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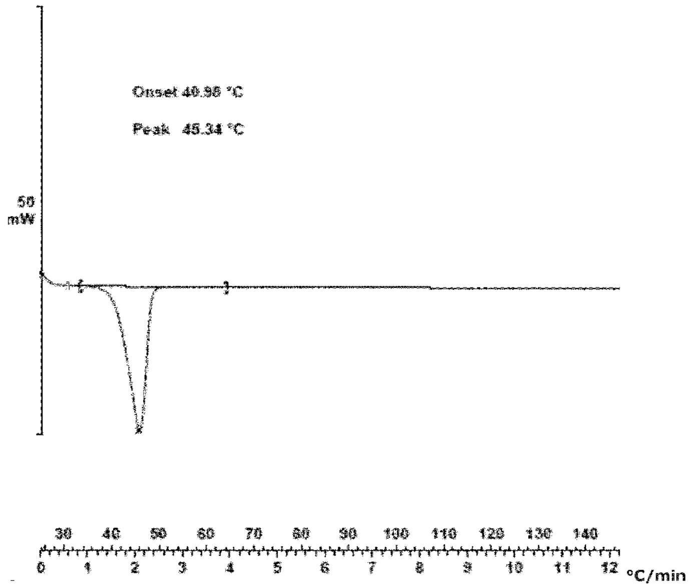
(54) Title: NOVEL SOLID FORM OF BIS(2,4,6-TRIMETHYLBENZOYL)-n-OCTYL-PHOSPHINE OXIDE

Figure 2



DSC diagram

(57) **Abstract:** The present invention relates to a novel physical form of bis(2,4,6- trimethylbenzoyl)-n-octyl-phosphine oxide, to a process for its preparation and to its use as photoinitiator in photopolymerization compositions. The invention also relates to a process for the photopolymerization of compositions comprising said photoinitiator as well as its use in articles of manufacture, including printed, coated, and fabricated assemblies.

[Continued on next page]

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"NOVEL SOLID FORM OF BIS(2,4,6-TRIMETHYLBENZOYL)-n-OCTYL-PHOSPHINE OXIDE"

***

PRIOR ART

Bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide is a known photoinitiator. The role of a photoinitiator (PI) is to convert light to chemical energy in the form of reactive intermediates. Said intermediates are radicals able to initiate radical polymerization of double bonds present in the formulation to be cured.

Bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide has been disclosed in a non-solid form. For instance, said compound has been disclosed as a resin in GB2259704 (Compound 7), as an oil in US5534559 (Example 6) and as a viscous oil in WO00/32612 (Example 10).

AIMS OF THE INVENTION

It is a first aim of the invention to provide for a novel physical form of bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide, for a process for its preparation and for its use as a photoinitiator.

It is a further aim of the invention to provide for photocurable compositions comprising the novel photoinitiator of the invention.

Is a further aim of the invention to provide for processes for photocuring ethylenically unsaturated compounds using the novel photoinitiator of the invention, as well as articles of manufacture obtained by said processes.

SUMMARY OF THE INVENTION

The Applicant surprisingly found that it is possible to prepare bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide in a solid form and, moreover, observed said novel physical solid form allows for better performances in photopolymerization processes with respect to the known non-solid forms of the same photoinitiator disclosed in the prior art.

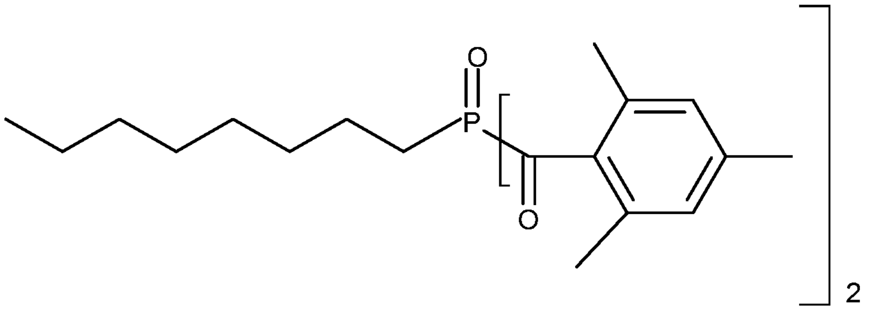
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows photographs of bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide of the prior art (A) (viscous oil poured on a surface) and of the invention (B) (solid product).

