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PHOTOINITIATOR COPOLYMERS

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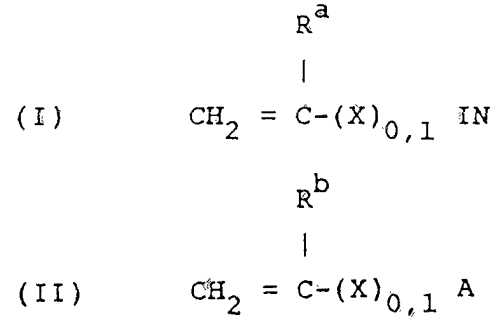
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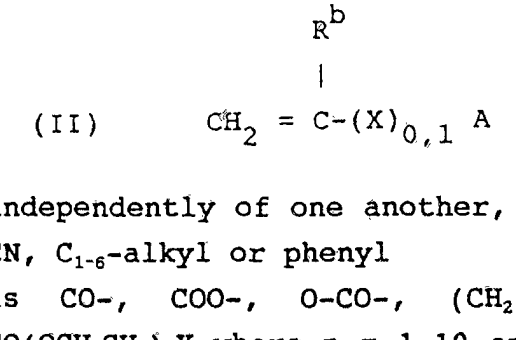
(56) Prior Art Documents
AU 12624/88 C08F 2/50 C07C 49/84
US 4672079

(57) Claim

1. Photoinitiator copolymers having molecular weights between 500 and 1,000,000, ~~obtainable~~ obtained by copolymerization of at least two different monomer units of the formulae I and II in the I/II ratio ~~1:100~~ of 1 to 100



(I) $CH_2 = C-(X)_{0,1}$ IN



(II) $CH_2 = C-(X)_{0,1}$ A

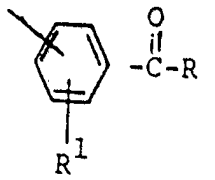
in which

R^a and R^b, independently of one another, are each H, Cl, CN, C_{1-6}-alkyl or phenyl

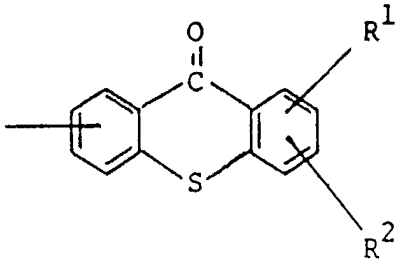
X is CO-, COO-, O-CO-, $(CH_2)_nY$, $COO(CH_2)_nY$, $CO(OCH_2CH_2)_nY$ where n = 1-10 and Y is a single bond, -O-, -S-, -CO-, -COO-, -OCO-, -NH- or $-N(C_{1-6}$-alkyl$)-$,

IN is one of the basic photoinitiator structures

.../2



or



in which

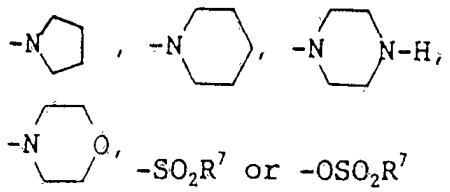
R is $-CR^3R^4R^5$ or $-\overset{O}{\overset{\|}{P}}(R^6)_2$,

and

R^1 and R^2 are H, halogen, C_{1-12}-alkyl or C_{1-12}-alkoxy,

R^3 and R^4 independently of one another, are each H, C_{1-12}-alkyl, C_{1-12}-alkenyl, C_{1-12}-alkoxy or together are C_{2-6}-alkylene,

R^5 is -OH, C_{1-6}-alkoxy, C_{1-6}-alkanoyloxy, $-N(C_{1-6}$-alkyl$)_2$,



$-SO_2R^7$ or $-OSO_2R^7$

R^6 is C_{1-6}-alkyl, C_{1-6}-alkanoyl, phenyl or benzoyl, in each case optionally substituted by halogen, C_{1-6}-alkyl or C_{1-6}-alkoxy,

R^7 is C_{1-6}-alkyl or phenyl,

A is one of the basic photoinitiator structures IN as defined above, or H, C_{1-12}-alkyl, C_{1-12}-alkenyl, phenyl, styryl, halogen, NCO, NCS, N_3, SO_3H, SO_2Cl,

$CR^c=CR^dR^e$ or  where R^c, R^d and R^e are each H or CH_3, or is $SiR^fR^gR^h$ where R^f, R^g and R^h are each Cl, C_{1-12}-alkyl, C_{1-12}-alkoxy or C_{1-12}-alkanoyloxy.

7. Radiation-curable systems essentially comprising one or more copolymers according to Claim 1.

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Patents Act

FORM 10

COMPLETE SPECIFICATION

(ORIGINAL)

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Lodged:

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Related Art:

Applicant(s): Merck Patent Gesellschaft Mit Beschrankter Haftung
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Actual Inventors: Dr. Manfred Kohler
Dr. Dieter Dorsch
Dr. Ohngemach
Prof. Dr. Gerhard Greber

Complete specification for the invention entitled "Photoinitiator copolymers".

