invention

[0036]

The present invention will be specifically explained

below by referring to the following Examples, Comparative Examples and Referential Examples. However, the present invention is never limited by those examples.

[0037]

5 Example 1

Into a 500 mL-four necked flask equipped with a stirrer, a thermometer, a nitrogen blowing tube and a condenser, were placed 45 g (0.625 moles) of acrylic acid; 0.45 g of BLEMMA VMA70 manufactured by NOF CORPORATION (a mixture comprising
10 10-20 parts by weight of stearyl methacrylate, 10-20 parts by weight of eicosanyl methacrylate, 59-80 parts by weight of behenyl methacrylate and 1 part by weight or less of tetracosanyl methacrylate) as alkyl (meth)acrylate which comprises an alkyl group having a carbon number of 18-24;
15 150 g of normal hexane and 0.081 g (0.00035 moles) of 2,2'-azobismethylisobutylate. The mixture was stirred and mixed uniformly followed by blowing a nitrogen gas into the solution in order to remove oxygen existing in the upper room of the reactor vessel, the raw materials and the
20 solvent. Then, a reaction was conducted for 4 hours at 60-65 °C under a nitrogen atmosphere. After the reaction completed, the formed slurry was heated at 90 °C to evaporate normal hexane and, further, the resultant was dried under reduced pressure at 10 mmHg at 110 °C for 8 hours
25 to obtain 43 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0038]

Example 2

The manner in Example 1 was followed but the amount of BLEMMER VMA70 manufactured by NOF CORPORATION was
5 changed to 1.35 g to obtain 44 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0039]

Example 3

10 The manner in Example 1 was followed but the amount of BLEMMER VMA70 manufactured by NOF CORPORATION was changed to 2.25 g to obtain 45 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

15 [0040]

Example 4

The manner in Example 1 was followed but 0.02 g of pentaerythritol allyl ether was added in addition to 45 g (0.625 moles) of acrylic acid, 0.45 g of BLEMMER VMA70
20 manufactured by NOF CORPORATION, 150 g of normal hexane and 0.081 g (0.00035 moles) of 2,2'-azobismethylisobutylate to obtain 43 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0041]

25 Example 5

The manner in Example 4 was followed but the amount

of BLEMMER VMA70 manufactured by NOF CORPORATION was changed to 1.35 g to obtain 44 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

5 [0042]

Example 6

The manner in Example 4 was followed but the amount of BLEMMER VMA70 manufactured by NOF CORPORATION was changed to 2.25 g to obtain 45 g of the water-soluble
10 copolymer having alkyl-modified carboxyl groups as white fine powder.

[0043]

Comparative Example 1

Into a 500 mL-four necked flask equipped with a stirrer,
15 a thermometer, a nitrogen blowing tube and a condenser, were placed 45 g (0.625 moles) of acrylic acid; 0.09 g of pentaerythritol allyl ether; 150 g of normal hexane and 0.081 g (0.00035 moles) of 2,2'-azobismethylisobutylate. The mixture was stirred and mixed uniformly followed by
20 blowing a nitrogen gas into the solution in order to remove oxygen existing in the upper room of the reactor vessel, the raw materials and the solvent. Then, a reaction was conducted for 4 hours at 60-65 °C under a nitrogen atmosphere. After the reaction completed, the formed
25 slurry was heated at 90 °C to evaporate normal hexane and, further, the resultant was dried under reduced pressure at

10 mmHg at 110 °C for 8 hours to obtain 42 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0044]

5 Comparative Example 2

The manner in Comparative Example 1 was followed but 0.9 g of stearyl methacrylate was added in addition to 45 g (0.625 moles) of acrylic acid, 0.09 g of pentaerythritol allyl ether, 150 g of normal hexane and 0.081 g (0.00035
10 moles) of 2,2'-azobismethylisobutylate to obtain 44 g of the water-soluble copolymer having alkyl-modified carboxyl groups as white fine powder.

[0045]

Comparative Example 3

15 The manner in Example 1 was followed but 0.42 g of stearyl methacrylate, 0.42 g of eicosanyl methacrylate and 1.86 g of behenyl methacrylate were used in place of 0.45 g of BLEMMEER VMA70 manufactured by NOF CORPORATION to obtain 46 g of the water-soluble copolymer having alkyl-modified
20 carboxyl groups as white fine powder.

[0046]

Main raw materials and their amounts used in Examples 1-6 and Comparative Examples 1-3 are summarized in Tables 1 and 2.

