

## Description

The present invention relates to a novel, high water-absorptive soft contact lens, and more particularly to a high water-absorptive soft contact lens made of a copolymer prepared by copolymerizing an acrylate polymer or a methacrylate polymer (hereinafter referred to as "(meth)acrylate polymer") having hydrophilic groups and at least one polymerizable group and hydrophilic monomers as main components.

It has been well-known that among various materials for contact lens use, a material having a property that it is swollen to soften by absorbing water, is preferred in obtaining a soft contact lens having a good sensation of wearing.

Material mainly composed of polyhydroxyalkyl methacrylate, polyvinylpyrrolidone, or the like has been used in the above mentioned materials. The material mainly composed of polyvinylpyrrolidone is excellent in water-absorptive property and gas-permeability, and has a high safety for eyes from the physiological point of view because oxygen physiologically required for cornea is supplied enough from the open air to the cornea through water impregnated in a contact lens.

The material mainly composed of polyvinylpyrrolidone has excellent properties as mentioned above. However, because it has a high water content, it shows remarkable deterioration of dynamical properties when it is swollen with water, and consequently, it has a problem in durability of being easily damaged when formed into a lens.

In order to solve the above mentioned problems in durability, it is disclosed in Japanese Examined Patent Publication No. 43085/1982 to produce a comb-type block polymer by introducing suitably the side chain having a size within a certain range of polymethyl methacrylate into the main chain of a hydrophilic polymer, thereby improving mechanical strength, while maintaining the preferable nature of the hydrophilic polymer.

However, the polymethyl methacrylate having a polymerizable group in one end of the molecule which is disclosed in the above mentioned publication has the disadvantages in productivity. That is to say, it is difficult to control the reaction so as to produce only the polymethyl methacrylate in good efficiency in the industrial production thereof, particularly in large quantities, the mixture of a polymethyl methacrylate having a polymerizable group in the molecular chain end and a polymethyl methacrylate not having a polymerizable group is apt to be produced. Accordingly, when a hydrophilic monomer is copolymerized with the polymethyl methacrylate, the produced comb-type block copolymer contains the polymethyl methacrylate not copolymerized with hydrophilic monomer, thus the devitrification-phenomena may appear when impregnated with water and the yield of the copolymer having good qualities is decreased.

The water content of the material mainly composed of polyhydroxyalkyl methacrylate is about 30 to 40 % by weight, and therefore, this material is superior in the dynamical properties to the material mainly composed of polyvinylpyrrolidone. However, it has such problems that the water content is low and oxygen required for cornea is not enough supplied from the open air to the cornea through water impregnated in a contact lens.

EP-A-0 129 840 discloses a method of manufacturing a shaped article of hydrogel by the polymerization in a mold of a mixture comprising:

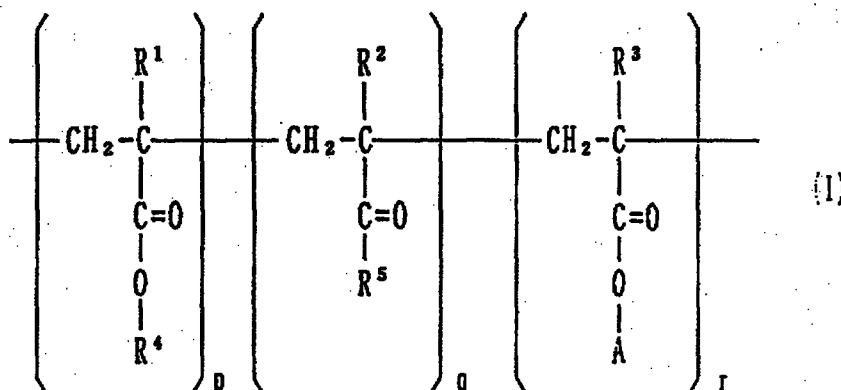
- A. an alkylene glycol mono(meth)acrylate or a monomer mixture consisting preponderantly of an alkylene glycol mono(meth)acrylate,
- B. a polymer synthesized from a component A and possessing a polymerizable double bond in the molecular unit thereof,
- C. a water-soluble dipolar aprotic solvent, and
- D. at least one member selected from the group consisting of a) water-soluble organic acids, (b) surface active agents, and (c) water-soluble organic substances which are poor solvents or non-solvents of the component B, and having the weight ratio of the component A to the component B in the range of 45 : 55 to 20 : 80.

The present invention is accomplished in order to obtain a high water-absorptive soft contact lens which does not have the remarkable deterioration of dynamical properties when it is swollen with water and which is excellent in transparency.

In accordance with the present invention, there is provided a high water-absorptive soft contact lens made of a copolymer comprising

- (A) 10 to 40 parts by weight of an acrylate or methacrylate polymer having a hydrophilic group and at least one polymerizable group in its molecule and
- (B) 90 to 60 parts by weight of a hydrophilic monomer selected from the group consisting of N-vinylactam, acrylamide, N-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative;

the total amount of the components (A) and (B) being 100 parts by weight, characterized in that said component (A) is a compound having the formula (I):



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are the same or different and each is hydrogen atom or methyl group,  $\text{R}^4$  is an alkyl group having 1 to 4 carbon atoms,  $\text{R}^5$  is an alkoxy group having hydroxyl group, hydroxyl group or  $-\text{N}(\text{CH}_3)_2$ , A is a polymerizable group, and p, q and r are integers to show a containing ratio of hydrophilic groups and polymerizable groups, satisfying the formula:

$$0.01 \leq \frac{q}{p + q + r} \leq 0.3 \text{ and}$$

$$0.002 \leq \frac{r}{p + q + r} \leq 0.05,$$

which copolymer is prepared by copolymerizing

- (a) 98.8 to 65 % by mole of an alkyl acrylate or methacrylate,
- (b) 1 to 30 % by mole of a monomer having a hydrophilic group and
- (c) 0.2 to 5 % by mole of a monomer having at least 2 polymerizable groups in its molecule.

In the present invention, there can be obtained a high water-absorptive soft contact lens excellent in transparency because the above mentioned (meth)acrylate polymer, that it is a reinforcing material, has a hydrophilic group and at least one polymerizable group in the molecule, and is suitably copolymerized with the above mentioned hydrophilic monomers, and moreover, the copolymer is not formed in phase separation structure.

In the present invention, (meth)acrylate polymer having a hydrophilic group and at least one polymerizable group in the molecule is a component in order to reinforce a formed copolymer without remarkable deterioration of strength and devitrification-phenomena when the hydrophilic polymer which is derived from a hydrophilic monomer selected from the group consisting of an N-vinylactam, acrylamide, N-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative is impregnated with water. The hydrophilic group and at least one polymerizable group are introduced into the (meth)acrylate polymer in order to reinforce the copolymer effectively without causing devitrification-phenomena.

