Claims

1. A method for the manufacture of a gel, said method comprising the steps of:

   a. providing a matrix composition comprising a polymeric photoinitiator of the general formula III:

$$\text{Polymer-}[CR_2\text{-}CHR\text{-}O\text{-Spacer}(PI)_n]_m \qquad \text{(III)}$$

   wherein m is an integer from 1-5000;

   n is a real number above 0 and below 5; and

   PI is a benzophenone photoinitiator moiety;

   the polymer is a polyalkylether;

   and wherein each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

   b. curing the matrix composition obtained in step a. by exposing it to UV radiation;

   c. exposing the matrix composition to a swelling medium, thus providing a gel;

wherein step c. may take place before or after step b.

2. The method according to claim 1, wherein the matrix composition additionally comprises one or more hydrophilic gel-forming polymers and/or hydrophilic gel-forming monomers.

3. The method according to any one of the preceding claims, wherein the polymer in formula III has a molecular weight in the range of 50-500,000 Da.

4. The method according to any one of the preceding claims, wherein the spacer is selected from the group consisting of a single bond, C1-C25 linear alkylene, C3-C25

branched alkylene, C3-C25 cycloalkylene, arylene, heteroarylene, amines, amides, alcohols, ethers, esters, thioethers, sulfones and derivatives thereof, sulfonic esters and derivatives thereof, sulfoxides and derivatives thereof and carbonates, ketones and esters.

5. The method according to any one of claims 1-3, wherein the spacer is a polymeric entity.

6. The method according to claim 5, wherein the spacer is selected from the group consisting of polyolefines, polyacrylates, polyurethanes, polyesters, polyamides, polydialkylsiloxanes, polyalkyloxides or various copolymers comprising blocks or repeatable units of the mentioned polymers.

7. The method according to any one of the preceding claims, wherein the photoinitiator units are pendant on the polymer.

Claims

1. A method for the manufacture of a hydrophilic gel, said method comprising the steps of:

   a. providing a matrix composition comprising a polymeric photoinitiator of the general formula I:

   $$\text{Polymer-}[CR_2\text{-CHR-Spacer}(PI)_n]_m \qquad (I)$$

   wherein m is an integer from 1-5000;

   n is a real number above 0 and below 5; and

   PI is a photoinitiator moiety;

   and wherein each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. -CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups),

   b. curing the matrix composition obtained in step a. by exposing it to UV radiation,

   c. exposing the matrix composition to a swelling medium, thus providing a hydrophilic gel,

   wherein step c. may take place before or after step b.

2. A method for the manufacture of a gel, said method comprising the steps of:

   a. providing a matrix composition comprising a polymeric photoinitiator of the general formula I:

   $$\text{Polymer-}[CR_2\text{-CHR-Spacer}(PI)_n]_m \qquad (I)$$

   wherein m is an integer from 1-5000;

n is a real number above 0 and below 5; and

PI is a photoinitiator moiety;

the polymer is selected from the group consisting of polyacrylates, polyalkylethers, polyurethanes, polyethylene vinyl acetates, polyvinylpyrrolidone and co-polymers and blends thereof;

and wherein each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. -CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups),

b. curing the matrix composition obtained in step a. by exposing it to UV radiation

c. exposing the matrix composition to a swelling medium, thus providing a gel

wherein step c. may take place before or after step b.

3. The method according to any one of the preceding claims, wherein the matrix composition additionally comprises one or more hydrophilic gel-forming polymers and/or hydrophilic gel-forming monomers.

4. The method according to any one of the preceding claims, wherein the gel-forming polymer is selected from the group consisting of polyacrylates, polyalkylethers, polyurethanes, polyethylene vinyl acetates, polyvinylpyrrolidone and co-polymers and blends thereof.

5. The method according to claim 3, wherein the gel-forming monomer is selected from the group consisting of acrylate monomers, N-vinylpyrrolidone, and epoxide monomers.

6. The method according to any one of the preceding claims, wherein the polymer in formula I is selected from the group consisting of polyolefines, polyacrylates, polyesters, polyurethanes, polyamides, polyalkyloxides, polydialkylsiloxanes or various copolymers comprising blocks or repeatable units of these polymers.

