Claims

1. A method for fabricating a silicone-containing copolymer molded article comprising a silicone monomer unit, hydrophilic monomer unit, and crosslinking monomer unit, and having a hydrophilic surface;

by polymerizing a monomer solution containing (a) at least one silicone monomer comprising a (meth)acryloyl group; (b) at least one hydrophilic monomer comprising a vinyl group; (c) at least one crosslinkable monomer; and (d) at least one polymerization initiator;

in a cavity of a mold having a hydrophobic cavity surface;

wherein the polymerization initiator has a 10-hour half-life temperature (abbreviated to T10 hereinafter) of 70°C or higher and 100°C or lower, and

the polymerization is conducted by means of a step P1 of maintaining a temperature within a range of from the T10 of the polymerization initiator contained in the monomer solution to 35°C below T10 for one hour or more; and a step P2 of maintaining a temperature higher than the T10 of the polymerization initiator contained in the monomer solution for one hour or more.

2. The method according to claim 1, wherein the temperature maintained in step P1 is in a temperature range of from a temperature 10°C lower than T10 to a temperature 35°C lower than T10.

3. The method according to claim 1 or 2, wherein the temperature maintained in step P2 is in a temperature range of from a temperature 5°C higher than T10 to a temperature 50°C higher than T10.

4. The method according to any one of claims 1 to 3, wherein the polymerization initiator is an azo polymerization initiator or an organic peroxide polymerization initiator.

5. The method according to any one of claims 1 to 4, wherein the content of silicone monomer (a) units in the silicon-containing copolymer molded article is in a range of 20

to 56 mass%, the content of hydrophilic monomer (b) units is in a range of 40 to 60 mass%, and the content of crosslinkable monomer (c) units is in a range of 0.02 to 4 mass%.

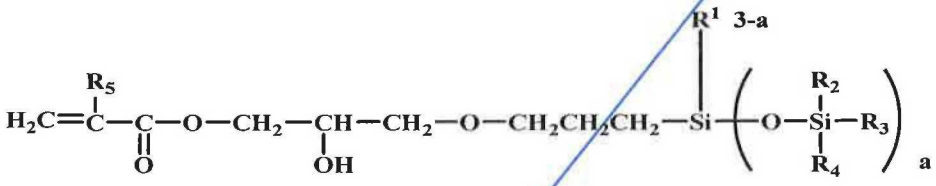
6. The method according to any one of claims 1 to 5, wherein silicone monomer (a) is at least one monomer selected from the group consisting of (a1) and (a2) below:

(a1) one or two or more silicone monomers containing at least one hydroxyl group and 1 to 4 silicon atoms per molecule; and

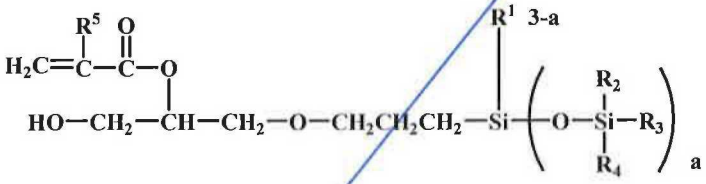
(a2) one or two or more silicone monomers containing at least one polyethylene glycol group and 1 to 4 silicon atoms per molecule.

7. The method according to claim 6, wherein silicone monomer (a1) is a monomer denoted by general formula (a1-1) or (a1-2) below:

[Chem. 1]



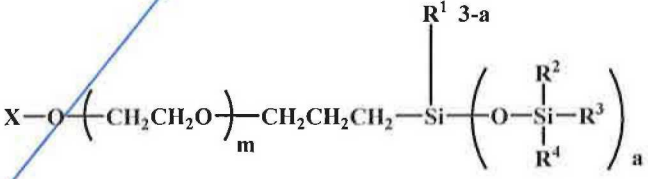
(a1-1)



(a1-2);

wherein R^1, R^2, R^3, and R^4 denote methyl groups, R^5 denotes a hydrogen atom or a methyl group, and *a* denotes an integer of from 1 to 3 and