The (meth)acrylate polymer is prepared, for instance, by copolymerizing an alkyl (meth)acrylate monomer (a) which is used in order to form the skeleton of the polymer, a (meth)acrylic monomer having a hydrophilic group (b) which is used in order to introduce a hydrophilic group into the molecule of the polymer and a monomer having at least two polymerizable groups (c) which is used in order to introduce at least one polymerizable group into the molecule of the polymer.

The alkyl (meth)acrylate monomer (a), the (meth)acrylic monomer having a hydrophilic group (b) and the monomer having at least two polymerizable groups are explained below.

The alkyl (meth)acrylate monomer (a) is one having linear, branched or cyclic alkyl group, which may be substituted with a halogen atom such as fluorine atom. Representative examples of the alkyl (meth)-

acrylate monomer (a) are, for instance, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, trifluoroethyl (meth)acrylate and pentafluoroethyl meth(acrylate). The alkyl (meth)acrylate monomers may be employed alone or in admixture thereof.

The (meth)acrylic monomer having a hydrophilic group (b) is one having a hydrophilic group such as hydroxyl, carboxyl or an N-dimethyl-substituted amide.

Representative examples of the (meth)acrylic monomer having a hydrophilic group (b) are, for instance, a (meth)acrylate having a hydroxyl group such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, dihydroxypropyl (meth)acrylate, dihydroxypropyl (meth)acrylate, dihydroxybutyl (meth)acrylate, (meth)acrylic acid; N,N-dimethyl (meth)acrylamide. Also, a ketalized dihydroxyalkyl (meth)acrylate in which 2 hydroxyl groups are ketalized such as 2,3-o-isopropylidene glycerol (meth)acrylate, 2-methyl-2-ethyl-4-(meth)acryloxymethyl-1,3-dioxolane or methyl-2,3-o-isopropylidene glycerol, can be employed in the invention as the monomer (b) to obtain substantially the same effects as those produced by the above-mentioned monomers. In that case, the ketal group is eliminated to produce hydroxyl groups by acid treatment after the polymerization. These monomers (b) may be employed alone or in admixture thereof.

Representative examples of the monomer having two polymerizable groups (c) are, for instance, ethylene glycol di(meth)acrylate, allyl (meth)acrylate, vinyl (meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, and the like. These monomers (c) may be employed alone or in admixture thereof.

When the (meth)acrylate polymer having a hydrophilic group and at least one polymerizable group in the molecule (A) used in the present invention is prepared, a lower alkyl (meth)acrylate is preferably used as a component of the alkyl (meth)acrylate monomer in order to make the copolymerization of the (meth)acrylate polymer (A) and the hydrophilic monomer selected from the group consisting of an N-vinylactam, acrylamide, n-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative good without causing steric hindrance. Also, since the copolymerizability is different between vinyl group and (meth)acryloyl group or between allyl group and (meth)acryloyl group, it is preferable to select the monomer (c) with giving a consideration to the copolymerizability between the polymerizable group of the polymer (A) and the polymerizable group of the hydrophilic monomer (B).

For instance, when the N-vinylactam is employed as the hydrophilic monomer (B), it is preferable that a (meth)acrylate monomer having a vinyl group such as allyl (meth)acrylate or vinyl (meth)acrylate is employed as the component (c). When the (meth)acrylamide in which hydrogen atom bonded to nitrogen atom which may be substituted is employed as the hydrophilic monomer (B), it is preferable that a (meth)acrylate monomer having a (meth)acryloyl group such as ethylene glycol di(meth)acrylate or diethylene glycol di(meth)acrylate is employed as the component (c). When the N-vinylactam and the (meth)acrylamide in which hydrogen atom bonded to nitrogen atom which may be substituted are employed at the same time, it is preferable that the (meth)acrylate monomer having vinyl group and the (meth)acrylate monomer having a (meth)acryloyl group are employed at the same time.

The (meth)acrylate polymer having a hydrophilic group and at least one polymerizable group in its molecule (A) used in the present invention can be obtained by copolymerizing the monomers (a), (b) and (c). However, it is necessary to control the copolymerization condition so that all polymerizable groups in the monomer (c) which is employed in order to introduce polymerizable groups into the obtained copolymer, do not participate in polymerization, in other words, cross-linking reaction does not occur, at the time when the monomers (a), (b) and (c) are copolymerized. Therefore, a solution polymerization is preferably employed as a polymerization method.

Any solvents can be used in the above solution polymerization, so long as they well dissolve and do not hinder the polymerization. For instance, benzene, acetone and the like can be used and may be employed alone or in admixture thereof. The amount of the solvent varies depending on the polymerization conditions. A suitable amount of the solvent is employed.

The polymerization reaction condition cannot be wholly determined because there is correlation between reaction temperature and reaction time. Therefore, it is practically preferable that the copolymerization reaction is carried out at comparatively low temperatures, e.g. at a temperature of 50° to 80° C, for several minutes to several hours.

When polymerizing the monomers (a), (b) and (c), usual polymerization initiators such as azobisisobutyronitrile, azobisdimethyl valeronitrile, t-butyl hydroperoxide, cumene hydroperoxide and benzoyl peroxide can be employed. The amount of the polymerization initiator is from about 0.001 to about 5 parts by weight, preferably, from about 0.01 to about 2 parts by weight based on the 100 parts by weight of all of the monomers used in the polymerization.

It is possible to control the composition of the (meth)acrylate polymer (A), that is, it is possible to control the numbers of polymerizable groups and hydrophilic groups in the polymer (A) by adjusting the amount of each of the monomers (a), (b) and (c) when preparing the (meth)acrylate polymer (A) used in the present invention.

For giving the excellent reinforcing effect, it is preferable that the proportion of the monomer (c) used to introduce polymerizable groups is about 0.2 to about 5 % by mole based on the total amount of the monomers used and the proportion of the monomer (b) used to introduce hydrophilic groups is about 1 to about 30 % by mole based on the total amount of the monomers used.

Regarding the proportion of the monomer (c) as the number of polymerizable groups, it is necessary that the number of polymerizable groups is at least one in one (meth)acrylate polymer molecule for giving the reinforcing effect. In case that the number average molecular weight is 10,000 to 50,000, it is preferable that the number of polymerizable groups is at most about 5. When the number of polymerizable groups is more than the above range it is hard to obtain the preferable copolymer having high water content because the cross-linking density of the copolymer prepared by copolymerizing the (meth)acrylate polymer (A) with the hydrophilic monomer (B) rises too high, thus resulting in lowering of the water content of the obtained copolymer.