Figure 2 shows the DSC diagram of a compound of formula (I) according to the invention.

DESCRIPTION OF THE INVENTION

According to one of its aspects, the present invention relates to bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide (herein after also referred to as "n-octyl-BAPO") of formula (I)



(I)

characterized in that is it in a solid form at ambient temperature and pressure.

Preferably, n-octyl-BAPO of the invention is a white/light yellow powder, having a melting point higher than 38°C.

Preferably, n-octyl-BAPO of the invention shows a DSC (Differential Scanning Calorimetry) onset from 38 to 50°C, more preferably from 38 to 48°C, for instance from 39 to 45°C.

Preferably, n-octyl-BAPO of the invention shows a DSC peak from 40 to 50°C, more preferably from 41 to 48°C, for example at about 41°C, about 42°C, about 43°C, about 44°C, about 45°C, about 46°C, about 47°C or about 48°C.

Preferably, n-octyl-BAPO of the invention is a white/light yellow powder having a HPLC (area%) higher than 99%.

Preferably, n-octyl-BAPO of the invention is a white/light yellow powder, with a melting point higher than 38°C and having a HPLC (area%) higher than 99%.

Preferably, n-octyl-BAPO of the invention shows a DSC onset from 38 to 50°C, more preferably from 38 to 48°C, for instance from 39 to 45°C and has a HPLC (area%) higher than 99%.

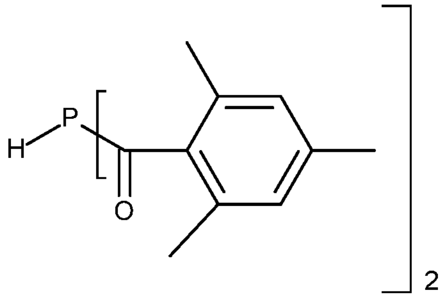
Preferably, n-octyl-BAPO of the invention shows a DSC peak from 40 to 50°C, more preferably from 41 to 48°C, for example at about 41°C, about 42°C, about 43°C, about 44°C, about 45°C, about 46°C, about 47°C or about 48°C and has a HPLC (area%) higher than 99%.

Ambient temperature and pressure are here intended as 25°C and 1 atm (101325 Pa).

The term "about" herein indicates that the mentioned values may vary of 1-1.2%. For instance, "45°C" may include temperatures from 44.5 and 45.4°C, and the like.

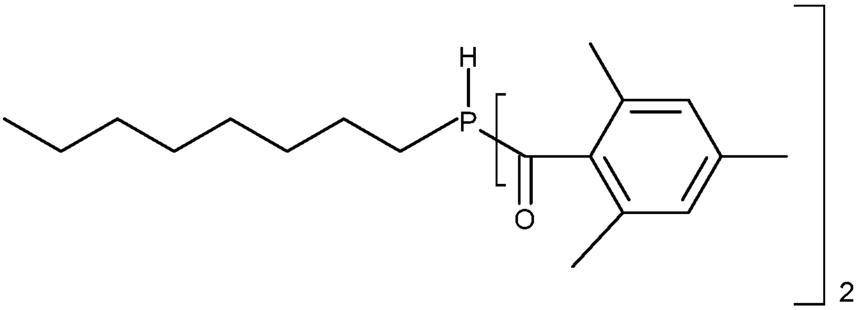
According to another of its aspects, the present invention relates to a process for the manufacture of n-octyl-BAPO in a solid form which comprises the following steps:

1. reacting compound of formula (II)



(II)

with a n-octyl-Hal, wherein Hal represents a halogen atom, in a suitable solvent, thus obtaining compound of formula (III)



(III)

2. oxidating compound of formula (III) in a suitable solvent, thus providing compound of formula (I) in a solid form.

According to the invention, the term "solvent" includes a single solvent, a mixture of solvents as well as solutions.

Unless otherwise indicated, reactions are preferably carried out under stirring.