The following statement is a full description of this invention, including the best method of performing it known to me:-

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Ciba-Geigy Aktiengesellschaft
~~Merck Patent Gesellschaft~~
mit beschränkter Haftung

6100 D a r m s t a d t

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Photoinitiator copolymers

The invention relates to photoinitiator copolymers constructed from at least two different monomer units, of which at least one carries a structural unit with a photoinitiating effect. Polymeric compounds of this type are used as free-radical-forming photoinitiators in the photopolymerization of ethylenically unsaturated compounds or systems containing such compounds. Photoinitiator copolymers exhibit a number of advantages, many of which are unexpected, compared with conventional monomeric photoinitiators or also homopolymeric photoinitiators derived therefrom.

Photochemically induced polymerization reactions have achieved great importance in industry, in particular when rapid curing of thin layers is important, such as, for example, in the curing of paint coats and plastic coatings on paper, wood, metal and plastic or in the drying of printing inks. Here, radiation curing in the presence of photoinitiators is distinguished by a saving in raw materials and energy, a low thermal load of the substrate, and, in particular, by high speed, compared with conventional methods of drying or curing coatings. However, the production of polymeric materials per se by polymerization of corresponding unsaturated monomeric starting materials is also frequently carried out photochemically and using photoinitiators, with customary processes, such as solution and emulsion polymerization, being used.

In addition, photoinitiators are frequently used in photopolymerizable compositions for photolithographic processes, such as, in particular, in negative photoresists in semiconductor electronics and in optoelectronics.

Since none of the reactants is generally capable of adequately absorbing the photochemically active radiation in the reactions mentioned, photoinitiators must be added which are capable either of absorbing incident, high-energy radiation, usually UV light, and at the same time of forming active initiator free radicals which in turn initiate the photopolymerization, or of transmitting the energy absorbed for free-radical formation to one of the polymerizable reactants. The initiators do not normally take part in the actual polymerization reaction.

Photoinitiators which are suitable for these purposes are predominantly compounds of the aromatic ketone type, such as benzophenones, benzoin ethers, benzil monoketals, dialkoxyacetophenones, thioxanthones, bisacylphosphine oxides or hydroxyalkylphenones, or derivatives derived from these types of structure. Hydroxyalkylphenone photoinitiators, as described in German Patent 2,722,264 and European Patent 3,002, have proven particularly advantageous, principally due to their high reactivity, but also because of the excellent shelf life in the dark of the radiation-curable systems to which they are added, and the low tendency towards yellowing of the layers cured using these systems.

The continuing diversification and specialization of processes and products in the sector of coating technology using polymeric materials and the increasing demand for tailor-made problem solutions is accompanied by the fact that greater and more specific demands are also being made on the photoinitiators. Frequently, conventional photoinitiators do not satisfy the demands made of them today, or at least do not do so in an optimal manner. Increasingly, these demands are that photoinitiators should be capable of more than merely forming free radicals which initiate only the photopolymerization or photocrosslinking. Essential problem areas here are, for example, the compatibility in a very wide variety of systems, in particular also those which, in order to achieve certain material properties, also

contain non-photopolymerizable components (so-called hybrid systems), and, in addition, the migration-resistant incorporation of photoinitiator or photolysis products thereof into the photopolymerized end product. At the same time, the additional properties must not influence the photoreactivity of the initiator; a long shelf life in the dark of the systems provided therewith is likewise of high importance for usability in practice.

Further developments in these directions have already been carried out, principally starting from the hydroxyalkylphenone photoinitiators, which have a particularly high performance with respect to photoreactivity. Thus, for example, the photoinitiators described in German Offenlegungsschrift 3,512,179 are particularly suitable for use in aqueous systems. The photoinitiators of German Offenlegungsschrift 3,534,645 and European Offenlegungsschrift 161,463, which are provided with unsaturated functions, and the particularly versatile, coreactive photoinitiators of German Patent Applications P 3,707,891 and P 3,738,567 enable migration-resistant incorporation into the product by the photochemically and non-photochemically induced coreaction with a very wide variety of system components, with themselves or with the substrate, before, during or even after the actual photopolymerization.

However, these further developments, which are very promising as far as the principle is concerned, are still in many cases in need of improvement. Thus, predominantly only individual specific additional properties can be achieved in each of the modified photoinitiators of the specifications cited above. For this reason, various applications and uses require a large number of appropriately modified photoinitiators to be synthesized from first principles and kept ready, which requires high expense and is therefore not very economical.

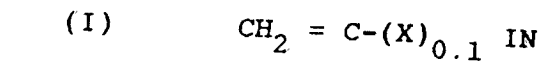
The invention therefore had the object of finding and providing high-performance photoinitiators using which, on the one hand, a large number of tailor-made additional properties can be achieved and which, however,

are on the other hand easily accessible, for example starting from a few universally applicable basic components.

