(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 February 2009 (19.02.2009)

PCT

(10) International Publication Number
WO 2009/022358 A1

(51) International Patent Classification:
C08B 15/00 (2006.01) ***C08J 3/24*** (2006.01)
C08B 11/20 (2006.01)

(21) International Application Number: PCT/IT2007/000584

(22) International Filing Date: 10 August 2007 (10.08.2007)

(25) Filing Language: Italian

(26) Publication Language: English

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)***:** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)***:** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report*

WO 2009/022358 A1

(54) Title: SUPERABSORBENT POLYMER HYDRO GELS AND A METHOD OF PREPARING THEREOF

(57) Abstract: The invention relates to a method for the preparation of a superabsorbent polymer hydrogel, comprising crosslinking a precursor comprising a carboxymethylcellulose salt optionally in combination with hydroxyethylcellulose, using citric acid as the crosslinking. agent and in the presence of a molecular spacer, subsequently washing the gel in a polar organic solvent and finally drying the gel by phase inversion in a non-solvent for cellulose. The invention further concerns the superabsorbent hydrogel obtainable by the method of the invention and the use thereof in a number of different applications.

Superabsorbent polymer hydrogels and a method of preparing thereof

The present invention relates to superabsorbent polymer hydrogels and a method of preparing thereof.

Polymer hydrogels are cross-linked hydrophilic polymers which are capable of absorbing high amounts of water. In particular, hydrogels capable of absorbing an amount of water in excess of 95% of their overall weight are defined as "superabsorbent". Some of these materials are even capable of absorbing over 1 litre of water per gram of dry polymer.

The crosslinks or cross-linking knots, i.e. the physical or chemical bonds between the macromolecular chains forming the hydrogel network, guarantee the structural integrity of the polymer-liquid system, on the one hand preventing the complete solubilisation of the polymer, and on the other hand allowing the retention of the aqueous phase within the molecular mesh.

The superabsorbent hydrogels which are currently available on the market are characterised not only by their marked absorbent properties, but also by their biocompatibility, which is probably due to the high water content, and above all by the possibility of adjusting their absorption properties according to the external stimuli. Consequently, such hydrogels may be used as intelligent materials, for example for the manufacture of sensors or actuators for a number of industrial applications. Besides the usual applications as absorbent cores in the field of personal hygiene absorbent products, there are more recent and innovative applications such as for example in the biomedical field, for the development of controlled release drugs, artificial muscles, sensors, etc., and in agriculture and horticulture, for example in devices for the controlled release of water and nutrients in arid soils.

However, the superabsorbent hydrogels currently available are almost exclusively acrylic-based products, and hence not biodegradable.

Given the growing interest in environmental protection issues, over recent years, a vast amount of interest has been focussed on the development of biodegradable polymer-based superabsorbent materials, having properties which are similar to those of the traditional superabsorbent polyacrylics.

Examples of biodegradable polymers used to obtain superabsorbent hydrogels are the starch and cellulose derivatives.

In 1990 Anbergen and Oppermann [1] proposed a method for the synthesis of a superabsorbent material made entirely from cellulose derivatives. Particularly, they used hydroxyethylcellulose (HEC) and a carboxymethylcellulose sodium salt (CMCNa), chemically crosslinked in a basic solution with divinylsulphone. However, the absorption properties of such materials are not high if compared to those of the acrylic-based superabsorbent materials.

In 1996 Esposito and co-workers [2], resuming the synthetic process proposed by Anbergen and Opperman, developed a method for increasing the absorption properties of the gel, acting mainly on the physical properties of the material. The basic idea was the induction of a microporosity into the polymer structure, so as to promote absorption and retention of water by capillarity. Said microporosity was induced during the drying step, which was carried out by phase inversion in a nonsolvent for the polymer, and the absorption properties of the material thus obtained were markedly superior than those of the air-dried gel.