On the other hand, in case that the proportion of the hydrophilic groups in the (meth)acrylate polymer (A) is less than the above range, the devitrification-phenomena occurs in the obtained contact lens when the lens is impregnated with water, and in case that the proportion of the hydrophilic groups in the (meth)acrylate polymer (A) is more than the above range, the (meth)acrylate polymer (A) cannot have the sufficient reinforcing effect.

The monomers (a), (b) and (c) are employed in the above-mentioned method for preparing the (meth)acrylate polymer (A). However, the (meth)acrylate polymer (A) can be synthesized by the following methods which are the methods introducing a polymerizable groups into the copolymer without employing the monomer (c).

1 A (meth)acrylate having epoxy group such as glycidyl (meth)acrylate is copolymerized with the monomer (a) and (b), and then polymerizable group is introduced into the copolymer by the reaction of the obtained copolymer and a compound which reacts with epoxy group such as methacrylic acid or hydroxystyrene.

2 The monomers (a) and (b) and an alkyl (meth)acrylate having hydroxyl group are copolymerized, and then the obtained copolymer is reacted with a predetermined amount of an acid halide having a polymerizable group such as (meth)acryloyl chloride to introduce polymerizable groups into the copolymer. As the alkyl (meth)acrylate having hydroxyl group, there are used those exemplified for the monomer (b).

3 (Meth)acrylic acid is copolymerized with the monomers (a) and (b), and then a polymerizable group is introduced into the copolymer by the reaction of the obtained copolymer and a compound having epoxy group and polymerizable group such as glycidyl (meth)acrylate.

In the above-mentioned processes 1 to 3, the reaction is carried out in two stages, but the before-mentioned process in which the monomers (a), (b) and (c) are copolymerized, is preferable from the view point of obtaining the (meth)acrylate polymer (A) in high industrial productivity, since the (meth)acrylate polymer (A) can be obtained in one stage reaction.

The thus synthesized (meth)acrylate polymer (A) is colorless and transparent in the form of a solution thereof in a solvent and is white powder in the dry state. According to a gel permeation chromatography (hereinafter referred to as "GPC") using polystyrene calibration curve, the number average molecular weight ( $\bar{M}_n$ ) of the (meth)acrylate polymer (A) is from about 5,000 to about 100,000. The molecular weight of the (meth)acrylate polymer (A) influences the dynamical properties of an obtained high water-absorptive soft contact lens and the larger the molecular weight is, the better the dynamical properties become. However, when the molecular weight is too large, it is difficult to obtain a homogeneous copolymer because the (meth)acrylate polymer (A) and the hydrophilic monomer (B) such as N,N-dimethyl (meth)acrylamide or N-vinyl-2-pyrrolidone are not uniformly admixed upon the copolymerization. Therefore, the preferable range of the number average molecular weight is from about 10,000 to about 50,000.

The copolymer employed in the soft contact lens of the present invention is prepared by copolymerizing the thus obtained (meth)acrylate polymer (A) and the hydrophilic monomer (B) selected from the group consisting of an N-vinyl lactam, acrylamide, N-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative.

Examples of the N-vinyl lactams are, for instance, N-vinylpyrrolidone, N-vinylpiperidone, N-vinylcaprolactam, and their derivatives in which the lactam ring has at least one lower alkyl substituent having 1 to 4 carbon atoms. However, these N-vinyl lactams are not limited to the exemplified ones. Other compounds

having similar properties to those of the above-mentioned N-vinyl lactams, namely those having polymerizing groups and proving hydrophilic properties to the produced copolymer, can be used in the invention as well as the N-vinyl lactam. Accordingly, the term "N-vinyl lactam" as used herein means the above mentioned N-vinyl lactam and the compounds having similar properties e.g. N-vinyl heterocyclic compounds such as  $\alpha$ -methylene-N-methylpyrrolidone. These compounds may be employed together with or instead of N-vinyl lactams.

Examples of the above-mentioned (meth)acrylamide in which hydrogen atoms attached to the nitrogen atom may be substituted are, for instance, (meth)acrylamide, N-methyl (meth)acrylamide, N-ethyl (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N,N-diethyl (meth)acrylamide, N-ethyl-N-aminoethyl (meth)acrylamide, and the like, but these (meth)acrylamides are not limited to the exemplified ones.

These hydrophilic monomers may be employed alone or in admixture thereof.

The proportion of the hydrophilic monomer (B) and the (meth)acrylate polymer (A) is about 90 : about 10 to about 60 : about 40 by weight, preferably about 85 : about 15 to about 70 : about 30.

The (meth)acrylate polymer (A) is used to reinforce the resulting copolymer prepared by copolymerization of the (meth)acrylate polymer (A) and the hydrophilic monomer (B). It is necessary that the amount of the (meth)acrylate polymer (A) is not less than 10 parts by weight based on 100 parts by weight of the total of the (meth)acrylate polymer (A) and the hydrophilic monomer (B). On the other hand, it is necessary that the amount is not more than 40 parts by weight based on 100 parts by weight of the total of the (meth)acrylate polymer (A) and the hydrophilic monomers (B) for maintaining high water-absorptive property of the soft contact lens.

When the high water-absorptive soft contact lens of the invention is prepared, as occasion demands, usual hydrophilic monomers such as (meth)acrylic acid, hydroxyethyl (meth)acrylate, dihydroxypropyl (meth)acrylate and alkoxypolyethylene glycol mono(meth)acrylate may be employed instead of the part of the above-mentioned hydrophilic monomer (B). In such a case, it is preferable that the amount of the above-mentioned usual hydrophilic monomers is not more than about 20 parts by weight based on 100 parts by weight of the total amount of the above-mentioned usual hydrophilic monomers and the hydrophilic monomer (B) in order to maintain the water-absorptive property of the obtained copolymer high. Of course, the ratio of the hydrophilic monomer and the (meth)acrylate polymer (A) should be within the above-mentioned range.

Moreover, it is possible that hydrophobic monomers such as methyl (meth)acrylate and styrene are admixed with the hydrophilic monomers, and an usual cross-linking agent such as ethylene glycol dimethacrylate or allyl methacrylate is employed from the view point of the compatibility.

When the copolymer used in the invention is prepared, a usual bulk polymerization process is preferably applicable for obtaining the soft contact lens of the invention in high productivity, and, if necessary, a solution polymerization process may be applied.

In the both of the above-mentioned polymerization methods, it is preferable to employ a temperature-elevation method, e.g. a method in which the heat-polymerization is carried out at about 40° to about 50° C for several hours to several tens of hours, and then polymerization is completed by heating at a rate of about 10° C/several hours.

The amount of the polymerization initiator employed in the preparation of the (meth)acrylate polymer (A) is about 0.001 to about 5 parts by weight, preferably about 0.01 to about 2 parts by weight based on 100 parts by weight of the whole amounts of the polymerizable monomers.