25

[0047]

Table 1

Main raw material	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
acrylic acid [g]	45 (100)	45 (100)	45 (100)	45 (100)	45 (100)	45 (100)
alkyl (meth)acrylate [g]	BLEMER VMA70 0.45 (1)	BLEMER VMA70 1.35 (3)	BLEMER VMA70 2.25 (5)	BLEMER VMA70 0.45 (1)	BLEMER VMA70 1.35 (3)	BLEMER VMA70 2.25 (5)
pentaerythritol allyl ether [g]	-	-	-	0.02 (0.044)	0.02 (0.044)	0.02 (0.044)

The numerical number in a parenthesis indicates an amount of the respective raw materials in parts by weight with assuming the amount of the acrylic acid used as 100 parts by weight.

[0048]

Table 2

Main raw material	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
acrylic acid [g]	45 (100)	45 (100)	45 (100)
alkyl (meth)acrylate [g]	-	stearyl methacrylate 0.9 (2)	stearyl methacrylate, eicosanyl methacrylate, behenyl methacrylate 2.7 (6) [Sum]
pentaerythritol allyl ether [g]	0.09 (0.2)	0.09 (0.2)	-

The numerical number in a parenthesis indicates an amount of the respective raw materials in parts by weight with assuming the amount of the acrylic acid used as 100 parts by weight.

[0049]

Evaluations

In order to evaluate properties as a thickening agent
5 of water-soluble copolymers having alkyl-modified carboxyl

groups obtained in Examples 1-6 and Comparative Example 1-3, viscosity and transmittance measurements were carried out regarding 1 weight %-neutralized viscous liquids of respective copolymers and electrolyte-added solutions prepared by adding sodium chloride to the liquids and mixing. Further, among these electrolyte-added solutions, those showing the highest viscosity were subjected to a moisture sensory test.

[0050]

10 (1) Preparation of evaluation samples

Three grams of each of the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Example 1-6 and Comparative Examples 1-3 was gradually added and dissolved to 280 g of pure water (deionized water) with stirring. To the solution was added 17 g of 6 weight %-sodium hydroxide to form 1 weight %-neutralized viscous liquids with a pH of 6.5-7.5. In addition, 0.25-5 weight %-electrolyte-added solutions were prepared by adding 0.75 g, 1.5 g, 2.25 g, 3 g, 6 g, 9 g, 12 g or 15 g of sodium chloride to 300 g of 1 weight %-neutralized viscous liquids obtained according to the manner as the same as above in order to evaluate properties of these neutralized viscous liquids in the presence of electrolytes.

25 [0051]

In the following evaluations, these 1

weight %-neutralized viscous liquids and the various weight %-electrolyte-added solutions were used as evaluation samples after standing for one hour.

[0052]

5 (2) Viscosity measurement

With respect to each of the evaluation samples, viscosity was measured at 25 °C after one minute rotating at a rotational speed of 20 rpm by using a BH type rotational viscometer with a spindle rotor No. 6. Measurement results
10 are shown in Tables 3-7.

[0053]

(3) Transmittance measurement

With respect to each of the evaluation samples, a transmittance was measured at a wavelength of 425 nm in a
15 cell with a light path length of 1 cm after degassed by centrifuging at 2000 rpm for 30 minutes. Usually, a liquid is considered to be transparent by visual observation when a transmittance is 90 % or higher. Measurement results are shown in Tables 3-7.

20 [0054]

(4) Sensory Evaluation on Texture

Respective evaluation samples which exhibited the highest viscosity in viscosity measurements with respect to each of the water-soluble copolymers having
25 alkyl-modified carboxyl groups obtained in Examples 1-6 and Comparative Examples 1-3 were applied on skins of panelists

consisting of 5 men and 5 women. Texture was evaluated based on feeling when the sample was spread with fingers.

Evaluation criteria are as follows:

- A: moisture
- 5 B: relatively moisture
- C: no impression
- D: sticky

[0055]

Additionally, when 70 % or more of the panelists score
10 "A: moisture" or "B: relatively moisture" to a sample, the sample is considered to show moisture texture. The evaluation results are shown in Tables 8-9.