CMCNa may be chemically crosslinked with any reagent which is bifunctional with respect to cellulose. Besides the divinylsulphone used in the synthetic process according to Anbergen and Opperman, the use of epichlorhydrin, formaldehyde and various diepoxides is also known. However, such compounds are highly toxic in their unreacted states [3]. Some carbodiimides are known amongst the unconventional crosslinking agents. Particularly, the use of carbodiimides in order to crosslink salified or non-salified carboxymethylcellulose (CMC) was described in [4]. Carbodiimide induces the formation of ester bonds between cellulose macromolecules, without participating in the bonds themselves, but simply giving rise to an urea derivative having a very low toxicity [5]. A superabsorbent hydrogel obtained cross-linking carboxymethylcellulose sodium salt and hydroxyethylcellulose with carbodiimide as the cross-linking agent is disclosed in the international patent application WO 2006/070337 [6].

However, the carbodiimide used as a cross-linking agent in WO 2006/070337 has the disadvantage of being extremely expensive. Moreover, during the cross-linking reaction with CMCNa, this substance turns into a slightly toxic urea derivative, which has to be removed during the washing step, thereby further increasing the costs and the complexity of the production process. These drawbacks are extremely unfavourable, particularly in connection with those applications which require large scale production of the hydrogels and which, consequently, involve high costs both with respect to the purchase of the starting materials and with respect to the disposal of the toxic substances which are produced during synthesis.

Furthermore, the formation of substances having a certain degree of toxicity, although very low, is a key factor for ruling out the possibility of using such polymers in biomedical and pharmaceutical applications.

Therefore, the object of the present invention is to provide superabsorbent polymer hydrogels which overcome the above-mentioned drawbacks which result from the use of carbodiimide as a cross-linking agent.

These and other objects are achieved by the superabsorbent hydrogel and the method of preparing thereof as defined in the appended claims. The hydrogel of the invention is based on the replacement of carbodiimide with citric acid as the cross-linking agent, as well as on the use of a molecular spacer.

Citric acid (3-carboxy-3-hydroxy-1,5-pentanedioic acid), hereinafter designated as CA, is a naturally occurring substance which is non-toxic and available on the market at low costs. CA is used in the prior art as a cross-linking agent for polymers such as cellulose, hydroxypropylmethylcellulose and starch, in textile and food applications [7-11].
However, the possibility of using CA in order to cross-link carboxymethylcellulose for preparing superabsorbent hydrogels was never shown before.

The method of preparing a superabsorbent hydrogel according to the present invention comprises the step of cross-linking an aqueous solution of a precursor comprising a carboxymethylcellulose salt, optionally in combination with a further and different cellulose derivative polymer, with citric acid as the cross-linking agent and in the presence of a molecular spacer.

The carboxymethylcellulose salt is preferably carboxymethylcellulose (CMCNa) sodium salt. The further and different cellulose derivative polymer is preferably hydroxyethylcellulose (HEC).

In a preferred embodiment of the method of the invention, which results in the formation of superabsorbent hydrogels having a particularly high swelling ratio (SR), the total precursor concentration in the aqueous solution is of at least 2% by weight referred to the weight of the water of the starting aqueous solution, and the concentration of the cross-linking agent is comprised between 1% and 5% by weight referred to the weight of the precursor.

In the present description, the term "precursor" indicates the whole amount of the cellulose derivative polymers used as the precursors for the formation of the hydrogel polymer network (i.e., preferably, the sum of CMCNa and HEC).

The swelling ratio (SR) is a measure of the hydrogel ability to absorb water. SR is obtained through swelling measurements at the equilibrium (using, for example, a Sartorius micro scale with a sensibility of 10^{-5}) and it is calculated with the following formula:

$$\mathbf{SR = (W_s - W_d)/W_d}$$

wherein W_s is the weight of the hydrogel after immersion in distilled water for 24 hours, and W_d is the weight of the hydrogel before immersion, the hydrogel having been previously dried in order to remove any residual water.

According to a preferred embodiment of the invention, the molecular spacer used to synthesise the superabsorbent hydrogel is selected from the group consisting of sorbitol, sucrose and plant glycerol.

A molecular spacer is a substance which, although not taking part into the reaction resulting in the formation of the hydrogel polymer network, exerts the function of increasing the length of the cross-linking bridge, thereby enhancing the possibility of the polymer network to expand so as to greatly increase the hydrogel absorption properties.

According to a particularly preferred embodiment of the method of the invention, sorbitol is used as the molecular spacer, at a concentration within the range of 0,5 to 10% by weight referred to the weight of water, preferably within the range of 2 to 8% by weight referred to the weight of water, still more preferably at a concentration of 4% by weight referred to the weight of water.

