US4861916 discloses photoinitiators for the photopolymerization of ethylenically unsaturated compounds, in particular in aqueous systems.

EP 2130817 discloses polymerizable Type II photoinitiators. Radiation curable compositions and inks including the multifunctional Type II photoinitiator are also disclosed.

Despite previous efforts, there remains a need for novel photoinitiators which can reduce by-products of low molecular weight in a polymerization process, particularly polymerization to form polyurethanes. In addition, it would prove useful to reduce or completely remove the need for low molecular weight polymerization catalysts or co-reagents in the polymerization process.

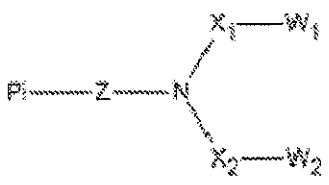
The present invention provides polymer photoinitiators in which the photoinitiator moiety itself becomes an integral part of the polymer, and remains so, during and after the polymerization process. Leaching of photoinitiator and photoinitiator by-products is therefore reduced or even eliminated.

At the same time, the particular design of the photoinitiator monomer allows a reduction in the amount of or even the elimination of co-reagents and catalysts in the polymerization process. In that such substances are minimised or eliminated, their concentrations in the resulting polymers are also reduced, so that leaching of such substances is correspondingly reduced or eliminated. Polymers likely to improve medical safety are thereby obtained.

SUMMARY ~~OF THE INVENTION~~

In an aspect, there is~~It is an object of embodiments of the invention to~~ provided a polymeric photoinitiator, being a co-polymer of at least one monomer (A) with at least one monomer (B), wherein:

- monomer (A) is a photoinitiator monomer (A) of the formula (I):



(I)

in which:

Pi is a photoinitiator moiety;

Z is a linker moiety;

X_1 and X_2 are independently selected from optionally substituted C_1-C_{12} alkylene, optionally substituted C_1-C_{12} alkenylene, optionally substituted heterocyclyl, -O-, -S-, -NR^2-, -C(=O)-, -C(=NR^2)-, -Si(R^2)$_2$-O-, optionally substituted aryl, and combinations thereof, wherein R^2 is H or optionally substituted C_1-C_{12} alkyl;

wherein X_1 and X_2 or a part thereof may be linked to one another or to Z to form one or more ring structures;

wherein Z, X_1 and X_2 are selected such that N is a tertiary amine;

W_1 and W_2 are functional groups independently selected from alcohol, primary amine, secondary amine, thiol, alkoxy silane, silane esters of carboxylic acids, isocyanate, isothiocyanate, carboxylic acid, chloroformate, primary amide, secondary amide, urethane or urea groups;

- monomer (B) comprises at least two functional groups W_3 and W_4, said W_3 and W_4 being independently selected from alcohol, primary amine, secondary amine, thiol, alkoxy silane, silane esters of carboxylic acids, isocyanate, isothiocyanate, carboxylic acid, chloroformate, primary amide, secondary amide, urethane or urea groups;

wherein W_1, W_2, W_3 and W_4 are selected such that – in the co-polymerization of monomers (A) and (B) – W_1 reacts with W_3 to form a urethane, thiourethane, urea, thiourea, ester, ether, amide, carbonate, allophanate or biuret moiety, and W_2 reacts with W_4 to form a urethane, thiourethane, urea, thiourea, ester, ether, amide, carbonate, allophanate or biuret moiety.

Co-polymerization using photoinitiator moieties having the general formula (I) are able to at least partially replace nucleophilic low molecular weight amine catalysts (e.g. DABCO) in polyurethane polymerization processes. The physical and chemical properties of the polymeric photoinitiators of the present disclosure~~invention~~ can be tailored as required, e.g. by varying the relative amounts and the nature of each monomer (A) or (B).

Furthermore, in other aspects, there are provided~~the invention provides~~ a method for producing the polymeric photoinitiator, said method comprising step-growth co-polymerization of at least one monomer (A) with at least one monomer (B), wherein (A) and (B) have the structures described herein, a method of cross-linking the polymeric photoinitiator by exposing the polymeric photoinitiator to~~means of~~ UV radiation and/or heat, and the use of the polymeric photoinitiator as a photoinitiator of radical polymerization.

Further embodimentaspects of the present disclosureinvention are presented in the dependent claims.

FIGURES

Fig. 1 shows the changes of rheological properties of a pristine sample of a PU made from 2 wt% 4-{[bis(2-hydroxyethyl)amino]methyl}benzophenone, 85 wt% PEG 2000 and 13 wt% 4,4' -methylenebis(cyclohexyl isocyanate) subjected to UV light.

Fig. 2 is an illustration of swelled hydrogel formed by subjecting a PU made from 2 wt% 4-{[bis(2-hydroxyethyl)amino]methyl}benzophenone, 85 wt% PEG 2000 and 13 wt% 4,4' -methylenebis(cyclohexyl isocyanate) to UV light.

Fig. 3 is a scheme of various synthesis routes to photoinitiator monomers (A) of structure Ib.

DETAILED DISCLOSURE OF THE INVENTION

Definitions

In the following, when a part of a molecule is described as *"optionally substituted"* it is meant that said part may be substituted by one or more substituents selected from: C_1-C_6 linear, branched or cyclic alkyl, aryl, -OH, -CN, -NO_2, halogens, amines, amides, alcohols, ethers, thioethers, sulfones and derivatives thereof, sulfoxides and derivatives thereof, carbonates, isocyanates, nitrates and acrylates.

The term "heterocyclyl" means a non-aromatic monocyclic or multicyclic ring system comprising about 3 to about 10 ring atoms, preferably about 5 to about 10 ring atoms, in which one or more of the atoms in the ring system is an element other than carbon, for example nitrogen, oxygen or sulfur, alone or in combination. Preferred heterocyclyls contain about 5 to about 6 ring atoms. The prefix aza, oxa or thia before the heterocyclyl root name means that at least a nitrogen, oxygen or sulfur atom, respectively, is present as a ring atom. The heterocyclyl can be optionally substituted as described above. The nitrogen or sulfur atom of the heterocyclyl can be optionally oxidized to the corresponding N-oxide, S-oxide or S,S-dioxide. Non-limiting examples of suitable monocyclic heterocyclyl rings include piperidyl, pyrrolidinyl, piperazinyl, morpholinyl, thiomorpholinyl, thiazolidinyl, 1,3-dioxolanyl, 1,4-dioxanyl, tetrahydrofuranyl, tetrahydrothiophenyl, tetrahydrothiopyranyl, and the like.