WO 03/033492 discloses thioxanthone derivatives attached to a polyhydroxy residue. However, these polyhydroxy groups have only up to 6 hydroxy groups present in the chain.

As a final example of polymeric photoinitiators described in the patent literature, US 4,602,097 details an invention related to water soluble photoinitiators where two photoinitiator moieties are bridged together by a polyalkylether of sufficient length to make it water soluble.

Common to all of the inventions described above from the patent literature, is that the active photoinitiator sites are present as end-groups on for example a polyethylene glycol which falls outside the present invention. The present invention details polymeric photoinitiators in which the photoinitiator moiety itself is an integral part of the repeating unit in the polymeric photoinitiator.

OBJECT OF THE INVENTION

It is an object of embodiments of the present invention to provide novel polymeric photoinitiators as well as to provide means and methods for their production. The invention also provides a method for curing a matrix composition and a cured matrix composition obtainable via said method.

SUMMARY ~~OF THE INVENTION~~

One embodiment~~aspect~~ of the present disclosure~~invention~~ is to provide access to polymeric photoinitiators with the general motif shown in Figure 1, in particular systems with a polyalkylether as the backbone polymer on which pendant photoinitiators moieties are covalently attached.

So, in a broad aspect, the present disclosure~~invention~~ relates to a polyalkylether photoinitiator of the general formula I

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

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 cycloalky groups or aryl groups or are independently at each occurrence selected from H, OH, CN, halogens, amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups), amides (e.g. –CONR'R" or R'CONR"-, where R' and R" are alkyl groups, suitably C1-C25 alkyl groups), alcohols, ethers, thioethers, sulfones and derivatives thereof, sulfonic acid and derivatives thereof, sulfoxides and derivatives thereof, carbonates, isocyanates, nitrates, acrylates, polyethylenes, polypropylenes, polyesters, polyamides, polyacrylates 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,

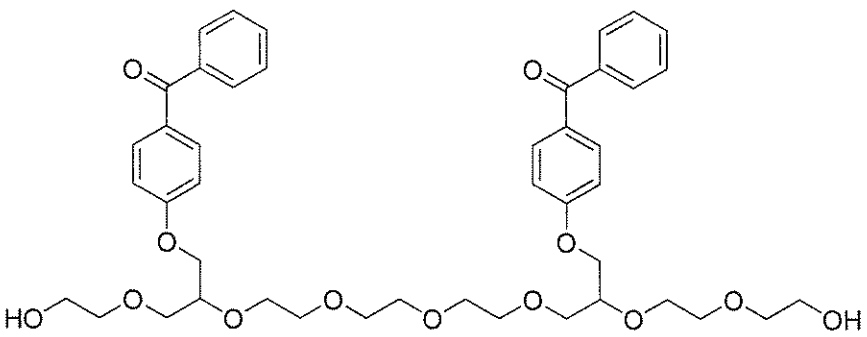
provided that m + n > 0;

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.

The indices m, n, o, p, r and s in the general formula I represent an average/sum and the formula I thereby represents alternating, periodic, statistical/random, block and grafted copolymers. As an example of a random copolymer may be mentioned the copolymer ABAAABABBABA having the formula A_7B_5.

An example of the identity of formula I applied to a photoinitiator described in the present disclosure~~invention~~ is given in Scheme 1.



chain alkyl group, C3-C8 branched or cyclic alkyl group. Photoinitiator moieties can be covalently linked to R_1 and/or R_4 as designated by $R_1(A_1)$ and $R_4(A_4)$, where A_1 and A_4 can be any of the photoinitiator moieties described above.

The indices m, n, o, p, r and s are defined as follows:

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.

Suitably, o and p are each from 0-3000, preferably 0-2000. Suitably, o and p are each independently 1 or greater, e.g. 10 or greater. The integers m and n may be from 0-8, preferably 0-5, provided that m + n > 0. Suitably, m + n ≥ 1. In a particular aspect, m = 1 and/or n = 1. When m = 1 and n = 0, the ratio o:p may be at least 1:1000, preferably at least 1:500.

Typically, r and s are each from 0-4, preferably 0-2. Suitably, r and s are independently 1 or greater, e.g. 1 or 2.

The polyalkylether photoinitiator according to the present disclosure~~invention~~ may have a molecular weight between 5 and 10,000 kDa, preferably between 10 kDa and 1,000 kDa, more preferably between 15 kDa and 500 kDa.

The photoinitiator moieties can be selected from 2-hydroxy-2-methyl-propiophenone, benzophenone, thioxanthone, benzil, anthraquionone, camphorquinone, benzoin ether, acylphosphine oxide and silane derivatives but the choice of photoinitiator moieties is not restricted to these classes of compounds. As one example of moieties potentially present in the polymeric photoinitiator is amines (e.g. -NR'R", where R' and R" are alkyl groups, suitably C1-C25 alkyl groups). More details concerning the separate moieties are provided below under the discussion in the detailed disclosure of the invention.

The present disclosure~~invention~~ comprises embodiment~~aspects~~ of coating formation employing the polymeric photoinitiators through UV curing of either polymeric photoinitiator/matrix polymer composition and/or solely of the polymeric photoinitiator. This application extends among other things to paints and lacquers, rubbers and protective coatings.

Ultimately, an embodiment~~aspect~~ of the present disclosure~~invention~~ is to use the polymeric photoinitiator solely in the coating composition eliminating the need for mixing a photoinitiator and a matrix in the coating composition. In an aspect, there is provided the use of a polyalkylether photoinitiator as defined herein for curing a matrix composition. In another aspect, there is provided a method for curing a matrix composition, said method comprising the steps of: a. mixing the polyalkylether photoinitiator as defined herein with a matrix composition; b. curing the mixture obtained in step a. by exposing it to UV radiation.

LEGENDS TO THE FIGURE

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.

DETAILED DISCLOSURE OF THE INVENTION

The present invention provides fabrication and applications of polymeric photoinitiators.

Photoinitiator and photoinitiator moieties

In the present invention, a photoinitiator is defined as a substance (other than a reactant) which, on absorption of light, generates reactive species (ions or radicals) and initiates one or several chemical reactions or transformation. One preferred property of the photoinitiator is good overlap between the UV light source spectrum and the photoinitiator absorption spectrum. Another desired property is a minor or no overlap between the photoinitiator absorption spectrum and the intrinsic combined absorption spectrum of the other components in the matrix. Good compatibility of the polymeric photoinitiator in the matrix consisting of material to be cured is also a property of interest.