According to the preparation method of the invention, the cross-linking reaction is preferably carried out at a temperature comprised between about 60°C and 120°C. Variating the temperature during this stage of the process will enable to increase or decrease the cross-linking degree of the polymer network. A cross-linking temperature of about 80°C is preferred.

As mentioned above, the precursor used to form the polymer network is a carboxymethylcellulose salt, preferably carboxymethylcellulose sodium salt (CMCNa), optionally in combination with a further and different cellulose derivative polymer, preferably hydroxyethylcellulose (HEC). In that case, if a mixture of carboxymethylcellulose sodium salt (CMCNa) and hydroxyethylcellulose (HEC) is used, the preferred weight ratio of CMCNa to HEC will be 3/1.

Hydroxyethylcellulose is used in order to stabilise the polymer network and to improve its mechanical properties. Carboxymethylcellulose alone, in fact, tends to create intramolecular rather than intermolecular cross-links, resulting in the creation of a gel with poor mechanical properties.

The material obtained with the cross-linking reaction is a hydrogel. This material is then purified by washing in a polar organic solvent. The hydrogel immersed into the solvent swells up releasing everything that was not incorporated into the polymer network. Water is preferred as the organic solvent, distilled water is still more preferred. The volume of water required during this step in order to reach the maximum swelling degree of the gel, is approximately 10- to 20-folds the initial volume of the gel itself. Taking into account the huge amounts of water which would be involved during this step on an industrial scale, as well as their disposal and/or recycling, the importance of avoiding the presence of any toxic by-products in the synthetic process becomes evident.

The hydrogel washing step may be repeated more than once, optionally changing the organic solvent employed. Fore example, methanol followed by distilled water may be used as the organic solvent in the washing step.

The subsequent step in the synthesis process is the hydrogel drying. The drying step is carried out by phase inversion in a cellulose nonsolvent. A suitable cellulose nonsolvent is for example acetone or ethyl alcohol. Drying by phase inversion results in a final micro porous structure which improves the absorption properties of the gel by capillarity. Moreover, if the porosity is interconnected or open, i.e. the micropores communicate with one another, the absorption/desorption kinetics of the gel will be improved as well. When a completely swollen gel is immersed into a nonsolvent, the gel undergoes phase inversion with the expulsion of water, until the gel precipitates in the form of a vitreous solid as white coloured granules. Various rinses in the nonsolvent may be necessary in order to obtain the dried gel in a short period of time.

At the end of the process, further air drying or oven drying may be useful in order to eliminate any residual traces of nonsolvent. The latter drying step may be carried out at a temperature of e.g. approximately 30-45°C until the residual nonsolvent is completely removed.

The hydrogels obtainable by the method of the invention possess a number of advantages over the polyacrylic hydrogels which have bee employed up to now in consumer products, such as for example in the filed of the absorbent products for personal care (i.e., babies' napkins, sanitary towels, etc.) and in the field of the products for agriculture (e.g., devices for the controlled release of water and nutrients). Such advantages are essentially associated with the biodegradability and the complete absence of any toxic by-products during the manufacturing process. Such features enable a real employment of the superabsorbent hydrogels of the invention in the biomedical and pharmaceutical fields as well.

The absorption properties of these materials, which depend on the amount of carboxymethylcellulose employed and which may be improved by the induction of a microporosity in the gel structure, are comparable to those of polyacrylic gels. The hydrogels obtainable by the method of the present invention therefore possess mechanical properties which make them suitable for use in all of the above-mentioned fields.

Thus, the scope of the present invention also includes the use of the polymer hydrogels obtainable by the method of the invention as an absorbent material in products which are capable of absorbing water and/or aqueous solutions and/or which are capable of swelling when brought into contact with water and/or an aqueous solution.