[0056]

Table 3

Amount of NaCl added [g]	Ex. 1			Ex. 2		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	100	99		270	98	
0.75	950	98		10350	98	
1.5	1650	98		15900	98	Sample for S.E.
2.25	2100	96		15000	98	
3	1000	95		14500	97	
6	700	94		13350	94	
9	5000	92		3950	60	
12	15000	90	Sample for S.E.	400	--	phase sep.
15	10750	88		50	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0057]

Table 4

Amount of NaCl added [g]	Ex. 3			Ex. 4		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	900	99		110	99	
0.75	25850	98	Sample for S.E.	1000	98	
1.5	20750	96		1800	98	
2.25	17800	94		2250	98	
3	14500	92		1500	95	
6	3600	70		900	94	
9	---	--	phase sep.	5100	92	
12	---	--	phase sep.	15250	90	Sample for S.E.
15	---	--	phase sep.	10400	87	

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0058]

Table 5

Amount of NaCl added [g]	Ex. 5			Ex. 6		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	470	98		1500	99	
0.75	10300	98		26000	98	Sample for S.E.
1.5	16000	98	Sample for S.E.	20500	95	
2.25	15500	97		18000	94	
3	16000	96		13500	92	
6	15050	94		2800	68	
9	7850	60		--	--	phase sep.
12	900	37		--	--	phase sep.
15	50	--	phase sep.	--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0059]

Table 6

Amount of NaCl added [g]	Comp. Ex. 1			Comp. Ex. 2		
	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks	Viscosity [mPa·s]	Transmi- ttance [%]	Remarks
0	50	99		6800	95	
0.75	50	99	Sample for S.E.	9750	93	
1.5	50	98		11150	93	Sample for S.E.
2.25	50	98		10500	91	
3	50	97		9550	87	
6	50	96		6150	63	
9	50	93		1700	13	
12	50	92		400	4	
15	50	89		--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0060]

Table 7

Amount of NaCl added [g]	Comp. Ex. 3		
	Viscosity	Transmi-	Remarks
	[mPa·s]	ttance	
		[%]	
0	13750	98	
0.75	26650	29	Sample for S.E.
1.5	23500	--	
2.25	19500	--	
3	15000	--	
6	--	--	phase sep.
9	--	--	phase sep.
12	--	--	phase sep.
15	--	--	phase sep.

* S.E.: Sensory Evaluation

* phase sep.: phase separation

[0061]

Table 8

Criteria	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
	[people]	[people]	[people]	[people]	[people]	[people]
A	9	10	8	9	9	8
B	1	0	2	1	1	1
C	0	0	0	0	0	1
D	0	0	0	0	0	0

[0062]

Table 9

Criteria	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
	[people]	[people]	[people]
A	10	7	0
B	0	2	2
C	0	1	0
D	0	0	8

5 [0063]

From Tables 3-9, it is understood that the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-6 produced a neutralized viscous liquid in which although its viscosity is very low when no electrolyte exists, the viscosity greatly increases when electrolytes are added, which has a high viscosity and a high transmittance and which has moist textures without stickiness even in the presence of a relatively high concentration of electrolytes.

10 [0064]

Thus, it is demonstrated that the water-soluble copolymers having alkyl-modified carboxyl groups obtained in Examples 1-6 can be used as a thickening agent having excellent properties as described above.

15 [0065]

Referential Example 1

Components 1-6 shown below were added at the respective percentages and uniformly mixed by stirring. Further, components 7-10 were added and uniformly mixed by stirring and solubilized to prepare lotion.

1. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 6)	0.1%
2. Sodium hydroxide	0.28%
25 3. 2-glucoside ascorbate	2.0%
4. Citric acid	0.01%

	5. Sodium hydrogenphosphate	0.1%
	6. Distilled water	balance to 100 % sum
	7. Ethanol	8.0%
	8. POE(30) POP(6) decyl tetradecyl ether	0.3%
5	9. Preservative	q.s.
10	10. Incense	q.s.

* q.s.: quantus sufficiat

[0066]

Referential Example 2

10 Components 1-8 shown below were added at the respective percentages and heated at 80 °C. Further, components 9-17 were added and heated at 80 °C followed by stirring to emulsify. Then, emulsion was prepared by cooling with stirring.