The high water-absorptive soft contact lens of the present invention can be prepared by the methods, that is, conducting the (meth)acrylate polymer (A) and the hydrophilic monomer (B) into a mold corresponding to the predetermined shape of a contact lens to give a contact lens having the predetermined shape, or preparing a copolymer by copolymerizing the (meth)acrylate polymer (A) and the hydrophilic monomer (B) and processing the copolymer by a mechanical method such as cutting or polishing to give a contact lens shape, then impregnating the obtained copolymer with water to give the desired high water-absorptive property.

When employing the (meth)acrylate polymer having ketalized dihydroxyalkyl groups in its molecule, it is necessary that the contact lens is subjected to the deketalation, (a reaction that ketal groups are converted into hydroxyl groups) by employing usual acids after molding the contact lens, as described in Japanese Unexamined Patent Publication (Tokkyo Kokai) No. 176618/1983.

The present invention is more specifically described and explained by means of the following Examples in which all percents and parts are by weight unless otherwise noted.

Reference Example 1

A three necked round bottom flask was charged with 7.5 g (5 parts) of 2-hydroxyethyl methacrylate, 142.5 g (95 parts) of methyl methacrylate, 0.93 g (0.62 part) of allyl methacrylate, 0.73 g (0.49 part) of ethylene glycol dimethacrylate, 2.0 g (1.3 parts) of azobisisobutyronitrile as a polymerization initiator and 600 ml of benzene as a solvent, and the polymerization reaction was carried out at a temperature of 70 °C for 1.5 hours with stirring. Then, the reaction mixture was poured into n-hexane to give a precipitate, and the obtained precipitate was dried under reduced pressure. The precipitate dissolved in benzene was poured into a large amount of n-hexane, and then it was reprecipitated, purified and dried under reduced pressure to give a (meth)acrylate polymer having a hydrophilic group and a polymerizable group in its molecule.

The molecular weight of the obtained (meth)acrylate polymer was measured according to the following method.

The results are shown in Table 1 with yields.

[Molecular weight]

The measurement of molecular weight is carried out by using a Trirotor III GPC analyzer (made by Japan Spectroscopic Co., Ltd.), (detector: Shodex RI SE-31 made by Showa Denko Kabushiki Kaisha; column: Shodex PAK GPC KF-804 made by Showa Denko Kabushiki Kaisha; medium: tetrahydrofuran) in conditions of a column temperature of 40 °C and a flow rate of 1.0 ml/min.

Reference Examples 2 to 14

The procedure of Reference Example 1 was repeated except that components and amounts shown in Table 1 were employed to prepare a (meth)acrylate polymer having a hydrophilic group and a polymerizable group in its molecule and a methyl (meth)acrylate polymer not having a hydrophilic group in its molecule, respectively. Molecular weights of the obtained (meth)acrylate polymers and methyl (meth)acrylate polymers were respectively measured in the same manner as in Reference Example 1.

The results are shown in Table 1 with yields.

Table 1

| Ref. Ex. No.                      | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    |
|-----------------------------------|------|------|------|------|------|------|------|------|
| Components (parts)                |      |      |      |      |      |      |      |      |
| HEMA (1)                          | 5    | 5    | 5    | -    | -    | -    | 10   | 15   |
| HBMA (2)                          | -    | -    | -    | 5    | 5    | 5    | -    | -    |
| MAA (3)                           | -    | -    | -    | -    | -    | -    | -    | -    |
| DMAA (4)                          | -    | -    | -    | -    | -    | -    | -    | -    |
| MMA (5)                           | 95   | 95   | 95   | 95   | 95   | 95   | 90   | 85   |
| AMA (6)                           | 0.62 | 1.25 | 0.93 | 1.23 | 0.93 | 0.92 | 0.61 | 0.61 |
| EDMA (7)                          | 0.49 | 0.49 | 0.73 | 0.48 | 0.49 | 0.72 | 0.49 | 0.48 |
| AIBN (8)                          | 1.3  | 1.3  | 1.3  | 1.7  | 1.3  | 1.7  | 1.3  | 1.3  |
| $\overline{Mn}$ ( $\times 10^4$ ) | 3.0  | 3.0  | 3.0  | 3.0  | 3.1  | 3.2  | 2.8  | 2.8  |
| $\overline{Mw}/\overline{Mn}$     | 2.3  | 2.0  | 2.1  | 2.2  | 2.1  | 2.1  | 2.4  | 2.4  |
| Yield (%)                         | 50   | 40   | 45   | 40   | 40   | 45   | 50   | 50   |

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| Ref. Ex. No.                      | 9    | 10   | 11   | 12   | 13   | 14   |
|-----------------------------------|------|------|------|------|------|------|
| Components (parts)                |      |      |      |      |      |      |
| HEMA (1)                          | 15   | -    | -    | -    | -    | -    |
| HBMA (2)                          | -    | -    | -    | -    | -    | -    |
| MAA (3)                           | -    | 5    | -    | 2.5  | 5    | -    |
| DMAA (4)                          | -    | -    | -    | -    | -    | 15   |
| MMA (5)                           | 85   | 95   | 100  | 97.5 | 95   | 85   |
| AMA (6)                           | -    | -    | 0.63 | 0.93 | 0.93 | 0.93 |
| EDMA (7)                          | 0.71 | 0.75 | 0.49 | 0.49 | 0.49 | 0.49 |
| AIBN (8)                          | 1.3  | 1.3  | 1.3  | 1.3  | 1.3  | 1.3  |
| $\overline{Mn}$ ( $\times 10^4$ ) | 3.3  | 3.1  | 3.0  | 2.5  | 2.6  | 2.4  |
| $\overline{Mw}/\overline{Mn}$     | 2.4  | 3.0  | 2.2  | 2.1  | 2.2  | 2.0  |
| Yield (%)                         | 30   | 47   | 45   | 46   | 46   | 43   |

- (Note) (1): 2-Hydroxyethyl methacrylate.  
 (2): Hydroxybutyl methacrylate  
 (3): Methacrylic acid  
 (4): N,N-dimethyl acrylamide  
 (5): Methyl methacrylate  
 (6): Allyl methacrylate  
 (7): Ethylene glycol dimethacrylate  
 (8): Azobisisobutyronitrile  
 $\overline{M}_n$ : Number average molecular weight  
 $\overline{M}_w$ : Weight average molecular weight

#### Examples 1 to 23 and Comparativ Example 1

The hydrophilic monomer, (meth)acrylate polymer and polymerization initiator shown in Table 2 were admixed in amounts shown in Table 2 to give a mixture. In Examples 11 to 23, the obtained mixture dried with anhydrous sodium sulfate overnight. A polypropylene test tube having an inside diameter of 18 mm was charged with the mixture and the polymerization was stepwise carried out at 35°C for 40 hours, at 50°C for 8 hours and then, the test tube was heated up to 110°C at the rate of 10°C/90 min. After the product was taken out from the test tube and cured at 90°C for 2 hours, the obtained rod was subjected to mechanical processing to give a lens. The obtained lens dipped with physiological saline solution was transparent, excellent in strength and flexible when it was impregnated with water.