The superabsorbent hydrogels of the present invention may be used as the absorbent materials in the following fields, which are provided by way of non-limiting example:

- dietary supplements (for example, as the bulking agents in dietary supplements for hypocaloric diets capable of conferring a sensation of lasting satiety being retained into the stomach for a limited period of time, or as water and low molecular weight compounds supplements, such as mineral salts or vitamins, to be included into drinks in a dry or swollen form);
- in agricultural products (for example, in devices for the controlled release of water and/or nutrients and/or phytochemicals, particularly for cultivation in arid, deserted areas and in all cases where it is not possible to carry out frequent irrigation; such products, mixed in a dry form with the soil in the areas surrounding the plant roots, absorb water during irrigation and are capable of retaining it, releasing it slowly together with the nutrients and phytochemicals

useful for cultivation);

- in personal hygiene and household absorbent products (such as for example, as the absorbent cores in babies'napkins, sanitary towels and the like);

- in the field of toys and gadgets (such as for example in products which are capable of significantly changing their size once brought into contact with water or an aqueous solution);

- in the biomedical field (for example, in biomedical and/or medical devices such as absorbent dressings for the treatment of highly exudative wounds, such as ulcers and/or burns, or in slow-release polymeric films suitable to slowly release liquids adapted for use in ophthalmology);

- in the body fluid management field, i.e., for controlling the amount of liquids into the organism, for example in products capable of promoting the elimination of fluids from the body e.g. in the case of oedema, CHF (chronic heart failure), dialysis,etc.

The above-mentioned products, containing a superabsorbent hydrogel obtainable by the method of the present invention as the absorbent material, also fall within the scope of the invention.

The following examples are provided to further illustrate the invention and are not to be construed as limiting its scope.

EXAMPLES

Materials and methods

All the materials employed were provided by Aldrich Italia and were used without any further modification. The devices used in the characterisation, in addition to the standard laboratory glassware, cupboards and counters for standard synthesis, were a scanning electron microscope (SEM) JEOL JSM-6500F, a precision 10-5g Sartorius scale, an Isco mixer and an ARES rheometer.

The superabsorbent hydrogels were prepared cross-linking an aqueous solution of carboxymethylcellulose sodium salt (CMCNa) with hydroxyethylcellulose (HEC), using citric acid (CA) as the cross-linking agent and sorbitol as the molecular spacer. The composition of a gel is given by the nominal amount of the reagents in the starting solution. The parameters used to define said composition are the following:

(i) the precursor weight concentration (%) = the total mass of polymers in the solution (e.g. CMCNa + HEC) (g) x 100/mass of water (g);

(ii) the CMCNa to HEC weight ratio = mass of CMCNa (g) in the solution/mass of HEC in the solution (g);

(iii) the cross-linking agent (CA) weight concentration (%) = mass of CA in the solution (g) x 100/mass of the precursors in the solution (g); and

(iv) the molecular spacer (e.g. sorbitol) weight concentration (%) = mass of molecular spacer (g) x 100/mass of water (g).

The laboratory tests demonstrated that a polymer concentration lower than 2% and a CA concentration lower than 1% either do not allow to achieve cross-linking of the gel or lead to the synthesis of a gel having very poor mechanical properties. On the other hand, CA concentrations higher than about 5% significantly increase the cross-linking degree and polymer stabilization, but excessively reduce the absorption properties of the superabsorbent gel.

Since CMCNa is the polyelectrolyte species, it is possible to achieve the desired absorption properties adjusting the weight ratio of carboxymethylcellulose sodium salt (CMCNa) to hydroxyethylcellulose (HEC). A CMCNa/HEC weight ratio of between 0/1 and 5/1, preferably between 1/1 and 3/1, was observed to enable in any event the synthesis of a hydrogel having optimum absorption properties.

Examples relating to the synthesis of different hydrogels according to the invention, differing from one another in the weight percent (wt%) of citric acid and in the composition of the polymeric precursor, are provided below.

Preparation of gel A: in a beaker containing distilled water, sorbitol at a concentration of 4% by weight referred to the weight of distilled water is added and mixed until complete solubilisation, which occurs within a few minutes. The CMCNa and HEC polymers are added at a total concentration of 2% by weight referred to the weight of distilled water, with a CMCNa/HEC weight ratio of 3/1. Mixing proceeds until solubilisation of the whole quantity of polymer is achieved and the solution becomes clear. At this stage, citric acid at a concentration of 1% by weight referred to the weight of the precursor is added to the solution, whose viscosity has greatly increased. The solution thereby obtained is poured into a vessel and dried at 48°C for 48 hours. During this process, the macromolecules are stabilised into a polymeric network which is the backbone of the hydrogel. At the end of the cross-linking process, the hydrogel is washed with distilled water for 24 hours at room temperature. During this phase, the hydrogel swells up thereby eliminating the impurities. In order to obtain the maximum swelling degree and elimination of all of the impurities, at least 3 rinses with distilled water are performed during the 24 hours washing step. At the end of this washing step, the hydrogel is dried by phase inversion in acetone as the nonsolvent, until a glassy white precipitate is obtained. The precipitate is then placed into an oven at 45°C for about 3 hours, to remove any residual trace of acetone.