Step 1 is carried out in the presence of water and a phase transfer catalyst, preferably ammonium salts, more preferably *tert*-butylammonium bromide or tert-butylammonium chloride and a base, such as a tertiary amine or alkali metal base, such as alkali carbonate, alkali hydroxide, e.g. potassium or sodium carbonate, potassium or sodium hydroxide, triethyl amine, preferably potassium carbonate.

Step 1 is carried out at a temperature ranging from ambient temperature to the reflux temperature of the reaction mixture, preferably from 50°C to the reflux temperature of the reaction mixture, more preferably at 80-95°C, advantageously at 88-90°C.

Preferably the said base is added to the reaction mixture in the form of an aqueous solution, more preferably dropwise, advantageously over 1 to 3 hours, and subsequently the reaction may be kept at the above temperatures for further 1 to 3 hours at ambient temperature.

Compound (II) and n-octyl-Hal are reacted in an almost equivalent molar ratio, preferably with a slight excess of n-octyl-Hal.

Preferably, step 1 is carried out in an inert atmosphere, for instance under a nitrogen flow.

At the end of the reaction, the mixture is extracted with an organic, preferably non-polar solvent, preferably selected from a C6-C8 alkane and their mixtures, petroleum ether, toluene, xylene and cyclohexane, more preferably with a C6-C8 alkane and their mixtures, for instance n-heptane or heptane mixtures, according to the known methods.

In step 2, the compound of formula (III) in the organic phase is oxidated with a suitable oxidating agent, preferably an aqueous solution of hydrogen peroxide, preferably at a temperature ranging from ambient temperature to 60°C, preferably from 45°C to 60°C, more preferably at approximately 55-60°C, then the reaction may be kept at said temperature for approximately 2-4 hours.

Suitable oxidating agents may include air.

At the end of the reaction, the two phases are separated and the organic phase is preferably washed with water, with a sodium bicarbonate water solution and again with water. The two phases are separated and the organic phase is preferably filtered, optionally concentrated under reduced pressure, then cooled at -5 to 5°C.

Compound of formula (I) precipitates, generally in a few hours, in a solid form and is isolated preferably by filtration and optionally washed with the organic solvent previously used.

According to another of its aspects, the invention relates to a compound of formula (I) in a solid form, as above defined, obtainable or obtained by the process of the invention.

According to another of its aspects, the present invention relates to the use of compound of formula (II) as above defined for the preparation of compound of formula (I), preferably, but not limited to, for the preparation of compound of formula (I) in a solid form.

Details of the process are provided in the Experimental Section which follows, which also shows the unexpected advantages provided by the solid compound of the invention.

In addition, a solid compound is easier to handle, workable at room temperature, while a viscous liquid always needs to be warmed to be poured/used/weighted, etc.

According to another of its aspects, the present invention relates to a photopolymerizable composition comprising:

a) from 50 to 99.7%, preferably from 70 to 98.9% by weight, based on the total content of the composition, of at least one ethylenically unsaturated compound;

b) from 0.1 to 35%, preferably from 0.1 to 20%, and more preferably from 0.2 to 15% by weight, based on the total content of the composition, of compound of formula (I) as above defined; and

c) from 0 to 20% by weight, preferably from 0 to 15%, and more preferably from 0.2 to 15% by weight, based on the total content of the composition, of an accelerator and/or of a coinitiator.

According to the present invention, the terms "photocuring" and "photopolymerizing" and related terms, are synonyms.

The expression "based on the total content of the composition" means that the % weight amounts of any of the components is calculated with respect to the sum of the weight of all the components of the composition, including any possible further additional components (in addition to a), b) and c) above), but possible water and/or solvents which may be present in the composition are not considered for the calculation of said % weight amounts.

According to another of its aspects, the present invention relates to a process for photocuring photopolymerizable compositions coatings, adhesives and inks, which process comprises:

i. providing a photopolymerizable composition as above defined;
ii. coating or printing said photopolymerizable composition onto a substrate, and
iii. photocuring said coated or printed composition with a light source on said substrate.

According to another of its aspects, the present invention relates to a process for three-dimensional printing which comprising photocuring with a light source a mixture comprising the composition as above defined.

According to another of its aspects, the present invention relates to an article of manufacture obtained by the process of the invention.

According to a preferred embodiment, the photopolymerizable composition used the processes of the invention comprises at least components (a) and (b), more preferably at least (a), (b) and (c).

