SUMMARY ~~OF THE INVENTION~~

It has been found by the present inventors that polymeric photoinitiators with certain structures can be used in the formation of hydrophilic gels and medical devices, such as catheters.

The present ~~invention~~disclosure therefore relates to method for manufacturing a catheter comprising a hydrophilic gel, said method comprising the steps of:

a. combining a polymeric photoinitiator of the general formula I:

$$R_1(A_1)_r\text{-}(R_2(A_2)_m\text{-}O)_o\text{-}(R_3(A_3)_n\text{-}O)_p\text{-}R_4(A_4)_s \qquad (I)$$

with one or more gel-forming polymers and/or gel-forming monomers to form a matrix composition,

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

c. exposing the matrix composition to a swelling medium,

d. incorporating the hydrophilic gel/matrix composition into a catheter,

wherein steps b. and c. may take place in any order, provided that, if step d. is carried out first, step b. takes place before step c.

In the above polymeric photoinitiator of formula (I), R_2 and R_3 are independently at each occurrence identical or different, linear or branched alkylene or cycloalkylene groups; wherein R_2 and R_3 may be substituted with one or more substituents selected from CN; azides, esters; ethers; amides; halogen atoms; sulfones; sulfonic derivatives; NH_2 or $Nalk_2$, where alk is any C_1-C_8 straight chain alkyl group, C_3-C_8 branched or cyclic alkyl group.

R_1 and R_4 are independently at each occurrence identical or different, linear or branched alkyl or cycloalkyl groups or aryl groups or are independently at each occurrence selected from H, OH, CN, halogens, amines, amides, alcohols, ethers, thioethers, sulfones and derivatives thereof, sulfonic acid and derivatives thereof, sulfoxides and derivatives thereof, carbonates, isocyanates, nitrates, acrylates, polyethylenes, polyethylene oxides, polyvinyl pyrrolidones, polypropylenes, polyesters, polyamides, polyacrylates, polystyrenes, and polyurethanes; and

when R_1 and R_4 are alkyl and aryl groups, they may be substituted with one or more substituents selected from CN; OH; azides; esters; ethers; amides; halogen atoms; sulfones; sulfonic derivatives; NH_2 or $Nalk_2$, where alk is any C_1-C_8 straight chain alkyl group, C_3-C_8 branched or cyclic alkyl group.

o and p are each a real number from 0-5000 provided that o + p > 0. m and n are each a real number from 0-10, provided that m + n > 0; r and s are each a real number from 0-5; and A_1, A_2, A_3 and A_4 are identical or different photoinitiator moieties.

In an aspect, there is provided a method for manufacturing a catheter comprising a hydrophilic gel, said method comprising the steps of:

a. combining a polymeric photoinitiator of the general formula I:

$R_1(A_1)_r$-$(R_2(A_2)_m$-$O)_o$-$(R_3(A_3)_n$-$O)_p$-$R_4(A_4)_s$ (I)

wherein R_2 is -CH_2CH_2-, in which one or more H atoms may be replaced by A_2; and R_3 is -CH_2CH_2-, in which one or more H atoms may be replaced by A_3;

R_1 is OH and R_4 is H;

o and p are each a real number from 0-5000 provided that o + p > 0;

m=1 and n=0;

r and s are each 0; and

A_1, A_2, A_3 and A_4 are identical or different non-cleavable photoinitiator moieties

linked to R_1, R_2, R_3, and R_4, respectively, via a spacer group selected from alkylene ethers;

with one or more gel-forming polymers and/or gel-forming monomers to form a matrix composition,

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

c. exposing the matrix composition to a swelling medium,

d. incorporating the hydrophilic gel/matrix composition into a catheter,

wherein steps b. and c. may take place in any order, provided that, if step d. is carried out first, step b. takes place before step c.

A catheter is also provided which is obtainable via the method above. The ~~invention~~present disclosure also provides a catheter, wherein the hydrophilic gel is coated on at least a surface portion thereof.