It has now been found that these requirements are fulfilled in an excellent manner by photoinitiator copolymers having molecular weights between 500 and 1,000,000, obtainable by copolymerization of at least two different monomer units of the formulae I and II in the I/II ratio of 1 to 100 ~~1:100~~



(I)



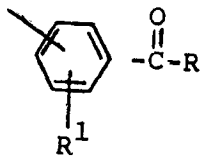
(II)

in which

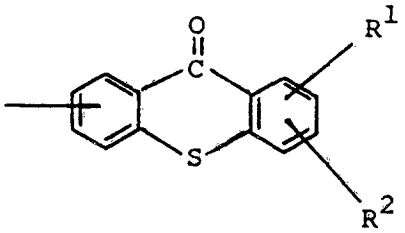
R^a and R^b, independently of one another, are each H, Cl, CN, C_{1-6}-alkyl or phenyl

X is CO-, COO-, O-CO-, $(CH_2)_nY$, $COO(CH_2)_nY$, $CO(OCH_2CH_2)_nY$ where n = 1-10 and Y is a single bond, -O-, -S-, -CO-, -COO-, -OCO-, -NH- or $-N(C_{1-6}\text{-alkyl})-$,

IN is one of the basic photoinitiator structures



or



in which

R is $-CR^3R^4R^5$ or $-\overset{O}{\overset{\|}{P}}(R^6)_2$,

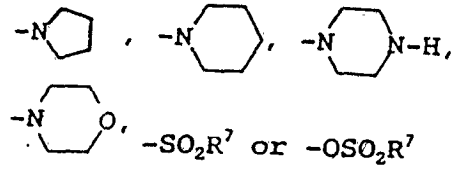
and

R^1 and R^2 are H, halogen, C_{1-12}-alkyl or C_{1-12}-alkoxy,

R^3 and R^4 independently of one another, are each H, C_{1-12}-alkyl, C_{1-12}-alkenyl, C_{1-12}-alkoxy or together are C_{2-6}-alkylene,

R^5 is -OH, C_{1-6}-alkoxy, C_{1-6}-alkanoyloxy, $-N(C_{1-6}\text{-alkyl})_2$,

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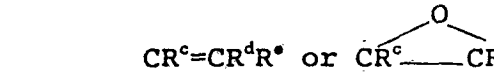


$-SO_2R^7$ or $-OSO_2R^7$

R^6 is C_{1-6}-alkyl, C_{1-6}-alkanoyl, phenyl or benzoyl, in each case optionally substituted by halogen, C_{1-6}-alkyl or C_{1-6}-alkoxy,

R^7 is C_{1-6}-alkyl or phenyl,

A is one of the basic photoinitiator structures IN as defined above, or H, C_{1-12}-alkyl, C_{1-12}-alkenyl, phenyl, styryl, halogen, NCO, NCS, N_3, SO_3H, SO_2Cl,



where R^c, R^d and R^e are each H or CH_3, or is $SiR^fR^gR^h$ where R^f, R^g and R^h are each Cl, C_{1-12}-alkyl, C_{1-12}-alkoxy or C_{1-12}-alkanoyloxy.

The copolymers according to the invention are high-performance, individually structurable photoinitiators for the photopolymerization or photocrosslinking of ethylenically unsaturated compounds or systems containing such compounds. However, they can also be employed themselves as simultaneously photoinitiating and film-forming components in radiation-curable systems.

The invention thus relates to photoinitiator copolymers having molecular weights of between 500 and 1,000,000, obtainable by copolymerization of monomer units of the formulae I and II defined above in the I/II ratio of 1 to 100 ~~= 1 : 100~~.

The invention furthermore relates to the use of these photoinitiator copolymers as photoinitiators for the photopolymerization of ethylenically unsaturated compounds or systems containing such compounds.

The invention additionally relates to a process for the preparation of photopolymerizable systems containing ethylenically unsaturated compounds, at least one of these photoinitiator copolymers being added to the mixture to be polymerized.

Finally, the invention relates to polymerizable

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systems containing at least one ethylenically unsaturated photopolymerizable compound and, optionally, further known and customary additives containing at least one of these photoinitiator copolymers.

The photoinitiator copolymers according to the invention are novel. They prove to be highly reactive photoinitiators whose specific properties can be specifically modified and varied through the quantitative and qualitative choice of the monomer units I and II. They are very simply accessible by thermal copolymerization of the appropriate monomer components. Due to their polymeric character, they have high migration resistance in the photopolymerizable system and in the photopolymerized end product.

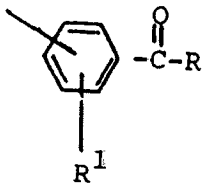
The photoinitiator copolymers according to the invention are built up from at least two different monomer units of the formulae I and II.

The monomer unit I contains a polymerizable, ethylenically unsaturated structural part in which the radical R^a can be hydrogen, chlorine, cyano, a C_{1-6}-alkyl group or a phenyl group. R^a is preferably hydrogen, and the unsaturated structural part is thus preferably a vinylic group. This unsaturated structural part is linked to any basic photoinitiator structure IN, as is, in principle, also present in conventional photoinitiators, either directly via a single bond or via a bridging group X.