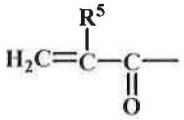
silicone monomer (a2) is a monomer denoted by general formula (a2-1) below:



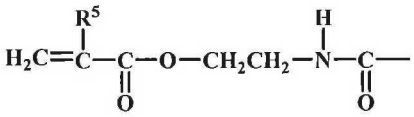
(a2-1);

wherein R^1, R^2, R^3, and R^4 denote methyl groups, a denotes an integer of from 1 to 3, m is 4 to 8, and X denotes one substituent selected from the substituents denoted by formula (Y1) or (Y2) below, wherein R^5 is a hydrogen atom or a methyl group,

[Chem. 3]



(Y1)



(Y2).

8. The method according to any one of claims 1 to 7, wherein hydrophilic monomer (b) is either one, or both, of N-vinyl-2-pyrrolidone and N-vinyl-N-methylacetamide.

9. The method according to any one of claims 1 to 8, wherein the crosslinkable monomer (c) is at least one monomer selected from the group consisting of (c1), (c2), and (c3):

(c1) one or two or more monomers containing two or more vinyl groups per molecule;

(c2) one or two or more monomers containing two or more allyl groups per molecule; and

(c3) one or two or more monomers containing two or more (meth)acrylate groups per molecule.

10. The method according to claim 9, wherein the monomer (c1) is one or two or more members selected from the group consisting of 1,4-butanediol divinyl ether, diethylene glycol divinyl ether, and triethylene glycol divinyl ether;

the monomer (c2) is one or two or more members selected from the group consisting of triallyl isocyanurate, trimethylol propane diallyl ether, and pentaerythritol triallyl ether; and

the monomer (c3) is one or two or more monomers selected from the group consisting of ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylol propane tri(meth)acrylate, and ethoxylated trimethylol propane tri(meth)acrylate.

11. The method according to any one of claims 1 to 10, wherein the monomer solution further contains at least one supplemental monomer selected from the group consisting of siloxane macromonomers, silicone monomers not containing hydroxyl groups or polyethylene glycol groups in the molecular structures thereof, and monomers not containing silicon atoms in the molecular structures thereof.

12. The method according to any one of claims 1 to 11, wherein the hydrophilic surface of the silicone-containing copolymer molded article exhibits a contact angle of 60° or less relative to pure water without the surface of the molded article having been subjected to post-processing to enhance the water wettability of the surface following polymerization, wherein the contact angle is the contact angle of a silicone hydrogel molded article obtained by hydrating the silicone-containing copolymer molded article.

13. The method according to any one of claims 1 to 12, wherein the mold having a hydrophobic cavity surface is a two-sided casting mold for use in polyalkylene contact lens molding and the silicone-containing copolymer molded article is a precursor for silicone hydrogel soft contact lens.

14. A silicone-containing copolymer molded article prepared by the method according to any one of claims 1 to 13.

15. A silicone-containing copolymer molded article comprised of at least one monomer unit selected from the group consisting of (a1) and (a2), a monomer unit (b),

and at least one monomer unit selected from the group consisting of (c1) to (c3) below, wherein molecular structure (g) may further contain monomer units not containing silicon atoms, wherein the monomers not containing silicon atoms in molecular structure (g) are one or more monomers selected from among 2-hydroxyethyl (meth)acrylate, methacrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, and 2-methacryloyloxyethyl phosphorylcholine); having a hydrophilic surface with a contact angle relative to pure water of 60°, wherein the contact angle is the contact angle of a silicone hydrogel molded article obtained by hydrating a silicone-containing copolymer molded article; wherein the content of silicone monomers (a1) and (a2) units is in a range of 20 to 56 mass%, the content of monomer (b) units is in a range of 40 to 60 mass%, and the content of monomers (c1) to (c3) units is in a range of 0.02 to 4 mass%, and the content of the monomer units not containing silicon atoms in molecular structure (g) is in a range of less than 10 mass%:

(a1) one or two or more units derived from silicone monomers containing at least one hydroxyl group and 1 to 4 silicon atoms per molecule, and having a molecular weight of less than 900;

(a2) one or two or more silicone monomer units containing at least one polyethylene glycol group and 1 to 4 silicon atoms per molecule, and having a molecular weight of less than 900;

(b) one or two or more units derived from hydrophilic monomers having a vinyl group;

(c1) one or two or more monomer units containing two or more vinyl groups per molecule;

(c2) one or two or more monomer units containing two or more allyl groups per molecule; and

(c3) one or two or more monomers having two or more (meth)acrylate groups per molecule.