Preparation of gel B: Gel B was prepared as gel A, with the only exception that the polymer is made only of CMCNa, and that the CMCNa concentration is 2% by weight referred to the weight of distilled water.

Preparation of gel C: Gel C was prepared as gel B, with the only exception that the citric acid concentration is 2% by weight referred to the weight of CMCNa.

Preparation of gel D: Gel D was prepared as gel B, with the only exception that the citric acid concentration is 0.5% by weight referred to the weight of CMCNa.

Absorption measurements

In order to test the absorption properties of the hydrogels prepared as described above, they were subjected to absorption measurements in distilled water. The absorption measurements essentially consist of placing the dry sample, obtained from the drying step, in distilled water, so that it swells up until an equilibrium condition is reached.

The absorption properties of the gel are assessed based on its swelling ratio (SR), defined according to the formula illustrated above. In order to minimise the influence of experimental errors, each test was performed on three samples from each gel, and then the mean value of the results of the three measurements was taken as the effective value.

Three dry samples were taken from each of the test gels, each having different weights and sizes. After recording the weights, the samples were swollen in abundant quantities of distilled water at room temperature. Upon reaching equilibrium after 24 hours, the samples were weighed once more in order to determine the swelling ratio.

Results

Table 1 below reports some of the results obtained, in terms of the swelling ratio, varying the concentrations of the reagents and the cross-linking times (6 hours, 13 hours, 18 hours, 24 hours).

Table 1

sample	CMCNa	HEC	CA	sorbitol	cross-linking time/swelling ratio			
-	75%	25%	-	-	6 hours	13 hours	18 hours	24 hours
g16	2%		1%	4%	nr	50	30	20
g17	4%		1%	4%	nr	25	10	5

nr = not cross-linked

It is pointed out that the increase in the polymer concentration exerts a negative effect on the swelling properties of the final product and it is also pointed out that the cross-linking time exerts a significant effect of the absorbing properties.

Thus, further experiments were carried out maintaining the polymer concentration fixed at 2% and varying the citric acid concentration. The results are reported in Table 2.

Table 2

sample	CMCNa	HEC	CA	sorbitol	cross-linking time/swelling ratio			
-	75%	25%	-	-	6 hours	13 hours	18 hours	24 hours
g21	2%		2%	4%	40	25	20	10
g22	2%		1%	4%	nr	50	30	20
g23	2%		0,5%	4%	nr	nr	50	30

nr = not cross-linked

Table 2 shows that the sample having the best swelling ratio is the sample designated as g22, which is characterised by a citric acid (CA) concentration of 1%.

Thus, further experiments were performed removing completely HEC from the solution. This should render the hydrogel more hydrophilic thereby leading to an increase of the swelling ratio. Table 3 shows some of the results obtained.

Table 3

sample	CMCNa	HEC	CA	sorbitol	cross-linking time/swelling ratio			
	100%	0%	-	-	6 hours	13 hours	18 hours	24 hours
g30	2%		2%	4%	nr	85	55	30
g31	2%		1%	4%	nr	100	75	40
g32	2%		0,5%	4%	nr	nr	70	50

nr = not cross-linked

The highest swelling ratio is associated with a cross-linking time of 13 hours and a citric acid concentration of 1%. It is also to be noticed that higher citric acid concentrations together with shorter cross-linking times lead to equally satisfactory swelling ratios, although the reaction is very fast and less easy to control.

Finally, the possibility to increase the swelling ratio creating a porosity into the material which could promote the absorbing properties, was evaluated. For that purpose, the sample g31, subjected to cross-linking for 12 hours, was swelled into distilled water for 24 hours and then dried by phase inversion in acetone. With this technique, a swelling ratio of 200 was obtained.