15

	1. POE(20) sorbitan monostearate	1.0%
	2. POE(40) sorbitol tetraoleate	1.5%
	3. Lipophilic glyceryl monostearate	1.0%
	4. Stearic acid	0.5%
20	5. Behenyl alcohol	1.5%
	6. Squalane	5.0%
	7. Cetyl 2-ethylhexanoate	5.0%
	8. Methyl polysiloxane	0.5%
25	9. Water-soluble copolymer having alkyl-modified carboxyl groups	

(Example 3) 0.1%

	10. Xanthan gum	0.1%
	11. Sodium hydroxide	0.05%
	12. Sodium lactate	1.0%
	13. Citric acid	0.01%
5	14. Sodium hydrogenphosphate	0.1%
	15. 1,3-butylene glycol	7.0%
	16. Preservative	q.s.
	17. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

10 [0067]

Referential Example 3

Components 1-11 shown below were added at the respective percentages and dissolved at room temperature to form a viscous liquid. Then, serum was prepared.

15

	1. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 5)	0.2%
	2. Sodium hydroxide	0.08%
	3. L-ascorbyl magnesium phosphate	3.0%
20	4. Sodium Citrate	0.5%
	5. Tetrasodium EDTA	0.1%
	6. 1,3-butylene glycol	7.0%
	7. Glycerin	8.0%
	8. Distilled water	balance to 100 % sum
25	9. Cosmetic component	q.s.
	10. Preservative	q.s.

11. Ethanol 5.0%

* q.s.: quantus sufficiat

[0068]

Referential Example 4

5 Components 1-6 shown below were added at the respective percentages and heated at 80 °C. Further, components 7-14 were added at the respective percentages, heated at 80 °C, and stirred to emulsify. Then, cream was prepared by cooling with stirring.

10

	1. Decaglyceryl pentaoleate	3.0%
	2. Beewax	2.0%
	3. Cetanol	2.0%
	4. Squalane	5.0%
15	5. Glyceryl tri-2-ethylhexanoate	2.0%
	6. Methyl polysiloxane	0.5%
	7. Glycerin	5.0%
	8. L-ascorbyl magnesium phosphate	3.0%
	9. Sodium citrate	0.5%
20	10. Tetrasodium EDTA	0.1%
	11. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 5)	0.15%
	12. Sodium hydroxide	0.06%
	13. Preservative	q.s.
25	14. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

[0069]

Referential Example 5

Components 1-4 shown below were added at the respective percentages and headed at 80 °C. Further, components 5-12 were added at the respective percentages, heated at 80 °C, and stirred to emulsify. Then, cream pack was prepared by cooling with stirring.

	1. POE(20) POP(4) cetyl ether	0.8%
10	2. Diglyceryl monostearate	0.2%
	3. Glyceryl tri-2-ethylhexanoate	1.0%
	4. Meduhome oil	1.0%
	5. Glycerin	5.0%
	6. 1,3-butylene glycol	3.0%
15	7. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 2)	0.1%
	8. Sodium hydroxide	0.28%
	9. Hydroxyethyl cellulose	0.3%
	10. 2-Glucoside ascorbate	2.0%
20	11. Preservative	q.s.
	12. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

[0070]

Referential Example 6

25 Components 1-7 shown below were added at the respective percentages and headed at 80 °C. Further, components 8-13

were added at the respective percentages, heated at 80 °C, and stirred to emulsify. Then, massage cream was prepared by cooling with stirring.

5	1. POE(20) cetyl ether	2.0%
	2. Lipophilic glyceryl monostearate	4.0%
	3. Cetanol	2.0%
	4. White vaseline	6.0%
	5. Squalane	30.0%
10	6. Glyceryl tri-2-ethylhexanoate	5.0%
	7. Methyl polysiloxane	0.5%
	8. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 2)	0.1%
	9. Sodium hydroxide	0.04%
15	10. Glycerin	5.0%
	11. Sodium PCA	1.0%
	12. Preservative	q.s.
	13. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

20 [0071]

Referential Example 7

Components 1-7 shown below were added at the respective percentages and heated at 80 °C. Further, components 8-13 were added at the respective percentages, heated at 80 °C, stirred to emulsify. Then, cleansing cream was prepared by cooling with stirring.

	1. POE(20) sorbitan monostearate	2.0%
	2. POE(40) sorbitol tetraoleate	1.0%
	3. Self-emulsifying glyceryl monostearate	2.0%
5	4. Stearic acid	4.0%
	5. Cetanol	2.0%
	6. Liquid paraffin	30.0%
	7. Glyceryl tri-2-ethylhexanoate	10.0%
	8. 1,3-butylene glycol	5.0%
10	9. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 6)	0.1%
	10. Sodium hydroxide	0.04%
	11. L-serine	1.0%
	12. Preservative	q.s.
15	13. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

[0072]

Referential Example 8

Components 1-10 shown below were added at the
 20 respective percentages and uniformly mixed at room
 temperature to form gel. Then, cleansing gel was prepared.