7. The method according to claim 6, wherein the polymer in formula I is selected from the group consisting of polyolefines, polyacrylates, polyesters, polyurethanes, polyamides, polyalkyloxides and polydialkylsiloxanes.

8. The method according to claim 7, wherein the polymer in formula I is a polyolefin or polyalkyloxide, preferably a polyalkyloxide.

9. The method according to any one of the preceding claims, wherein the polymer in formula I has a molecular weight in the range of 50-500,000 Da.

10. The method according to any one of the preceding claims, wherein the spacer is selected from the group consisting of a single bond, C1-C25 linear alkylene, C3-C25 branched alkylene, C3-C25 cycloalkylene, arylene, heteroarylene, amines, amides, alcohols, ethers, esters, thioethers, sulfones and derivatives thereof, sulfonic esters and derivatives thereof, sulfoxides and derivatives thereof and carbonates, ketones and esters.

11. The method according to claim 10, wherein the spacer is selected from the group consisting of C1-C25 linear alkylene, C3-C25 branched alkylene, C3-C25 cycloalkylene, and esters.

12. The method according to any one of claims 1-11, wherein the spacer is a polymeric entity.

13. The method according to claim 12, wherein the spacer is selected from the group consisting of polyolefines, polyacrylates, polyurethanes, polyesters, polyamides, polydialkylsiloxanes, polyalkyloxides or various copolymers comprising blocks or repeatable units of the mentioned polymers.

14. The method according to any one of claims 12-13, wherein the spacer has a molecular weight in the range of 50-500,000 Da.

15. The method according to any one of the preceding claims, wherein the photoinitiator moiety is independently selected from the group consisting of benzoin ethers, phenyl hydroxyalkyl ketones, phenyl aminoalkyl ketones, benzophenones, thioxanthones, xanthones, acridones, anthraquinones, fluorenones, dibenzosuberones, benzils, benzil ketals, α-dialkoxy-acetophenones, α-hydroxy-alkyl-phenones, α-amino-alkyl-phenones, acyl-phosphine oxides, phenyl ketocoumarins, silanes, maleimides and derivatives thereof.

16. The method according to claim 15, wherein the photoinitiator moiety is optionally-substituted benzophenone or thioxanthone.

17. The method according to any one of the preceding claims wherein m is an integer from 1-3000, preferably from 1-1000.

18. The method according to any one of the preceding claims, wherein the polymeric photoinitiator of Formula I is synthesised by grafting photoinitiator moieties (PI) onto the polymer in the presence of a radical initiator.

19. The method according to claim 18, wherein the grafting of the photoinitiator moieties (PI) onto the polymer takes place in an extruder.

20. The method according to any one of claims 1-19, wherein the photoinitiator units are pendant on the polymer.

21. The method according to any one of claims 1-20, wherein the matrix composition additionally comprises an anti-oxidant.

22. The method according to any of claims 1-21, wherein the polymeric photoinitiator has the general formula II:

$$\text{Polymer-}[CR_2\text{-}CHR\text{-}C(=O)\text{-Spacer}(PI)_n]_m \qquad \text{(II)}$$

wherein m is an integer from 1-5000;

n is a real number above 0 and below 5;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

and PI is a photoinitiator moiety.

23. The method according to any of claims 1-22, wherein the polymeric photoinitiator has the general formula IIa:

Polymer-[CR_2-CHR-C(=O)-O-Spacer$(PI)_n]_m$ (IIa)

wherein m is an integer from 1-5000;

n is a real number above 0 and below 5;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

and PI is a photoinitiator moiety.

24. The method according to any of claims 1-22, wherein the polymeric photoinitiator has the general formula IIb:

Polymer-[CR_2-CHR-C(=O)-NH-Spacer$(PI)_n]_m$ (IIb)

wherein m is an integer from 1-5000;

n is a real number above 0 and below 5;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

and PI is a photoinitiator moiety.