The polymeric photoinitiators of the ~~invention~~present disclosure can also "self-cure" or "auto-cure". The ~~invention~~present disclosure therefore provides a method for the manufacture of a hydrophilic gel, said method comprising the steps of:

a. providing a polymeric photoinitiator of the general formula I:

$$R_1(A_1)_r\text{-}(R_2(A_2)_m\text{-}O)_o\text{-}(R_3(A_3)_n\text{-}O)_p\text{-}R_4(A_4)_s \qquad I$$

wherein R_2 and R_3 are independently at each occurrence identical or different, linear or branched alkylene or cycloalkylene groups; wherein R_2 and R_3 may be substituted with one or more substituents selected from CN; azides, esters; ethers; amides; halogen atoms; sulfones; sulfonic derivatives; NH_2 or $Nalk_2$, where alk is any C_1-C_8 straight chain alkyl group, C_3-C_8 branched or cyclic alkyl group;

R_1 and R_4 are independently at each occurrence identical or different, linear or branched alkyl or cycloalkyl groups or aryl groups or are independently at each occurrence selected from H, OH, CN, halogens, amines, amides, alcohols, ethers, thioethers, sulfones and derivatives thereof, sulfonic acid and derivatives thereof, sulfoxides and derivatives thereof, carbonates, isocyanates, nitrates, acrylates, polyethylenes, polyethylene oxides, polyvinyl pyrrolidones, polypropylenes, polyesters, polyamides, polyacrylates, polystyrenes, and polyurethanes; and when R_1 and R_4 are alkyl and aryl groups, they may be substituted with one or more substituents selected from CN; OH; azides; esters; ethers; amides; halogen atoms; sulfones; sulfonic derivatives; NH_2 or $Nalk_2$,

where alk is any C_1-C_8 straight chain alkyl group, C_3-C_8 branched or cyclic alkyl group;

o and p are each a real number from 0-5000 provided that o + p > 0;

m and n are each a real number from 0-10, provided that m + n > 0;

r and s are each a real number from 0-5; and

A_1, A_2, A_3 and A_4 are identical or different photoinitiator moieties;

b. exposing the polymeric photoinitiator from step a. to UV radiation, and

c. exposing the polymeric photoinitiator to a swelling medium,

wherein steps b. and c. may take place in any order.

In another aspect, there is provided a method for the manufacture of a gel precursor, said method comprising the steps of:

a. providing a polymeric photoinitiator of the general formula I:

$R_1(A_1)_r$-$(R_2(A_2)_m$-$O)_o$-$(R_3(A_3)_n$-$O)_p$-$R_4(A_4)_s$ (I)

wherein

R_2 is -CH_2CH_2-, in which one or more H atoms may be replaced by A_2;
R_3 is -CH_2CH_2-, in which one or more H atoms may be replaced by A_3;
R_1=OH;
R_4=H;

o and p are each a real number from 0-5000 provided that o + p > 0;

m = 1 and n=0;

r and s are each 0; and

A_1, A_2, A_3 and A_4 are identical or different non-cleavable photoinitiator moieties linked to R_1, R_2, R_3, and R_4, respectively, via a spacer group selected from alkylethers; and

b. exposing the polymeric photoinitiator from step a. to UV radiation,

thus providing a gel precursor.

In the case where the swelling medium is water, a hydrogel is obtained.

Further ~~aspects~~embodiments of the ~~invention~~present disclosure include a hydrophilic gel obtainable via the "auto-curing" method, a medical device comprising this hydrophilic gel.

LEGENDS TO THE FIGURES

Fig. 1 illustrates a general motif of polymeric photoinitiators, with photoinitiator moieties pendant on a polyalkylether.

Fig. 2 shows the ^{1}H-NMR spectrum of poly-co-ethyleneoxid-(4-(oxiran-2-ylmethoxy) phenyl)(phenyl)methanone using the polymerization procedure given for **1**.

Fig. 3 shows the ^{1}H-NMR spectrum of poly-co-ethyleneoxid-(4-(oxiran-2-ylmethoxy) phenyl)(phenyl)methanone using the polymerization procedure given for **2**.

Fig. 4 shows the curing profile for pristine poly-co-ethyleneoxid-(4-(oxiran-2-ylmethoxy) phenyl)(phenyl)methanone (**1**) at 120°C.

Fig. 5 shows the curing profile for pristine poly-co-ethyleneoxid-(4-(oxiran-2-ylmethoxy) phenyl)(phenyl)methanone (**2**) at 120°C.