The film of the copolymer which thickness was about 0.2 mm and a diameter was about 20 mm when impregnated with water, was processed from the rods, and the physical properties of the copolymer were measured by the following method.

The results are shown in Table 2.

#### [Appearance]

Appearance of equilibrium wet film is observed with the naked eyes.

#### [Water content]

Water content (%) is calculated on the basis of the following formula.

$$\text{Water content (\%)} = \frac{\begin{array}{c} \text{(Weight of} \\ \text{equilibrium} \\ \text{wet film (g))} \end{array} - \begin{array}{c} \text{(Weight of} \\ \text{dry film (g))} \end{array}}{\begin{array}{c} \text{Weight of equilibrium} \\ \text{wet film (g)} \end{array}} \times 100$$

## [Linear swelling ratio]

Linear swelling ratio (%) is calculated on the basis of the following formula.

Linear swelling ratio (%)

$$= \frac{(\text{Diameter of equilibrium wet film (mm)} - \text{Diameter of dry film (mm)})}{\text{Diameter of dry film (mm)}} \times 100$$

## 15 [Needle penetration strength]

A pressure needle having a diameter of 1/16 inch is put on the center of the film impregnated with water (a thickness: about 0.2 mm) and a weight (g) is measured at the time when the film is penetrated by employing an Instron compression tester.

## 20 [Elongation ratio]

Elongation ratio (%) of the film is measured at the time when needle penetration strength (g) is measured. The value shows the elongation at breaking.

## 25 [Strength index]

Strength index is calculated on basis of the following formula.

$$\text{Strength index} = \frac{(\text{Needle penetration strength (g)}) \times (\text{Elongation ratio (\%)})}{2 \times \text{Thickness of the film (\mu m)}}$$

Table 2

| components (parts)                  | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 |
|-------------------------------------|-------|-------|-------|-------|-------|-------|
| NVP.....                            | 39    | 15    | 39    | 15    | 19    | 39    |
| DMAA.....                           | 39    | 61    | 39    | 61    | 55    | 39    |
| MMA.....                            | -     | -     | -     | -     | -     | -     |
| EDMA.....                           | -     | -     | -     | -     | -     | -     |
| Polymer prepared in Ref. Ex. 1..... | 22    | -     | -     | -     | -     | -     |
| 2.....                              | -     | 24    | -     | -     | -     | -     |
| 3.....                              | -     | -     | 22    | -     | -     | -     |
| 4.....                              | -     | -     | -     | 24    | -     | -     |
| 5.....                              | -     | -     | -     | -     | 26    | -     |
| 6.....                              | -     | -     | -     | -     | -     | 22    |
| 7.....                              | -     | -     | -     | -     | -     | -     |
| 8.....                              | -     | -     | -     | -     | -     | -     |
| 9.....                              | -     | -     | -     | -     | -     | -     |
| 10...                               | -     | -     | -     | -     | -     | -     |
| 11...                               | -     | -     | -     | -     | -     | -     |
| 12...                               | -     | -     | -     | -     | -     | -     |
| 13...                               | -     | -     | -     | -     | -     | -     |
| 14...                               | -     | -     | -     | -     | -     | -     |
| V-65.....                           | 0.05  | 0.03  | 0.05  | 0.03  | 0.03  | 0.05  |
| Anhydrous sodium sulfate.....       | -     | -     | -     | -     | -     | -     |

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| components (parts)                 | Ex. 7 | Ex. 8 | Ex. 9 | Ex. 10 | Ex. 11 | Ex. 12 |
|------------------------------------|-------|-------|-------|--------|--------|--------|
| NVP.....                           | 56    |       |       | 19     | 18.5   | 19.5   |
| DMAA.....                          | 19    |       |       | 56     | 55.5   | 58.5   |
| MMA.....                           | -     |       | 71    | -      | -      | -      |
| EDMA.....                          | -     |       | -     | -      | -      | 0.3    |
| Polymer prepared in Ref. Ex. 1.... | -     |       | -     | -      | -      | -      |
| 2....                              | -     |       | -     | -      | -      | -      |
| 3....                              | -     |       | -     | -      | -      | -      |
| 4....                              | -     |       | -     | -      | -      | -      |
| 5....                              | -     |       | -     | -      | -      | -      |
| 6....                              | -     |       | -     | -      | -      | -      |
| 7.... 25                           | -     |       | -     | -      | -      | -      |
| 8....                              | 25    |       | -     | -      | -      | -      |
| 9....                              | -     |       | 29    | -      | -      | -      |
| 10....                             | -     |       | -     | 25     | -      | -      |
| 11....                             | -     |       | -     | -      | -      | -      |
| 12....                             | -     |       | -     | -      | -      | -      |
| 13....                             | -     |       | -     | -      | 26     | 22     |
| 14....                             | -     |       | -     | -      | -      | -      |
| V-65.....                          | 0.07  | 0.07  | 0.03  | 0.03   | 0.02   | 0.02   |
| Anhydrous sodium sulfate.....      | -     | -     | -     | -      | used   | used   |

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|                                    | Ex. 13 | Ex. 14 | Ex. 15 | Ex. 16 | Ex. 17 | Ex. 18 |
|------------------------------------|--------|--------|--------|--------|--------|--------|
| components (parts)                 |        |        |        |        |        |        |
| NVP.....                           | 19.5   | 18.5   | 19.5   | 19.5   | 20.25  | 20.25  |
| DMAA.....                          | 58.5   | 55.5   | 58.5   | 58.5   | 60.75  | 60.75  |
| MMA.....                           | 15     | -      | -      | 15     | 3      | 15     |
| EDMA.....                          | 0.3    | -      | 0.3    | 0.3    | 0.3    | 0.3    |
| Polymer prepared in Ref. Ex. 1.... | -      | -      | -      | -      | -      | -      |
| 2....                              | -      | -      | -      | -      | -      | -      |
| 3....                              | -      | -      | -      | -      | -      | -      |
| 4....                              | -      | -      | -      | -      | -      | -      |
| 5....                              | -      | -      | -      | -      | 19     | 19     |
| 6....                              | -      | -      | -      | -      | -      | -      |
| 7....                              | -      | -      | -      | -      | -      | -      |
| 8....                              | -      | -      | -      | -      | -      | -      |
| 9....                              | -      | -      | -      | -      | -      | -      |
| 10....                             | -      | -      | -      | -      | -      | -      |
| 11....                             | -      | -      | -      | -      | -      | -      |
| 12....                             | -      | 26     | 22     | 22     | -      | -      |
| 13....                             | 22     | -      | -      | -      | 26     | -      |
| 14....                             | -      | -      | -      | -      | -      | -      |
| V-65.....                          | 0.02   | 0.02   | 0.02   | 0.02   | 0.02   | 0.02   |
| Anhydrous sodium sulfate.....      | used   | used   | used   | used   | used   | used   |