The photoinitiators of the invention can be used in photocurable compositions comprising ethylenically unsaturated compounds (a). Said unsaturated compounds (a) can contain one or more olefinic double bonds. They can be low-molecular weight (monomeric) or high-molecular weight (oligomeric) compounds.

Examples of suitable low molecular weight monomers (monomeric compounds) having one double bond are alkyl or hydroxyalkyl acrylates or methacrylates, such as methyl-, ethyl-, butyl-, 2-ethylhexyl-,2-hydroxyethyl- or isobornyl-acrylate; and methyl or ethyl methacrylate. Further examples are resins modified with silicon or fluorine, e.g. silicone acrylates. Further examples of these monomers are acrylonitrile, acrylamide, methacrylamide, N-substituted (meth)acrylamides, styrene, alkylstyrenes and halogeno styrenes, vinyl esters such as vinyl acetate, vinyl ethers such as iso-butyl vinyl ether, N-vinylpyrrolidone, vinyl chloride or vinylidene chloride.

Examples of monomers having more than one double bond are the ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, hexamethylene glycol diacrylate, bisphenol A diacrylate, 4,4'-bis-(2-acryloyloxyethoxy)-diphenylpropane, trimethylolpropane triacrylate, pentaerythritol triacrylate or tetraacrylate, vinyl acrylate, divinyl benzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate or tris-(2-acryloylethyl) isocyanurate.

Examples of high-molecular weight (oligomeric) polyunsaturated compounds are acrylated epoxy resins, acrylated or vinyl-ether- or epoxy-group-containing polyesters, acrylated polyurethanes or acrylated polyethers. Further examples of unsaturated oligomers are unsaturated polyester resins which are usually prepared from maleic acid, phthalic acid and one or more diols and which have molecular weights of from approximately 500 Da to 3,000 Da. Such unsaturated oligomers can also be referred to as prepolymers.

Examples of compounds (a) which are particularly suitable for the implementation of the present invention, are esters of ethylenically unsaturated carboxylic acids and polyols or polyepoxides, and polymers containing ethylenically unsaturated groups in the chain or in side groups, e.g. unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, alkyl resins, polybutadiene and butadiene copolymers, polyisoprene and isoprene copolymers, polymers and copolymers having (meth)acrylic groups in side chains, as well as mixtures thereof.

Illustrative examples of unsaturated carboxylic acids or anhydrides, useful for the preparation of the above esters, are acrylic acid, methacrylic acid, maleic anhydride, crotonic acid, itaconic acid, cinnamic acid and unsaturated fatty acids such as linolenic acid and oleic acid. Acrylic and methacrylic acid are preferred.

Examples of polyols, which can also be esterified, are aromatic and aliphatic and cycloaliphatic polyols, preferably aliphatic and cycloaliphatic polyols.

Aromatic polyols are, for example, hydroquinone, 4,4'-dihydroxydiphenyl, 2,2-di(4-hydroxyphenyl) propane, as well as novolaks and resoles. Polyepoxides, which can be esterified, include those based on the said polyols, especially the reaction products between aromatic polyols and epichlorohydrin. Also suitable as polyols are polymers and copolymers that contain hydroxyl groups in the polymer chain or in side groups, for example polyvinyl alcohol and copolymers thereof or polymethacrylic acid hydroxyalkyl esters or copolymers thereof. Further suitable polyols are oligoesters carrying hydroxyl terminal groups.

Examples of aliphatic and cycloaliphatic polyols include alkylenediols containing preferably from 2 to 12 carbon atoms, such as ethylene glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-butanediol, pentanediol, hexanediol, octanediol, dodecanediol, diethylene glycol, triethylene glycol, polyethylene glycols having molecular weights of preferably from 200 Da to 1,500 Da, 1,3-cyclopentanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, 1,4-dihydroxymethyl cyclohexane, glycerol, tris(β-hydroxy-ethyl)amine, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol.