16. A silicone-containing copolymer molded article, comprising at least one monomer unit selected from the group consisting of (a1) and (a2) below, monomer unit (b) below, at least one monomer selected from the group consisting of (c1) to (c3), and the

siloxane macromonomer unit denoted by (e); having a hydrophilic surface with a contact angle of 60° or less relative to pure water; and having a water content of 35% or greater but less than 60%, wherein the contact angle and water content are the contact angle and water content of a silicone hydrogel molded article obtained by hydrating the silicone-containing copolymer molded article:

(a1) one or two or more units derived from silicone monomers containing at least one hydroxyl group and 1 to 4 silicon atoms per molecule, and having a molecular weight of less than 900;

(a2) one or two or more silicone monomer units containing at least one polyethylene glycol group and 1 to 4 silicon atoms per molecule, and having a molecular weight of less than 900;

(b) one or two or more units derived from hydrophilic monomers having a vinyl group;

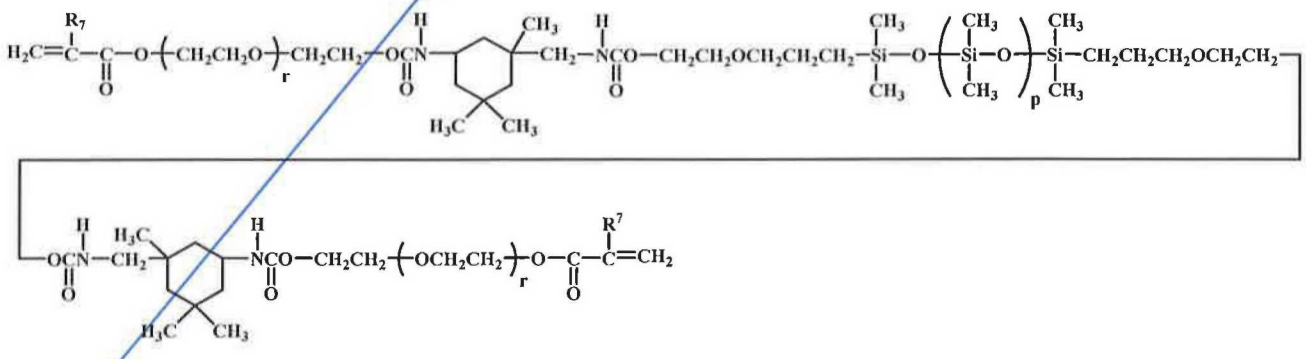
(c1) one or two or more monomer units containing two or more vinyl groups per molecule;

(c2) one or two or more monomer units containing two or more allyl groups per molecule;

(c3) one or two or more monomers having two or more (meth)acrylate groups per molecule; and

(e) one or two or more macromonomers of general formula (C1) and (C2);

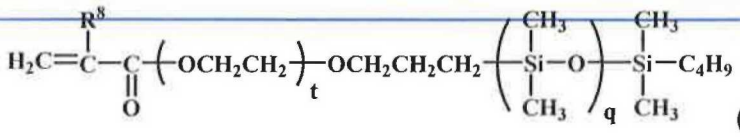
[Chem. 4]



(C1)

where in formula C1, R^7 denotes a hydrogen atom or a methyl group; r denotes 0 to 10; and p denotes 8 to 60;

[Chem. 5]



(C2)