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| components (parts)                 | Ex. 19 | Ex. 20 | Ex. 21 | Ex. 22 | Ex. 23 | Com. Ex. 1 |
|------------------------------------|--------|--------|--------|--------|--------|------------|
| NVP.....                           | 19.5   | 18.5   | 18.5   | 19.5   | 19.5   | 19         |
| DMAA.....                          | 58.5   | 58.5   | 55.5   | 58.5   | 58.5   | 56         |
| MMA.....                           | 3      | 15     | -      | -      | 15     | -          |
| EDMA.....                          | 0.3    | 0.3    | -      | 0.3    | 0.3    | -          |
| Polymer prepared in Ref. Ex. 1.... | -      | -      | -      | -      | -      | -          |
| 2....                              | -      | -      | -      | -      | -      | -          |
| 3....                              | -      | -      | -      | -      | -      | -          |
| 4....                              | -      | -      | -      | -      | -      | -          |
| 5....                              | 22     | 22     | -      | -      | -      | -          |
| 6....                              | -      | -      | -      | -      | -      | -          |
| 7....                              | -      | -      | -      | -      | -      | -          |
| 8....                              | -      | -      | -      | -      | -      | -          |
| 9....                              | -      | -      | -      | -      | -      | -          |
| 10....                             | -      | -      | -      | -      | -      | -          |
| 11....                             | -      | -      | -      | -      | -      | 25         |
| 12....                             | -      | -      | -      | -      | -      | -          |
| 13....                             | -      | -      | -      | -      | -      | -          |
| 14....                             | -      | -      | 26     | 22     | 22     | -          |
| V-65.....                          | 0.02   | 0.02   | 0.02   | 0.02   | 0.02   | 0.05       |
| Anhydrous sodium sulfate.....      | used   | used   | used   | used   | used   |            |

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| Physical properties                  | Ex. 1 | Ex. 2            | Ex. 3            | Ex. 4            | Ex. 5            | Ex. 6            |
|--------------------------------------|-------|------------------|------------------|------------------|------------------|------------------|
| Appearance.....trans-<br>parent      |       | trans-<br>parent | trans-<br>parent | trans-<br>parent | trans-<br>parent | trans-<br>parent |
| Water content (%).....               | 80.1  | 79.1             | 78.0             | 78.4             | 79.9             | 77.0             |
| Linear swelling ratio (%).....       | 70.9  | 71.9             | 65.1             | 70.2             | 73.0             | 63.3             |
| Needle penetration strength (g)..... | 143   | 152              | 163              | 179              | 122              | 186              |
| Elongation ratio (%).....            | 67    | 61               | 61               | 65               | 69               | 59               |
| Strength index (g·s/μm).....         | 24.1  | 23.2             | 25.0             | 28.8             | 21.1             | 27.5             |

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| Physical properties                                  | Ex. 7 | Ex. 8 | Ex. 9 | Ex. 10 | Ex. 11 | Ex. 12 |
|------------------------------------------------------|-------|-------|-------|--------|--------|--------|
| Appearance.....trans-<br>parent                      |       |       |       |        |        |        |
| Water content (%).....trans-<br>parent               |       | 79.6  | 79.6  | 79.2   | 78.7   | 78.5   |
| Linear swelling ratio (%).....trans-<br>parent       |       | 65.4  | 72.8  | 72.3   | 70.3   | 70.7   |
| Needle penetration strength (g).....trans-<br>parent |       | 140   | 141   | 152    | 147    | 161    |
| Elongation ratio (%).....trans-<br>parent            |       | 59    | 61    | 55     | 57     | 60     |
| Strength index (g·%/μm).....trans-<br>parent         |       | 20.2  | 21.5  | 20.9   | 21     | 25     |

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|                                      | Ex. 13 | Ex. 14 | Ex. 15 | Ex. 16 | Ex. 17 | Ex. 18 |
|--------------------------------------|--------|--------|--------|--------|--------|--------|
| Physical properties                  |        |        |        |        |        |        |
| Appearance.....trans-<br>parent      |        |        |        |        |        |        |
| Water content (%).....               | 76.8   | 78.3   | 78.3   | 76.7   | 80.8   | 79.1   |
| Linear swelling ratio (%).....       | 67.7   | 69.7   | 70.6   | 66.4   | 76.7   | 72.5   |
| Needle penetration strength (g)..... | 174    | 159    | 132    | 178    | 117    | 115    |
| Elongation ratio (%).....            | 71     | 59     | 51     | 69     | 62     | 65     |
| Strength index (g·s/μm).....         | 32     | 24     | 17     | 32     | 18     | 19     |

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| Physical properties                  | Ex. 19           | Ex. 20           | Ex. 21           | Ex. 22           | Ex. 23           | Com. Ex. 1 |
|--------------------------------------|------------------|------------------|------------------|------------------|------------------|------------|
| Appearance.....                      | trans-<br>parent | trans-<br>parent | trans-<br>parent | trans-<br>parent | trans-<br>parent | cloudy     |
| Water content (%).....               | 79.2             | 77.3             | 80.5             | 79.8             | 78.1             | 79.2       |
| Linear swelling ratio (%).....       | 70.2             | 66.5             | 75.2             | 73.7             | 69.6             | 71.1       |
| Needle penetration strength (g)..... | 114              | 151              | 142              | 126              | 148              | 166        |
| Elongation ratio (%).....            | 52               | 72               | 62               | 51               | 60               | 51         |
| Strength index (g·%/μm).....         | 15               | 27               | 22               | 16               | 23               | 22.4       |

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55 Comparative Example 2

The physical properties of a high water absorptive soft contact lens prepared from commercially available N-vinylpyrrolidone as a main component were measured in the same manner as in Example 1.

The soft contact lens had a water content of 78.0 % (a thickness: 0.2 mm), a needle penetration strength of 125 g, an elongation ratio of 84 % and a strength index of 20.