25. The method according to any of claims 1-21, wherein the polymeric photoinitiator has the general formula III:

Polymer-[CR_2-CHR-O-Spacer$(PI)_n]_m$ (III)

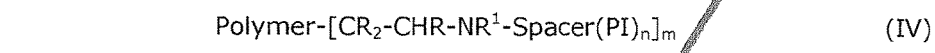
wherein m is an integer from 1-5000;

n is a real number above 0 and below 5;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

and PI is a photoinitiator moiety.

26. The method according to any of claims 1-21, wherein the polymeric photoinitiator has the general formula IV:



$$\text{Polymer-}[CR_2\text{-}CHR\text{-}NR^1\text{-Spacer}(PI)_n]_m \qquad \text{(IV)}$$

wherein m is an integer from 1-5000;

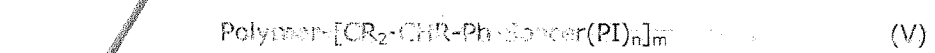
n is a real number above 0 and below 5;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

R^1 is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN and halogens;

and PI is a photoinitiator moiety.

27. The method according to any of claims 1-21, wherein the polymeric photoinitiator has the general formula V



$$\text{Polymer-}[CR_2\text{-}CHR\text{-Ph-Spacer}(PI)_n]_m \qquad \text{(V)}$$

wherein m is an integer from 1-5000;

n is a real number above 0 and below 5;

Ph is an optionally substituted phenyl group;

each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups);

and PI is a photoinitiator moiety.

28. The method according to claim 27, wherein the Ph group is substituted with one or more substituents independently selected from C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups).

29. The method according to any one of the preceding claims, wherein R is independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, preferably hydrogen.

30. The method according to any of the preceding claims, where the swelling medium is selected from the group consisting of water, C1-C5 alcohols, glycerol and polyethylene glycol (PEG), preferably PEG-2000.

31. The method according to claim 30, where the swelling medium comprises water, and the gel thus produced is a hydrogel.

32. The method according to any one of the preceding claims, wherein step c. takes place before step b.

33. A method for manufacturing a hydrophilic gel-precursor, said method comprising the steps of

a. providing a matrix composition consisting of a polymeric photoinitiator of the general formula I:

Polymer-[CR_2-CHR-Spacer$(PI)_n]_m$ (I)

wherein m is an integer from 1-5000;

n is a real number above 0 and below 5; and

PI is a photoinitiator moiety;

the polymer is selected from the group consisting of polyacrylates, polyalkylethers, polyurethanes, polyethylene vinyl acetates, polyvinylpyrrolidone and co-polymers and blends thereof;

and wherein each R group is a substituent independently selected from hydrogen, C1-C25 linear alkyl, C3-C25 branched alkyl, C3-C25 cycloalkyl, aryl, heteroaryl, -OH, -CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups) and amides (e.g. -CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups),

b. curing the matrix composition obtained in step a. by exposing it to UV radiation.

34. A method according to claim 33, wherein the polymeric photoinitiator has a structure as defined in any one of claims 6-29.

35. A hydrophilic gel-precursor obtainable via the method of any one of claims 33-34.

36. A method for the manufacture of a hydrophilic gel, said method comprising steps a. and b. as defined in any one of claims 33-34, said method comprising the additional step of

c. exposing the matrix composition to a swelling medium, thus providing a hydrophilic gel,

wherein step c. may take place before or after step b.

37. The method according to claim 36, where the swelling medium is selected from the group consisting of water, C1-C5 alcohols, glycerol and polyethylene glycol (PEG), preferably PEG-2000.

38. The method according to claim 37, where the swelling medium comprises water, and the gel thus produced is a hydrogel.

39. A gel obtainable via the method of any of claims 1-32 or 36-38.

40. A medical device comprising the gel of claim 39 or the hydrophilic gel precursor of claim 35.

41. A medical device according to claim 40 coated on at least a surface portion thereof with the gel of claim 39 or the hydrophilic gel precursor of claim 34.

42. The use of a polymeric photoinitiator, of the general formula I, II, IIa, IIb, III, IV or V, wherein m, n, PI, R, R^1, the Spacer and the polymer are as defined in any one of claims 1-29, in the manufacture of a gel.