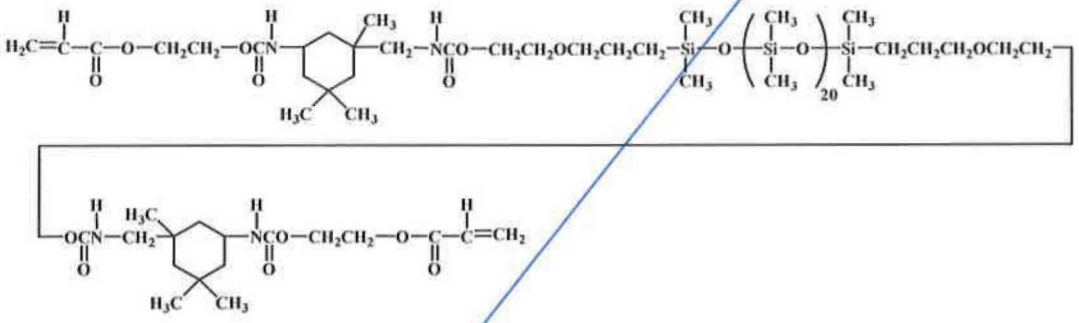
and where in formula C2, R^8 denotes a hydrogen atom or a methyl group, q denotes 9 to 15, and t denotes 0 to 3.

17. The silicone-containing copolymer molded article according to claim 16 wherein r is 0 to 8, p is 8 to 50, q is 9 to 13, and t is 0 to 2.

18. The silicone-containing copolymer molded article according to claim 16 wherein the siloxane macromonomer unit denoted by (e) is (E5) or (E6) below:

[Chem. 6]

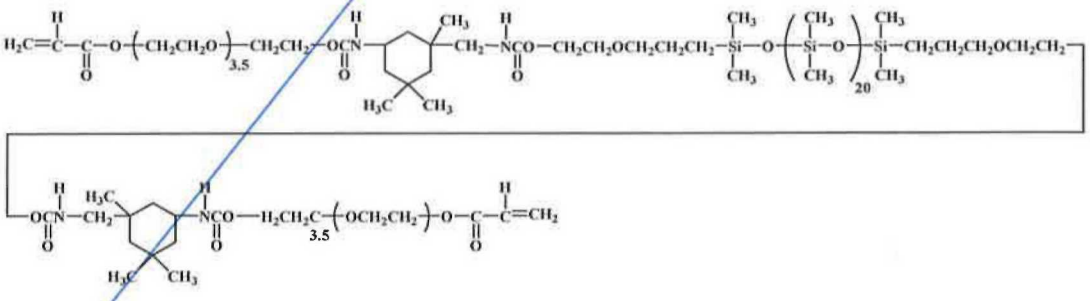
Macromer A



(E5)

[Chem. 7]

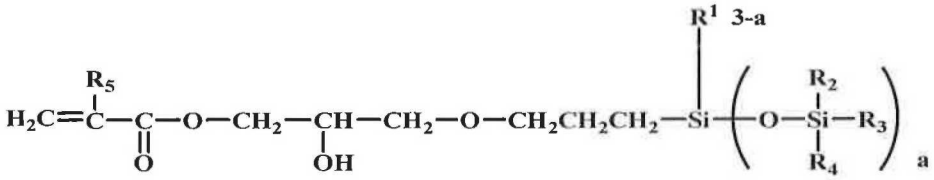
Macromer B



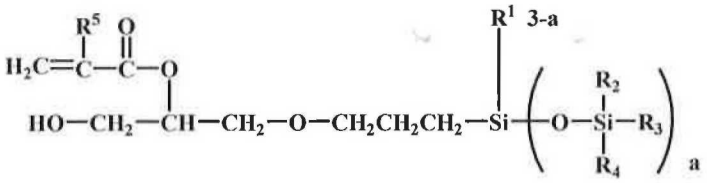
(E6).