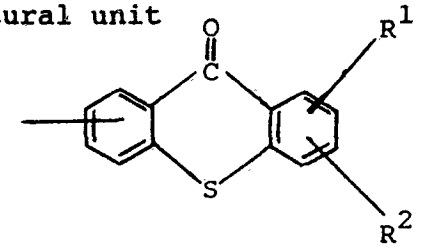
The bridging group X can be a carbonyl, carboxyl or alkylene group having 1-10 C atoms. It can alternatively be a carbonyloxy alkylene or carbonylpolyoxyethylene group, in each case having 1-10 methylene units or oxyethylene units respectively. The linking to the basic photoinitiator structure IN can take place via a single bond or via an oxygen, sulphur, carbonyl, carboxyl or amino group. Preferred linkings of unsaturated structural unit to basic photoinitiator structure IN are the single bond, the carbonyl group, the carbonyloxymethylenoxy group and the carbonyloxyethoxy group. In the case of linking via a single bond, vinyl-substituted

derivatives of customary photoinitiators result. In the other cases of preferred linkings, acrylated photoinitiator derivatives result.

IN is essentially the aromatic ketone structural unit or the thioxanthone structural unit



or



as present in most classical photoinitiators, but can alternatively be any other structures having photoinitiator properties.

If R is the $-CR^3R^4R^5$ group, the abovementioned definitions for R^3, R^4 and R^5 accordingly give the basic photoinitiator structures of the acyloin ethers, the dialkoxyacetophenones, the hydroxyalkylphenones and aminoalkylphenones and the α-sulphonyl ketones.

Copolymerizable hydroxyalkylphenone derivatives are particularly preferred monomer units of the formula I.

If R is the $-\overset{O}{\overset{\|}{P}}(R^6)_2$ group, the resultant photoinitiators belong to the class comprising the acylphosphine oxides.

Copolymerizable thioxanthone derivatives are likewise preferred monomer units of the formula I.

Numerous unsaturated derivatives of a very wide variety of photoinitiator groups, as represented by the formula I, are known, and some are also commercially available. This applies, in particular, to the hydroxyalkylphenone derivatives described in German Offenlegungsschrift 3,534,645 and European Offenlegungsschrift 161,463, and to the corresponding photoinitiators provided with unsaturated functions, of German Patent Applications P 3,707,891 and P 3,738,567. In principle, they can be prepared by standard methods of organic chemistry.

The reaction conditions here are given in the

standard works of preparative organic chemistry, for example HOUBEN-WEYL, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme Verlag, Stuttgart, or ORGANIC SYNTHESIS, J. Wiley, New York, London, Sydney.

In general, it is favourable to prepare the monomers of the formula I or corresponding precursors by proven synthetic methods as customary for the basic photoinitiators. It is advantageous here to start directly from the known photoinitiators as starting materials and to link the unsaturated structural unit to these using customary reactions, such as substitution reactions, in one or more steps. However, precursors of the known photoinitiators which already have suitable substituents can also be used and the actual photoinitiator active structure only produced in these when the unsaturated structural part is already present.

Particularly suitable precursors for photoinitiators which have been provided with unsaturated functions are the photoinitiator derivatives described in German Patent Applications P 3,707,891 and P 3,738,567, which carry substituents having reactive functional groups.

Of these, the hydroxyethoxy- and hydroxyethylthio-substituted photoinitiator derivatives are preferred since they can easily be converted into the corresponding (meth)acrylic acid esters. Typical photoinitiator derivatives which have been provided with unsaturated functions and can be used as monomer components of the formula I for the photoinitiator copolymers according to the invention are, for example,

4-vinylphenyl 2-hydroxy-2-propyl ketone (Ia)

4-allyloxyphenyl 2-hydroxy-2-propyl ketone (Ib)

4-2-allyloxyethoxyphenyl 2-hydroxy-2-propyl ketone (Ic)

vinyl 4-(2-hydroxy-2-methylpropionyl)phenoxyacetate (Id)

4-acryloyloxyphenyl 2-hydroxy-2-propyl ketone (Ie)

4-methacryloyloxyphenyl 2-hydroxy-2-propyl ketone (If)

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4-2-acryloyloxyethoxyphenyl 2-hydroxy-2-propyl ketone (Ig)

4-2-methacryloyloxyethoxyphenyl 2-hydroxy-2-propyl ketone (Ih)

4-2-acryloyloxydiethoxyphenyl 2-hydroxy-2-propyl ketone (Ii)

4-2-acryloyloxyethylthiophenyl 2-hydroxy-2-propyl ketone (Ij)

4-2-acryloyloxyethylthiophenyl 2-N-morpholino-2-propyl ketone (Ik)

2-[2-(acryloyloxy)ethylthio]thioxanthone (Il)

2-[2-(acryloylamino)ethylthio]thioxanthone (Im)

2-[2-(allyloxyethylthio]thioxanthone (In)

2-[2-(allylamino)ethylthio]thioxanthone (Io)

4-[2-(methacryloyloxy)ethoxycarbonyl]thioxanthone (Ip)

The monomer unit of the formula II is built up entirely analogously to the monomer unit of the formula I. The group A linked in this unit to the unsaturated structural unit, either directly or via the bridging group X, can be a basic photoinitiator structure IN, as defined above, or alternatively hydrogen, C_{1-12}-alkyl, C_{1-12}-alkenyl, phenyl, styryl, halogen, such as, in particular, chlorine and fluorine, the isocyanate, isothiocyanate, azide, sulphonic acid or sulphonyl chloride group, a vinyl or oxiranyl group, which may also optionally be monosubstituted or polysubstituted by chlorine or methyl, or a silyl group in which the radicals bonded to silicon are chlorine and/or C_{1-12}-alkyl and/or C_{1-12}-alkoxy and/or C_{1-12}-alkanoyloxy.