	1. AQUPEC HV-501E (carboxyvinyl polymer)	0.1%
	2. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 1)	0.1%
25	3. Sodium hydroxide	0.08%

	4. Sodium PCA	1.0%
	5. Hydroxypropyl cellulose	0.5%
	6. POE(30) cetyl ether	16.0%
	7. POE(5) lauryl ether	12.0%
5	8. 1,3-butylene glycol	10.0%
	9. Distilled water	balance to 100 % sum
	10. Preservative	q.s.

* q.s.: quantus sufficiat

[0073]

10 Referential Example 9

Components 1-8 shown below were added at the respective percentages and heated at 80 °C. Further, components 9-14 were added at the respective percentages, heated at 80 °C and mixed. Then, cleansing foam was prepared by cooling
15 with stirring.

	1. Myristic acid	15.0%
	2. Palmitic acid	5.0%
	3. Stearic acid	3.0%
20	4. Beewax	3.0%
	5. Polyethylene glycol 6000	2.0%
	6. Ethylene glycol distearate	2.0%
	7. Diethanolamide cocoate	3.0%
	8. Concentrated glycerin	15.0%
25	9. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 3)	0.1%

10.	Sodium hydroxide	0.04%
11.	Potassium hydroxide	5.5%
12.	Sodium PCA	0.5%
13.	Sodium <i>N</i> -lauroylsarcosine	10.0%
5 14.	Distilled Water	balance to 100 % sum
	[0074]	

Referential Example 10

Components 1-10 shown below were added at the respective percentages and heated at 80 °C. Further, components 11-16 were added at the respective percentages, heated at 80 °C and stirred to emulsify. Then, sunscreen was prepared by cooling with stirring.

15	1. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 4)	0.1%
	2. Sodium carboxymethylcellulose	0.3%
	3. Sodium hydroxide	0.28%
	4. 2-glucoside ascorbate	2.0%
	5. Citric acid	0.01%
20	6. Sodium hydrogenphosphate	0.1%
	7. Preservative	q.s.
	8. 1,3-butylene glycol	7.0%
	9. Glycerin	8.0%
	10. Distilled water	balance to 100 % sum
25	11. Sorbitan monostearate	0.5%
	12. Polyoxyethylene sorbitan POE(20) monooleate	0.5%

13. Sorbitan sesquioleate	0.5%
14. Cetanol	2.0%
15. 2-ethylhexyl paramethoxycinnamate	10.0%
16. Ethanol	10.0%

5 * q.s.: quantus sufficiat

[0075]

Referential Example 11

Components 1-6 shown below were added at the respective percentages and dissolved at room temperature. Then,
 10 styling gel was prepared by stirring to uniformly mix.

1. AQUPEC HV-505E (carboxyvinyl polymer)	0.1%
2. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 5)	0.1%
15 3. Sodium hydroxide	0.08%
4. Vinylpyrrolidone-vinyl acetate copolymer solution (H) (*1)	10.0%
5. Sodium PCA	1.0%
6. Distilled water	balance to 100 % sum

20 *1: PVP/VAE-735 manufactured by ISP Corporation

[0076]

Referential Example 12

Components 1-9 shown below were added at the respective percentages and dissolved at room temperature. Then,
 25 eyeliner was prepared by stirring to uniformly mix.

	1. Alkyl acrylate copolymer emulsion (*2)	30.0%
	2. 1,3-butylene glycol	15.0%
	3. Black iron oxide	15.0%
	4. Water-soluble copolymer having alkyl-modified carboxyl	
5	groups (Example 3)	0.1%
	5. Sodium hydroxide	0.04%
	6. Sodium carboxymethylcellulose	2.0%
	7. Sodium chloride	0.5%
	8. Preservative	q.s.
10	9. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

*2: YODOSOL GH810 manufactured by Nippon NSC Ltd.

[0077]

Referential Example 13

15 Components 1-10 shown below were added at the
 respective percentages and heated at 80 °C. Further,
 components 11-16 were added at the respective percentages,
 heated at 80 °C and stirred to emulsify. Then, mascara was
 prepared by cooling with stirring.