19. The silicone-containing copolymer molded article according to any one of claims 15 to 18, wherein silicone monomer (a1) is a monomer denoted by general formula (a1-1) or (a1-2):

[Chem. 8]



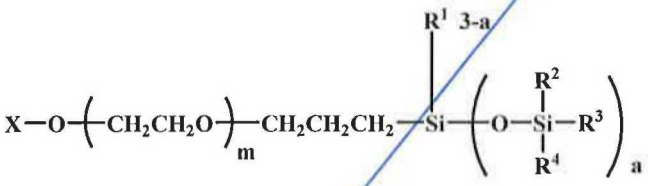
(a1-1)



(a1-2)

wherein R^1, R^2, R^3, and R^4 denotes methyl groups, R^5 denotes a hydrogen atom or methyl group, and *a* denotes an integer of 1 to 3 and silicone monomer (a2) is a monomer denoted by general formula (a2-1) below:

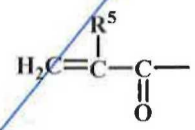
[Chem. 9]



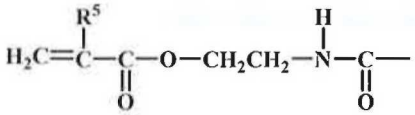
(a2-1)

wherein R^1, R^2, R^3, and R^4 denote methyl groups, *a* denotes an integer of from 1 to 3, m denotes 4 to 8, the X in the equation denotes a substituent selected from the substituents denoted by formulas (Y1) and (Y2) below (wherein R^5 denotes a hydrogen atom or a methyl group)):

[Chem. 10]



(Y1)



(Y2).

20. The silicone-containing copolymer molded article according to any one of claim 15 to 19, wherein hydrophilic monomer (b) is either N-vinyl-2-pyrrolidone or N-vinyl-N-methyl acetamide, or both.

21. The silicone-containing copolymer molded article according to any one of claims 15 to 20, wherein monomer (c1) is one or two or more selected from among 1,4-butanediol divinyl ether, diethylene glycol divinyl ether, and triethylene glycol divinyl ether;

monomer (c2) is one or two or more selected from among triallyl isocyanurate, trimethylol propane diallyl ether, and pentaerythritol triallyl ether; and

monomer (c3) is one or two or more monomer selected from among ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylol propane tri(meth)acrylate, and ethoxylated trimethylol propane tri(meth)acrylate.

22. The silicone-containing copolymer molded article according to any one of claims 16 to 21, wherein the content of silicone monomer (a1) and (a2) units is in a range of 20 to 56 mass%, the content of monomer (b) units is in a range of 40 to 60 mass%, and the content of monomer (c1), (c2), and (c3) units is in a range of 0.02 to 4 mass%.

23. The silicone-containing copolymer molded article according to any one of claims 16 to 22, wherein the content of siloxane macromonomer units (e) is 25 mass% or less.

24. The silicone-containing copolymer molded article according to any one of claims 16 to 23, further containing at least one additional monomer unit selected from the

group of silicone monomer units not containing hydroxyl groups or polyethylene glycol groups in the molecular structure thereof, and monomer units not containing silicon atoms in the molecular structure thereof.

25. The silicone-containing copolymer product of any one of claims 15 to 24, wherein the hydrophilic surface with a contact angle relative to pure water of 60° or less is obtained without post-processing the lens-forming material after polymerization to enhance the water wettability of the surface, wherein the contact angle is the contact angle of a silicone hydrogel molded article obtained by hydrating the silicone-containing copolymer molded article.

26. A precursor for silicone hydrogel soft contact lens in the form of the silicone-containing copolymer molded article according to any one of claims 14 to 25 and having a contact lens shape.

27. A silicone hydrogel soft contact lens obtained by rendering the silicone hydrogel soft contact lens precursor according to claim 26 a hydrated state with physiological saline or a preservation solution for soft contact lens.

28. The soft contact lens according to claim 27, wherein the hydrated silicone hydrogel soft contact lens exhibits a water content of 35% or greater and less than 60%.

29. The soft contact lens according to claim 27 or 28, wherein the hydrated silicone hydrogel soft contact lens is a soft contact lens with a maximum replacement frequency of up to one month.

30. The soft contact lens according to claim 29, wherein the hydrated silicone hydrogel soft contact lens is of a type with a replacement frequency of one day or two weeks.