A large number of unsaturated monomer units of the formula II which contain no photoinitiating structural parts IN are known from the field of polymer chemistry and are available. These are predominant vinyl and acrylic derivatives, i.e. customary, easily and inexpensively available, unsaturated monomer components.

Preferred monomer components of this type are, in particular, those which contain functional groups which are capable of further reactions, such as, in particular, hydroxyl, carboxyl, carboxamide, sulphonic acid,

isocyanate, olefinically unsaturated and silyl groups. Photoinitiator copolymers according to the invention having specific properties which are tailor-made for the particular use can be prepared through functionalized monomer components of this type. Thus, compatibility with a very wide variety of radiation-curable systems and, in particular, also with hybrid binder systems can be achieved. The functional groups impart the photoinitiator copolymers according to the invention with coreactivity as in P 3,707,891/P 3,738,567, i.e., in particular, with the ability to react with components of the radiation-curable systems or with the substrate.

Typical monomer units of the formula II of this type are, for example, (meth)acrylic acid, (meth)acrylamide, alkyl (meth)acrylate, hydroxyethyl methacrylate, alkenyl or epoxy (meth)acrylates, hexanediol diacrylate, acrylonitrile, styrene, divinylbenzene, methyl vinyl ketone, N-vinylpyrrolidone, 2-(N,N-dimethylamino)ethyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate.

In the case of monomer components of the formula II containing initiator groups, those are likewise preferred which have been indicated above as being preferred for the monomer units of the formula I. If the photoinitiator copolymers according to the invention are in each case built up only from initiator-containing monomers, the monomer units of the formula I and of the formula II are different from one another.

The preparation of the photoinitiator copolymers according to the invention from the monomer units of the formulae I and II is carried out in a manner known per se for the polymerization of olefinically unsaturated compounds of this type, namely in solution using customary thermally activatable free-radical initiators, such as, for example, benzoyl peroxide or azobisisobutyronitrile, with exclusion of light. The monomer units of the formulae I and II are employed here in amounts such that the I:II ratio is between 1 and 100, preferably between 2 and 10. Typical solvents of the polymerization are, for example tetrahydrofuran and toluene. The reac-

tion is normally carried out at the reflux temperature of the solvent. The photoinitiator copolymers are isolated by precipitation using a non-solvent, for example n-hexane. The photoinitiator copolymers can be purified by re-precipitation, repeated if necessary. As is customary for polymer products, the products obtained can be adequately characterized by their average molecular weight $\bar{M}w$, which can be determined by gel permeation chromatography and their glass transition temperature Tg, which can be determined by differential thermoanalysis. A random distribution of the various monomer units in the copolymer is assumed. The average molecular weight can be between 500 and 1,000,000 and is preferably between 1,000 and 10,000.

The photoinitiator copolymers according to the invention can very advantageously be used for the photopolymerization of ethylenically unsaturated compounds or systems containing such compounds as photoinitiators which have been provided with tailor-made additional properties. They are principally used analogously to conventional photoinitiators as UV curing agents for paint or polymer coatings, UV-curable binder or hybrid binder systems, printing inks and in the radiation curing of aqueous prepolymer dispersions. They are used in a customary manner, generally being added to the systems to be polymerized in amounts of 0.1-20% by weight, preferably 0.5-12% by weight. They are generally added by simply being stirred into the systems to be polymerized.

The photoinitiator copolymers according to the invention can in many cases also be used even as the only or the essential component of radiation-curable systems. In this case, they simultaneously take on both the film-forming and photoinitiating functions. Thus, for example, copolymers of 4-(2-acryloyloxyethoxy)phenyl 2-hydroxy-2-propyl ketone (Ig) with a 2-dimethylaminoethyl methacrylate or 3-(trimethoxysilyl)propyl methacrylate, applied as a layer to a substrate, can be photostructured principally using UV radiation. These materials are thus suitable for use as negative photoresists.

Using the photoinitiator copolymers according to the invention, polymer materials which cannot themselves be photocrosslinked or photostructured since they do not contain, for example, any ethylenically unsaturated double bonds can also be rendered photoreactive.

It is known that the action of numerous conventional photoinitiators can in some cases be considerably increased by mixing with photoinitiators of a different structure, i.e. coinitiators and/or sensitizers, such as, in particular, organic amines. Typical mixtures are, for example, mixtures of hydroxyalkylphenones with thioxanthones and, if appropriate, amino compounds, such as, for example, N-methyldiethanolamine.

A particularly preferred aspect of the invention is the combination of initiators with coinitiators or sensitizers in the photoinitiator copolymers according to the invention. This is because it has been shown, surprisingly, that photoinitiator copolymers of this type are more effective than mixtures of the basic conventional photoinitiators, coinitiators and sensitizers.