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CLAIMS

1. A method of preparing a superabsorbent polymer hydrogel, comprising the steps of:

(i) cross-linking an aqueous solution of a precursor comprising at least a carboxymethylcellulose salt, optionally in combination with a further and different cellulose derivative polymer, with citric acid as the cross-linking agent in the presence of a molecular specer;

(ii) washing at least once the gel obtaining by swelling in a polar organic solvent; and

(iii) drying the gel by phase inversion in a nonsolvent for cellulose.

2. The method according to claim 1, wherein the carboxymethylcellulose salt is carboxymethylcellulose sodium salt.

3. The method according to claim 1 or 2, wherein the further and different cellulose derivative polymer is hydroxyethylcellulose.

4. The method according to claim 3, wherein the weight ratio of carboxymethylcellulose salt to hydroxyethylcellulose is 3/1.

5. The method according to any of claims 1 to 4, wherein the total precursor concentration in the aqueous solution is at least 2% by weight referred to the weight of water.

6. The method according to any of claims 1 to 5, wherein the cross-linking agent concentration is comprised between 1% and 5% by weight referred to the weight of precursor.

7. The method according to any of claims 1 to 6, wherein the molecular spacer is sorbitol.

8. The method according to claim 7, wherein the sorbitol concentration is comprised between 0,5% and 10% by weight referred to the weight of water.

9. The method according to claim 8, wherein the sorbitol concentration is 4% by weight referred to the weight of water.

10. The method according to any of claims 1 to 9, wherein the polar organic solvent is selected from methanol and water.

11. The method according to any of claims 1 to 10, wherein the gel is washed with distilled water before being dried.

12. The method according to any of claims 1 to 11, wherein the nonsolvent for cellulose is acetone.

13. The method according to any of claims 1 to 12, wherein the cross-linking reaction is carried out at a temperature comprised between 60°C and 120°C.

14. The method according to claim 13, wherein the cross-linking temperature is about 80°C.

15. A superabsorbent polymer hydrogel obtainable by the method according to any of claims 1 to 14.

16. Use of a superabsorbent polymer hydrogel according to claim 15, as the absorbent material in products capable of absorbing water and/or aqueous solutions and/or capable of swelling when brought into contact with water and/or aqueous solutions, particularly dietary supplements, devices or pharmaceuticals for eliminating water and/or aqueous solutions from the organism, devices for the controlled release of water and/or nutrients and/or phytopharmaceuticals in agriculture, absorbent products for personal and household hygiene, toys and gadgets adapted to altering their size when brought into contact with water and/or aqueous solutions, biomedical devices, polymeric films capable of slowly releasing liquids in ophthalmology.

17. A product which is capable of absorbing water and/or aqueous solutions and/or capable of swelling when brought into contact with water and/or aqueous solutions, comprising a superabsorbent polymer hydrogel according to claim 15.

18. The product according to claim 17, selected from the group consisting of dietary supplements, devices or pharmaceuticals for eliminating water and/or aqueous solutions from the organism, devices for the controlled release of water and/or nutrients and/or phytopharmaceuticals in agriculture, absorbent products for personal and household hygiene, toys and gadgets adapted to altering their size when brought into contact with water and/or aqueous solutions, biomedical devices, particularly absorbent medications, polymeric films capable of slowly releasing liquids in ophthalmology.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2007/000584

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08B15/00 C08B11/20 C08J3/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/070337 A (AMBROSIO LUIGI [IT]; NICOLAIS LUIGI [IT]; SANNINO ALESSANDRO [IT]) 6 July 2006 (2006-07-06) cited in the application	1-5,7,8, 10-12, 15-18
Y	page 5 - page 6 page 7, last paragraph - page 8, last paragraph page 12, last paragraph - page 16, line 1	6,9,13, 14
Y	WO 01/87365 A (KIMBERLY CLARK CO [US]; QIN JIAN [US]) 22 November 2001 (2001-11-22) page 58; example IX	6,9,13, 14

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 25 April 2008	Date of mailing of the international search report 08/05/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Mazet, Jean-François

International application No
PCT/IT2007/000584

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ESPOSITO F ET AL: "WATER SORPTION IN CELLULOSE-BASED HYDROGELS" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 60, 1996, pages 2403-2407, XP008071224 ISSN: 0021-8995 cited in the application the whole document -----	1-18

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