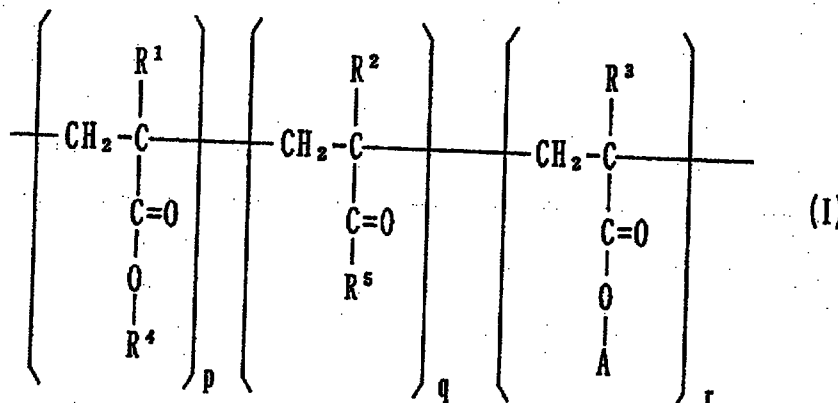
From the above-mentioned results, although the high water absorptive soft contact lens of the present invention has high water content (water content: about 75 to 80 %), it is confirmed that the contact lens is excellent in transparency and dynamical properties (mechanical strength or stability of shape when impregnated with water).

The high water-absorptive soft contact lens of the present invention has the following advantages.

- 1 It is possible to be used for a long period of time, because the contact lens has high water content (about 70 to about 90 %) and is excellent in oxygen permeability.
- 2 The remarkable lowered strength and lowered transparence (devitrification-phenomena) are not occurred in the contact lens when the contact lens is impregnated with water, and therefore, the contact lens is excellent in transparency and physical properties.

## Claims

1. A high water-absorptive soft contact lens made of a copolymer comprising
  - (A) 10 to 40 parts by weight of an acrylate or methacrylate polymer having a hydrophilic group and at least one polymerizable group in its molecule and
  - (B) 90 to 60 parts by weight of a hydrophilic monomer selected from the group consisting of N-vinylactam, acrylamide, N-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative;
 the total amount of the components (A) and (B) being 100 parts by weight, characterized in that said component (A) is a compound having the formula (I):



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are the same or different and each is hydrogen atom or methyl group,  $\text{R}^4$  is an alkyl group having 1 to 4 carbon atoms,  $\text{R}^5$  is an alkoxy group having hydroxyl group, hydroxyl group or  $-\text{N}(\text{CH}_3)_2$ , A is a polymerizable group, and p, q and r are integers to show a containing ratio of hydrophilic groups and polymerizable groups, satisfying the formula:

$$0.01 \leq \frac{q}{p + q + r} \leq 0.3 \text{ and}$$

$$0.002 \leq \frac{r}{p + q + r} \leq 0.05,$$

which copolymer is prepared by copolymerizing

- (a) 98.8 to 65 % by mole of an alkyl acrylate or methacrylate,
- (b) 1 to 30 % by mole of a monomer having a hydrophilic group and
- (c) 0.2 to 5 % by mole of a monomer having at least 2 polymerizable groups in its molecule.



The soft contact lens had a water content of 78.0 % (a thickness: 0.2 mm), a needle penetration strength of 125 g, an elongation ratio of 64 % and a strength index of 20.

From the above-mentioned results, although the high water absorptive soft contact lens of the present invention has high water content (water content: about 75 to 80 %), it is confirmed that the contact lens is excellent in transparency and dynamical properties (mechanical strength or stability of shape when impregnated with water).

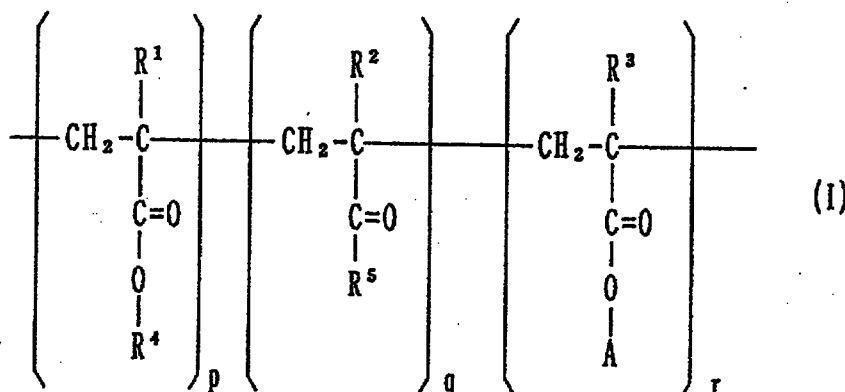
The high water-absorptive soft contact lens of the present invention has the following advantages.

1 It is possible to be used for a long period of time, because the contact lens has high water content (about 70 to about 90 %) and is excellent in oxygen permeability.

2 The remarkable lowered strength and lowered transparence (devitrification-phenomena) are not occurred in the contact lens when the contact lens is impregnated with water, and therefore, the contact lens is excellent in transparency and physical properties.

### Claims

1. A high water-absorptive soft contact lens made of a copolymer comprising
  - (A) 10 to 40 parts by weight of an acrylate or methacrylate polymer having a hydrophilic group and at least one polymerizable group in its molecule and
  - (B) 90 to 60 parts by weight of a hydrophilic monomer selected from the group consisting of N-vinylactam, acrylamide, N-substituted acrylamide derivative, methacrylamide and N-substituted methacrylamide derivative;
 the total amount of the components (A) and (B) being 100 parts by weight, characterized in that said component (A) is a compound having the formula (I):



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are the same or different and each is hydrogen atom or methyl group,  $\text{R}^4$  is an alkyl group having 1 to 4 carbon atoms,  $\text{R}^5$  is an alkoxy group having hydroxyl group, hydroxyl group or  $-\text{N}(\text{CH}_3)_2$ , A is a polymerizable group, and p, q and r are integers to show a containing ratio of hydrophilic groups and polymerizable groups, satisfying the formula:

$$0.01 \leq \frac{q}{p + q + r} \leq 0.3 \text{ and}$$

$$0.002 \leq \frac{r}{p + q + r} \leq 0.05,$$

which copolymer is prepared by copolymerizing

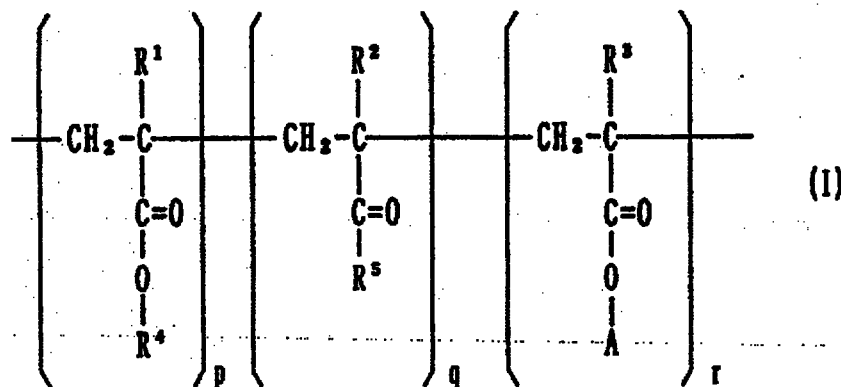
- (a) 98.8 to 65 % by mole of an alkyl acrylate or methacrylate,
- (b) 1 to 30 % by mole of a monomer having a hydrophilic group and
- (c) 0.2 to 5 % by mole of a monomer having at least 2 polymerizable groups in its molecule.