Thus, for example, copolymers of the unsaturated hydroxyalkylphenone derivative Ig and the unsaturated thioxanthone derivative Im prove to be considerably more effective than the corresponding mixture of the conventional hydroxyalkylphenone and thioxanthone photoinitiators. An explanation for this could be a direct, coinitiating interaction of the various initiator groups, caused by fixation in the copolymer structure.

Photoinitiator copolymers can very advantageously also be applied to the substrate material as a discrete photoinitiator layer and only then provided with a photopolymerizable layer material. Use in the form of two-layer systems of this type is carried out as in German Offenlegungsschrift 3,629,543 and German Offenlegungsschrift 3,702,897. Particularly advantageous here are photoinitiator copolymers having polar, optionally chelate-forming groups and having silyl groups. Better fixation to metal, semiconductor, glass and ceramic substrates is thereby achieved.

Copolymers having amino-group-containing monomer components of the formula II, for example containing 2-(N,N-dimethylamino)ethyl methacrylate, contain the frequently advantageous amine accelerators and are more reactive than the corresponding conventional systems.

Dyes which are capable of forming salts with amino groups can be incorporated into amino-group-containing photoinitiator copolymers of this type during preparation. Examples of suitable dyes are xanthene dyes, such as, for example, Bengal Pink. Surprisingly, the absorption maximum is thereby shifted into the longer-wave region, which means that photoinitiator copolymers modified in this way can also be activated using longer-wave radiation, for example between 500 and 600 nm.

In general, the photoinitiator copolymers according to the invention have excellent migration resistance due to their high-molecular character. This means that they do not migrate into or out of the corresponding radiation-curable systems, which is particularly important for numerous applications.

A system to be polymerized is taken to mean a mixture of monofunctional or polyfunctional, ethylenically unsaturated monomers which can be initiated by means of free radicals, oligomers, prepolymers, polymers or mixtures of these oligomers, prepolymers and polymers with unsaturated monomers, it also being possible, if necessary or desired, for the mixture to contain further additives, such as, for example, antioxidants, light stabilizers, dyes, pigments, but also further known photoinitiators and reaction accelerators. Suitable unsaturated compounds are all those whose C=C double bonds have been activated by, for example, halogen atoms, carbonyl, cyano, carboxyl, ester, amide, ether or aryl groups or by conjugated further double or triple bonds. Examples of such compounds are vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, methyl, ethyl, n- or tert.-butyl, cyclohexyl, 2-ethylhexyl, benzyl, phenyloxyethyl, hydroxyethyl, hydroxypropyl, lower alkoxyethyl or tetrahydro-

furfuryl acrylate or methacrylate, vinyl acetate, propionate, acrylate or succinate, N-vinylpyrrolidone, N-vinylcarbazole, styrene, divinylbenzene, substituted styrenes, and the mixtures of unsaturated compounds of this type. Polyunsaturated compounds, such as, for example, ethylene diacrylate, 1,6-hexanediol diacrylate, propoxylated bisphenol A diacrylate and dimethacrylate, trimethylolpropane diacrylate and pentaerythritol triacrylate can also be polymerized with the photoinitiators used according to the invention. Suitable photopolymerizable compounds are furthermore unsaturated oligomers, prepolymers or polymers and mixtures thereof with unsaturated monomers. These include, for example, unsaturated polyesters, unsaturated acrylic materials, epoxy materials, urethanes, silicones, aminopolyamide resins and, in particular, acrylated resins, such as acrylated silicone oil, acrylated polyesters, acrylated urethanes, acrylated polyamides, acrylated soybean oil, acrylated epoxy resin and acrylated acrylic resin, expediently mixed with one or more acrylates of the mono- di- or polyalcohol.

The expression "photopolymerization of ethylenically unsaturated compounds" should be understood in its broadest sense. It includes, for example, the further polymerization of or crosslinking between polymeric materials, for example of prepolymers, the homopolymerization, copolymerization and terpolymerization of simple monomers and also the combination of the types of reaction mentioned.

The photopolymerization can be initiated by the action of high-energy radiation, preferably UV light, on the photopolymerizable systems containing the photoinitiator copolymers according to the invention.

The photopolymerization is carried out by methods known per se by irradiation with light or UV radiation of the wavelength range from 250-500 nm, preferably 300-400 nm. Radiation sources which can be used are sunlight or artificial-light lamps. For example, mercury high-pressure, medium-pressure or low-pressure lamps and

xenon and tungsten lamps are advantageous.

The photopolymerization using the photoinitiator copolymers according to the invention can be carried out both batchwise and continuously. The duration of irradiation depends on the way in which the polymerization is carried out, on the type and amount of the polymerizable materials employed, on the type and concentration of the photoinitiators used, and on the intensity of the light source, and can be in the range from a few seconds to minutes, such as, for example, in the case of radiation-curing of coatings, but also in the region of hours in the case of large batches, such as, for example, in bulk polymerization.