20

	1. Stearic acid	2.0%
	2. Carnauba wax	2.0%
	3. Beewax	3.0%
	4. Polyoxyethylene sorbitan POE(20) monooleate	1.0%
25	5. Sorbitan sesquioleate	0.5%
	6. Alkyl acrylate copolymer emulsion (*2)	1.0%

	7. Triethanolamine	1.1%
	8. Propylene glycol	1.0%
	9. Black iron oxide	10.0%
	10. Kaolin	10.0%
5	11. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 1)	0.2%
	12. Sodium hydroxide	0.08%
	13. Sodium carboxymethylcellulose	2.5%
	14. Sodium chloride	0.1%
10	15. Preservative	q.s.
	16. Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

*2: YODOSOL GH810 manufactured by Nippon NSC Ltd.

[0078]

15 Referential Example 14

Components 1-11 shown below were added at the respective percentages and dispersed by roll milling. The resultant was run into a mold at a high temperature. Then, lipstick was prepared by filling the cooled and molded product into a container.

	1. Candelilla wax	5.0%
	2. Ceresin	5.0%
	3. Carnauba wax	3.0%
25	4. Microcrystalline wax	3.0%
	5. Glyceryl tri-2-ethylhexanoate	20.0%

	6. Isotridecyl isononanoate	20.0%
	7. Diisostearyl maleate	balance to 100 % sum
	8. Water-soluble copolymer having alkyl-modified carboxyl groups (Example 6)	1.0%
5	9. Silicic anhydride	1.0%
	10. Coloring agent	q.s.
	11. Preservative	q.s.

* q.s.: quantus sufficiat

[0079]

10 Referential Example 15

Components 1-11 shown below were added at the respective percentages and heated at 80 °C. Further, components 12-17 were added at the respective percentages, heated at 80 °C and mixed. Then, foundation was prepared
15 by cooling with stirring.

	1. Lipophilic glyceryl monostearate	1.0%
	2. Stearic acid	5.0%
	3. Behenyl alcohol	1.0%
20	4. Cetanol	0.5%
	5. Squalane	5.0%
	6. Titanium oxide	4.0%
	7. Red iron oxide	q.s.
	8. Yellow iron oxide	q.s.
25	9. Black iron oxide	q.s.
	10. Talc	4.0%

11.	Soy bean phospholipid	0.3%
12.	1,3-butylene glycol	8.0%
13.	Triethanolamine	1.5%
14.	Water-soluble copolymer having alkyl-modified carboxyl	
5	groups (Example 6)	0.2%
15.	Sodium hydroxide	0.08%
16.	Sodium PCA	1.0%
17.	Distilled water	balance to 100 % sum

* q.s.: quantus sufficiat

10 [0080]

The cosmetics which use the water-soluble copolymer having alkyl-modified carboxyl groups obtained in Examples 1-6 showed moisture texture without stickiness. In addition, cosmetics and the like which contained
15 electrolytes and the like showed similar properties.

What we claimed is:

1. A water-soluble copolymer having alkyl-modified carboxyl groups
5 which is obtained by polymerizing 100 parts by weight of
(meth)acrylic acid, 0.5-5 parts by weight of alkyl (meth)acrylate
comprising an alkyl group having a carbon number of 18-24, and 0-0.1
parts by weight of a compound having two or more of ethylenic
unsaturated groups, wherein a 1 weight %-neutralized viscous liquid
10 shows a viscosity of 1500 mPa·s or lower and a transmittance of 90 %
or higher, and when 0.25-5 parts by weight of sodium chloride is
added to 100 parts by weight of the neutralized viscous liquid, the
liquid shows a highest viscosity of 15000-40000 mPa·s and a
transmittance of 90 % or higher, and wherein viscosity is measured
15 at 25°C after one minute rotation at a rotational speed of 20 rpm by
using a BH type rotational viscometer with a spindle rotor No. 6,
and wherein transmittance is measured at a wavelength of 425 nm in a
cell with a light path length of 1 cm after being degassed by
centrifuging.

20

2. The water-soluble copolymer having alkyl-modified carboxyl groups
according to claim 1, wherein the compound having two or more of
ethylenic unsaturated groups is at least one selected from a group
consisting of pentaerythritol allyl ether, diethylene glycol diallyl
25 ether, polyethylene glycol diallyl ether and polyallyl saccharose.

3. A thickening agent comprising the water-soluble copolymer having alkyl-modified carboxyl groups according to claim 1 or 2.