31. A packaged soft contact lens product wherein the soft contact lens according to any one of claims 27 to 30 and physiological saline or soft-contact lens-use preservation solution are contained in a sealed container.

Claims

1. A method for fabricating a silicone-containing copolymer molded article comprising a silicone monomer unit, hydrophilic monomer unit, and crosslinking monomer unit, and having a hydrophilic surface;

by polymerizing a monomer solution containing (a) at least one silicone monomer comprising a (meth)acryloyl group; (b) at least one hydrophilic monomer comprising a vinyl group; (c) at least one crosslinkable monomer; and (d) at least one polymerization initiator;

in a cavity of a mold having a hydrophobic cavity surface;

wherein the polymerization initiator has a 10-hour half-life temperature (abbreviated to T10 hereinafter) of 70°C or higher and 100°C or lower, and

the polymerization is conducted by means of a step P1 of maintaining a temperature within a range of from the T10 of the polymerization initiator contained in the monomer solution to 35°C below T10 for one hour or more; and a step P2 of maintaining a temperature higher than the T10 of the polymerization initiator contained in the monomer solution for one hour or more.

2. The method according to claim 1, wherein the temperature maintained in step P1 is in a temperature range of from a temperature 10°C lower than T10 to a temperature 35°C lower than T10.

3. The method according to claim 1 or 2, wherein the temperature maintained in step P2 is in a temperature range of from a temperature 5°C higher than T10 to a temperature 50°C higher than T10.

4. The method according to any one of claims 1 to 3, wherein the polymerization initiator is an azo polymerization initiator or an organic peroxide polymerization initiator.

5. The method according to any one of claims 1 to 4, wherein the content of silicone monomer (a) units in the silicon-containing copolymer molded article is in a range of 20

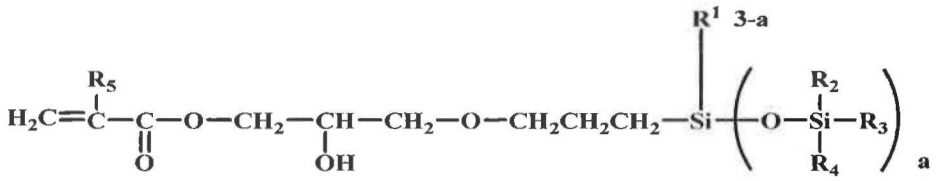
to 56 mass%, the content of hydrophilic monomer (b) units is in a range of 40 to 60 mass%, and the content of crosslinkable monomer (c) units is in a range of 0.02 to 4 mass%.

6. The method according to any one of claims 1 to 5, wherein silicone monomer (a) is at least one monomer selected from the group consisting of (a1) and (a2) below:

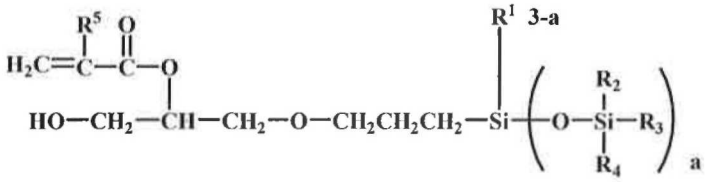
(a1) one or two or more silicone monomers containing at least one hydroxyl group and 1 to 4 silicon atoms per molecule; and

(a2) one or two or more silicone monomers containing at least one polyethylene glycol group and 1 to 4 silicon atoms per molecule.