The photoinitiator copolymers according to the invention are preferably used as photoinitiators in the UV curing of thin layers, such as, for example, paint coats, on all materials and carriers which are customary for this purpose. These can principally be paper, wood, textile carriers, plastic and metal. An important area of application is also the drying or curing of printing inks and screen-printing materials, of which the latter are preferably employed in surface coating or shaping of, for example, cans, tubes and metallic sealing caps. Due to the very substantial to complete absence of free initiator radicals or free photolysis products when the photopolymerization is complete in the systems to which the photoinitiator copolymers according to the invention have been added, they are particularly suitable in areas of application where diffusion of such radicals into media surrounding corresponding end products is to be excluded, for example if packing provided with photopolymerizable coatings comes into contact with foodstuffs.

Examples

A. Preparation of photoinitiator copolymers

General preparation procedure:

The monomeric starting materials in the appropriate molar amounts are dissolved in THF (150-300 ml/batch up to 100 mmol), and azobisisobutyronitrile

(150-300 mg/batch up to 100 mmol) is added. The mixture is refluxed for 12 hours. The solvent is then stripped off, the residue is taken up in ethyl acetate, and the solution is treated with activated charcoal and filtered. The photoinitiator copolymer is obtained by precipitation using n-hexane and re-precipitation from ethyl acetate/n-hexane.

Photoinitiator monomers used:

4-(2-acryloyloxyethoxy)phenyl 2-hydroxy-2-propyl ketone (Ig)

4-(2-methacryloyloxyethoxy)phenyl 2-hydroxy-2-propyl ketone (Ih)

4-(2-acryloyloxyethylthio)phenyl 2-(N-morpholino)-2-propyl ketone (Ik)

2-[2-(acryloyloxy)ethylthio]thioxanthone (Il)

4-[2-(methacryloyloxy)ethoxycarbonyl]thioxanthone (Ip)

Photoinitiator copolymers prepared:

Example No.	Monomers/	Molar amount	Mw	Tg (°C)
1	Ig	10		
	Il	1	3000	-
2	Ig	1		
	Il	1	3200	37.7
3	Ik	5		
	Il	1	1900	47.4
4	Ik	10		
	Il	1	1900	47.9
5	Ik	15		
	Il	1	1950	40.8
6	Ik	10		
	Ip	1	4100	38.5

Example No.	Monomers/	Molar amount	Mw	Tg (°C)
7	Ik	10		
	Ip	1	3000	32.7
	acrylic acid	2		
8	Ik	10		
	Ip	1	3050	35.3
	acrylic acid	5		
9*	Ig	3		
	2-dimethylamino-ethyl methacrylate	1	3450	36.5
	Bengal Pink (0.5 g/100 mmol batch)			
10	Ih	6		
	methyl methacrylate	1	2200	107
11	Ih	1		
	methyl methacrylate	1	2300	90.2
12	Ig	10		
	n-dodecyl acrylate	1	3400	28.3
13	Ig	5		
	acrylic acid	1	3300	35.9
14	Ig	10		
	acrylamide	1	3000	45.3
15	Ig	1		
	acrylamide	1	2300	62.9
16	Ig	3		
	3-(trimethoxysilyl)-propyl methacrylate	1	3100	(oil)

Example No.	Monomers/	Molar amount	Mw	Tg (°C)
17	Ig	6		
	3-(trimethoxysilyl)-propyl methacrylate	1	3100	(oil)

* Maximum absorption at λ = 550 nm

B. Applicational comparison experiments

The photoinitiator copolymers according to the invention to be tested and corresponding conventional photoinitiators or photoinitiator mixtures for comparison were stirred into samples of a pigmented, radiation-curable binder system comprising

75 parts by weight of polyester acrylate (Laromer EA 81, BASF)

25 parts by weight of hexanediol diacrylate

30 parts by weight of TiO_2

The initiator-containing systems were applied to glass plates (10 x 10 cm) in a film thickness of 24 μm.

The UV curing was then carried out by passing the coated plates on a variable-speed conveyor belt under Hg medium-pressure lamps (lamp power 2 x 80 W/cm; lamp distance 10 cm).

As a measure of the respective curing result at various belt speeds, the König pendulum hardness (DIN 53157) was determined after storage for 20 hours.

	Belt speed (m/min)			
Pendulum hardness (seconds)	5	10	15	20
Initiator/Content+				
Ex. No. 1 / 3 % by weight	124	83	71	58
Ex. No. 2 / 3 % by weight	133	95	81	62
Comparison + / 3 % by weight	92	66	53	41

\+ In all cases additionally 2% by weight of

N-methyldiethanolamine

+

+ Mixture of phenyl 2-hydroxy-2-propyl ketone and 2-isopropylthioxanthone/9:1 (Darocur 1664, E. Merck)

C. Application examples/photostructuring

The photoinitiator copolymers according to the invention, i.e., copolymers containing hydroxyalkyl phenone and thioxanthone units, furnish substantial better curing results, compared with mixtures of the respective basic photoinitiators.