2. The soft contact lens of Claim 1, wherein said N-substituted acrylamide derivative is an N-monosubstituted or N,N-disubstituted compound.
3. The soft contact lens of Claim 1, wherein said N-substituted methacrylamide derivative is an N-monosubstituted or N,N-disubstituted compound.

### Patentansprüche

1. Eine in hohem Maße wasserabsorbierende weiche Kontaktlinse, hergestellt aus einem Copolymer, das umfaßt
  - (A) 10 bis 40 Gewichtsteile eines Acrylat- oder Methacrylatpolymers mit einer hydrophilen Gruppe und wenigstens einer polymerisierbaren Gruppe in seinem Molekül und
  - (B) 90 bis 60 Gewichtsteile eines hydrophilen Monomers ausgewählt aus der Gruppe, die besteht aus N-Vinylactam, Acrylamid, N-substituiertem Acrylamidderivat, Methacrylamid und N-substituiertem Methacrylamidderivat,
 wobei die Gesamtmenge der Komponenten (A) und (B) 100 Gewichtsteile beträgt, dadurch gekennzeichnet, daß die genannte Komponente (A) eine Verbindung mit der Formel (I):



ist, worin  $\text{R}^1$ ,  $\text{R}^2$  und  $\text{R}^3$  gleich oder verschieden sind und jedes ein Wasserstoffatom oder eine Methylgruppe ist,  $\text{R}^4$  eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist,  $\text{R}^5$  eine Alkoxygruppe mit einer Hydroxylgruppe, eine Hydroxylgruppe oder  $-\text{N}(\text{CH}_3)_2$  ist, A eine polymerisierbare Gruppe ist und p, q und r ganze Zahlen sind, um ein Gehaltsverhältnis der hydrophilen Gruppen und der polymerisierbaren Gruppen zu zeigen, daß der Formel genügt:

$$0.01 \leq \frac{q}{p + q + r} \leq 0.3 \text{ und}$$

$$0.002 \leq \frac{r}{p + q + r} \leq 0.05,$$

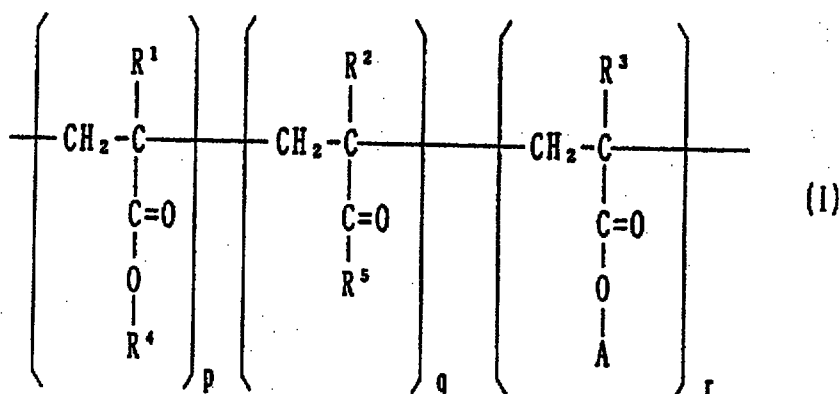
welches Copolymer hergestellt wird durch Copolymerisation von

- (a) 98,8 bis 65 Mol-% eines Alkylacrylats oder -methacrylats,
  - (b) 1 bis 30 Mol-% eines Monomers mit einer hydrophilen Gruppe und
  - (c) 0,2 bis 5 Mol-% eines Monomers mit wenigstens 2 polymerisierbaren Gruppen im Molekül.
2. Weiche Kontaktlinse nach Anspruch 1, in der das genannte N-substituierte Acrylamidderivat eine N-monosubstituierte oder N,N-disubstituierte Verbindung ist.
  3. Weiche Kontaktlinse nach Anspruch 1, bei der das genannte N-substituierte Methacrylamidderivat eine N-monosubstituierte oder N,N-disubstituierte Verbindung ist.



## Revendications

1. Lentille de contact souple présentant une haute absorption de l'eau, faite d'un copolymère comprenant
- (A) 10 à 40 parties en poids d'un polymère acrylate ou méthacrylate possédant un groupe hydrophile et au moins un groupe polymérisable dans sa molécule, et
- (B) 90 à 60 parties en poids d'un monomère hydrophile choisi dans le groupe constitué par le N-vinyl lactame, l'acrylamide, un dérivé d'acrylamide N-substitué, le méthacrylamide et un dérivé de méthacrylamide N-substitué ;
- la quantité totale des constituants (A) et (B) étant de 100 parties en poids, caractérisée en ce que ledit constituant (A) est un composé de formule (I) :



dans laquelle  $\text{R}^1$ ,  $\text{R}^2$  et  $\text{R}^3$  sont identiques ou différents et sont chacun un atome d'hydrogène ou un groupe méthyle,  $\text{R}^4$  est un groupe alkyle comportant 1 à 4 atomes de carbone,  $\text{R}^5$  est un groupe alcoxy comportant un groupe hydroxyle, un groupe hydroxyle ou  $-\text{N}(\text{CH}_3)_2$ , A est un groupe polymérisable et p, q et r sont des nombres entiers indiquant le taux de présence de groupes hydrophiles et de groupes polymérisables, satisfaisant à la formule :

$$0,01 \leq \frac{q}{p + q + r} \leq 0,3 \text{ et}$$

$$0,002 \leq \frac{r}{p + q + r} \leq 0,05,$$

ce copolymère étant préparé par copolymérisation

- (a) de 98,8 à 65% en moles d'un acrylate ou d'un méthacrylate d'alkyle,
- (b) de 1 à 30% en moles d'un monomère possédant un groupe hydrophile, et
- (c) de 0,2 à 5% en moles d'un monomère possédant, dans sa molécule, au moins 2 groupes polymérisables.

2. Lentille de contact souple selon la revendication 1, dans laquelle ledit dérivé acrylamide N-substitué est un composé N-mono-substitué ou N,N-di-substitué.
3. Lentille de contact souple selon la revendication 1, dans laquelle ledit dérivé méthacrylamide N-substitué est un composé N-mono-substitué ou N,N-di-substitué.