7. The method according to claim 6, wherein silicone monomer (a1) is a monomer denoted by general formula (a1-1) or (a1-2) below:



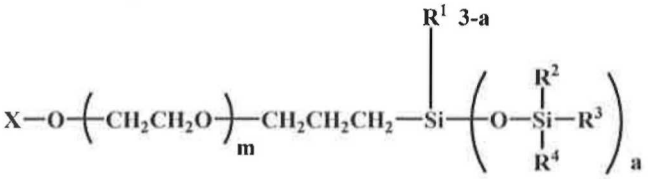
(a1-1)



(a1-2);

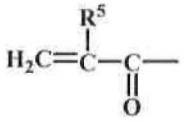
wherein R^1, R^2, R^3, and R^4 denote methyl groups, R^5 denotes a hydrogen atom or a methyl group, and *a* denotes an integer of from 1 to 3 and

silicone monomer (a2) is a monomer denoted by general formula (a2-1) below:

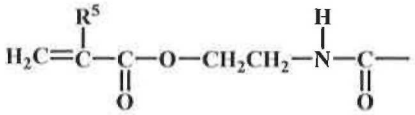


(a2-1);

wherein R^1, R^2, R^3, and R^4 denote methyl groups, *a* denotes an integer of from 1 to 3, m is 4 to 8, and X denotes one substituent selected from the substituents denoted by formula (Y1) or (Y2) below, wherein R^5 is a hydrogen atom or a methyl group,



(Y1)



(Y2).

8. The method according to any one of claims 1 to 7, wherein hydrophilic monomer (b) is either one, or both, of N-vinyl-2-pyrrolidone and N-vinyl-N-methylacetamide.

9. The method according to any one of claims 1 to 8, wherein the crosslinkable monomer (c) is at least one monomer selected from the group consisting of (c1), (c2), and (c3):

(c1) one or two or more monomers containing two or more vinyl groups per molecule;

(c2) one or two or more monomers containing two or more allyl groups per molecule; and

(c3) one or two or more monomers containing two or more (meth)acrylate groups per molecule.

10. The method according to claim 9, wherein the monomer (c1) is one or two or more members selected from the group consisting of 1,4-butanediol divinyl ether, diethylene glycol divinyl ether, and triethylene glycol divinyl ether;

the monomer (c2) is one or two or more members selected from the group consisting of triallyl isocyanurate, trimethylol propane diallyl ether, and pentaerythritol triallyl ether; and

the monomer (c3) is one or two or more monomers selected from the group consisting of ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylol propane tri(meth)acrylate, and ethoxylated trimethylol propane tri(meth)acrylate.

11. The method according to any one of claims 1 to 10, wherein the monomer solution further contains at least one supplemental monomer selected from the group consisting of siloxane macromonomers, silicone monomers not containing hydroxyl groups or polyethylene glycol groups in the molecular structures thereof, and monomers not containing silicon atoms in the molecular structures thereof.

12. The method according to any one of claims 1 to 11, wherein the hydrophilic surface of the silicone-containing copolymer molded article exhibits a contact angle of 60° or less relative to pure water without the surface of the molded article having been subjected to post-processing to enhance the water wettability of the surface following polymerization, wherein the contact angle is the contact angle of a silicone hydrogel molded article obtained by hydrating the silicone-containing copolymer molded article.

13. The method according to any one of claims 1 to 12, wherein the mold having a hydrophobic cavity surface is a two-sided casting mold made of polyalkylene and the silicone-containing copolymer molded article is a precursor for silicone hydrogel soft contact lens.

14. A silicone-containing copolymer molded article prepared by the method according to any one of claims 1 to 13.

15. A precursor for silicone hydrogel soft contact lens in the form of the silicone-containing copolymer molded article according to claim 14 and having a contact lens shape.

16. A silicone hydrogel soft contact lens obtained by rendering the silicone hydrogel soft contact lens precursor according to claim 15 a hydrated state with physiological saline or a preservation solution for soft contact lens.

17. The soft contact lens according to claim 16, wherein the hydrated silicone hydrogel soft contact lens exhibits a water content of 35% or greater and less than 60%.

18. The soft contact lens according to claim 16 or 17, wherein the hydrated silicone hydrogel soft contact lens is a soft contact lens with a maximum replacement frequency of up to one month.

19. The soft contact lens according to claim 18, wherein the hydrated silicone hydrogel soft contact lens is of a type with a replacement frequency of one day or two weeks.

20. A packaged soft contact lens product wherein the soft contact lens according to any one of claims 16 to 19 and physiological saline or soft-contact lens-use preservation solution are contained in a sealed container.