A 10% solution of the copolymer as in Ex. No. 9 in diethylene glycol dimethyl ether was spin-coated (30 seconds, 4500 rpm) onto a glass plate (5 x 5 cm). The coated plate was dried for 10 minutes at 150°C. The plate, half of which was covered, was irradiated for 4 minutes using a UV lamp (type TQ 180, Heraeus Original Hanau) at a distance of 5 cm. After the irradiation, the plate was treated with acetone to dissolve off the unexposed part of the coating. A highly adherent, cured, 0.4 µm thick coating which remained unchanged even after relatively long storage in acetone remained in the exposed region.

An analogous result was achieved using the copolymer as in Ex. No. 16.

An analogous result was achieved using a copolymer comprising monomer Ig, 3-(trimethoxysilyl)propyl methacrylate and methyl methacrylate in a molar ratio 3:1:5.

The claims defining the invention are as follows:

1. Photoinitiator copolymers having molecular weights between 500 and 1,000,000, ~~obtainable~~ obtained by copolymerization of at least two different monomer units of the formulae I and II in the I/II ratio ~~1:100~~ of 1 to 100

(I) $CH_2 = C-(X)_{0,1}$ IN

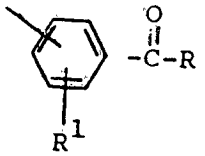
(II) $CH_2 = C-(X)_{0,1}$ A

in which

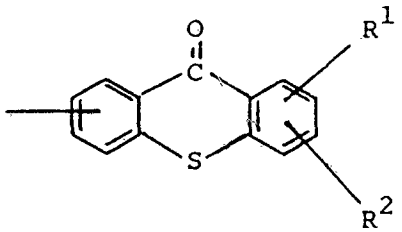
R^a and R^b, independently of one another, are each H, Cl, CN, C_{1-6}-alkyl or phenyl

X is CO-, COO-, O-CO-, $(CH_2)_nY$, $COO(CH_2)_nY$, $CO(OCH_2CH_2)_nY$ where n = 1-10 and Y is a single bond, -O-, -S-, -CO-, -COO-, -OCO-, -NH- or $-N(C_{1-6}\text{-alkyl})-$,

IN is one of the basic photoinitiator structures



or



in which

R is $-CR^3R^4R^5$ or $-\overset{O}{\overset{\|}{P}}(R^6)_2$,

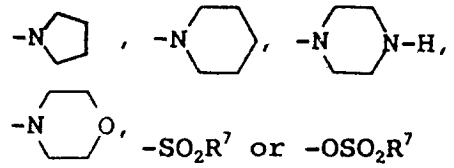
and

R^1 and R^2 are H, halogen, C_{1-12}-alkyl or C_{1-12}-alkoxy,

R^3 and R^4 independently of one another, are each H, C_{1-12}-alkyl, C_{1-12}-alkenyl, C_{1-12}-alkoxy or together are C_{2-6}-alkylene,

R^5 is -OH, C_{1-6}-alkoxy, C_{1-6}-alkanoyloxy, $-N(C_{1-6}\text{-alkyl})_2$,

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$-SO_2R^7$ or $-OSO_2R^7$

R^6 is C_{1-6}-alkyl, C_{1-6}-alkanoyl, phenyl or benzoyl, in each case optionally substituted by halogen, C_{1-6}-alkyl or C_{1-6}-alkoxy,

R^7 is C_{1-6}-alkyl or phenyl,

A is one of the basic photoinitiator structures IN as defined above, or H, C_{1-12}-alkyl, C_{1-12}-alkenyl, phenyl, styryl, halogen, NCO, NCS, N_3, SO_3H, SO_2Cl,



where R^c, R^d and R^e are each H or CH_3, or is $SiR^fR^gR^h$ where R^f, R^g and R^h are each Cl, C_{1-12}-alkyl, C_{1-12}-alkoxy or C_{1-12}-alkanoyloxy.

2. Use of copolymers according to Claim 1 as photoinitiators for the photopolymerization of ethylenically unsaturated compounds or systems containing such compounds.

3. Process for the preparation of photopolymerizable systems containing ethylenically unsaturated compounds, characterized in that at least one photoinitiator copolymer according to Claim 1 is added to the mixture to be polymerized.

4. Process according to Claim 3, characterized in that 0.1 to 20% by weight of a photoinitiator copolymer according to Claim 1 is added to the mixture to be polymerized.

5. Photopolymerizable systems containing at least one ethylenically unsaturated, photopolymerizable compound and, if appropriate, further known and customary additives, characterized in that they contain at least one photoinitiator copolymer according to Claim 1.

6. Use of copolymers according to Claim 1 as simultaneously photoinitiating and film-forming components in radiation-curable systems.

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7. Radiation-curable systems essentially comprising one or more copolymers according to Claim 1.

8. Process for the preparation of a radiation-cured coating on a substrate, the latter being coated with a photopolymerizable system and the curing being carried out by irradiation with UV light of a wavelength between 250 and 600 nm, characterized in that a system according to Claim 5 or 7 is used.

~~9. Any novel, starting or intermediate compound or process for the manufacture of same as herein described.~~

DATED the 27th day of APRIL, 1989

~~Merck Patent Gesellschaft~~
~~Mit Beschrankter Haftung~~
By its Patent Attorneys
ARTHUR S. CAVE & CO.
Ciba-Geigy Aktiengesellschaft

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