Further suitable ethylenically unsaturated compounds (a) are unsaturated polyamides obtained from unsaturated carboxylic acids and aromatic, aliphatic and cycloaliphatic polyamines having preferably from 2 to 6, preferably from 2 to 4, amino groups. Examples of such polyamines are: ethylenediamine, 1,2- or 1,3-propylenediamine, 1,2-, 1,3- or 1,4-butylenediamine, 1,5-pentylenediamine, 1,6-hexylenediamine, octylenediamine, dodecylene diamine, 1,4-diaminocyclohexane, isophoronediamine, phenylene diamine, bisphenylenediamine, di-(β-aminoethyl) ether, diethylene triamine, triethylenetetramine and di(β-aminoethoxy)- and di(β-aminopropoxy)ethane. Other suitable polyamines are polymers and copolymers which may contain additional amino groups in the side chain and oligoamides containing amino end groups.

Specific examples of such unsaturated polyamides are methylenebisacrylamide, 1,6-hexamethylene bisacrylamide, diethylenetriamine trismethacrylamide, bis(methacrylamidopropoxy) ethane and N-[(β-hydroxyethoxy)ethyl]-acrylamide.

Unsaturated polyurethanes are also suitable for the implementation of the present invention as components (a), for example those derived from saturated or unsaturated diisocyanates and unsaturated or saturated diols. Polybutadiene and polyisoprene and copolymers thereof may also be used. Suitable monomers include, for example, olefins, such as ethylene, propene, butene and hexene, (meth)acrylates, acrylonitrile, styrene and vinyl chloride. Polymers having unsaturated (meth)acrylate groups in the side chain can also be used as component (a). They may typically be reaction products of epoxy resins based on novolac with (meth)acrylic acid; homo- or copolymers of vinyl alcohol or hydroxyalkyl derivatives thereof that have been esterified with (meth)acrylic acid; and homo- and co-polymers of (meth)acrylates that have been esterified with hydroxyalkyl (meth)acrylates.

According to a preferred embodiment, the photocurable composition further comprises a coinitiators (c), also referred to as accelerators.

Suitable examples of accelerators/coinitiators (c) are alcohols, thiols, thioethers, amines or ethers that have an available hydrogen, bonded to a carbon adjacent to the heteroatom, disulfides and phosphines, e.g. as described in EP 438 123 and GB 2 180 358.

Suitable examples of amine accelerators/co-initiators include, but are not limited to, aliphatic, cycloaliphatic, aromatic, aryl-aliphatic, heterocyclic, oligomeric or polymeric amines. They can be primary, secondary or tertiary amines, for example butyl amine, dibutyl amine, tributyl amine, cyclohexyl amine, benzyldimethyl amine, di-cyclohexyl amine, N-phenyl glycine, triethyl amine, phenyl-diethanol amine, triethanolamine, piperidine, piperazine, morpholine, pyridine, quinoline, esters of dimethylamino benzoic acid, Michler’s ketone (4,4'-bis-dimethyl aminobenzophenone) and derivatives thereof.

As the amine accelerators/co-initiators, an amine-modified acrylate compound can be used; examples of such amine-modified acrylate include acrylates modified by reaction with a primary or secondary amine that are described in US 3,844,916, EP 280222, US 5,482,649 or US 5,734,002.

Multifunctional amine and polymeric amine derivatives are also suitable as co-initiators some examples are those presently marketed as Omnipol® ASA from IGM Resins B.V., Genopol® AB-2 from Rahn A.G., Speedcure® 7040 from Lambson Limited or those described in US2013/0012611.

The photocurable compositions of the present invention can also comprise one or more of the following components: (d) photosensitizers and/or (e) further photoinitiators and/or (f) conventional additives, in addition to compounds (a), (b) and, when present, (c).

The photocurable compositions of the present invention can also be formulated in compositions further comprising water and/or solvents, such as organic solvents.

Photosensitizers (d) can be present in an amount comprised between 0.01 and 15% by weight, based on the total content of the composition, preferably between 0.01 and 10% by weight.

Examples of photosensitizers are those commonly used in the art, aromatic carbonyl compounds, e.g. benzophenones, thioxanthones, anthraquinones, coumarins and 3-acylcoumarin derivatives, terphenyls, styryl ketones, and 3-(aroylmethylene)-thiazolines, camphorquinones and also eosin, rhodamine and erythrosine dyes.

Examples of thioxanthones are thioxanthone, 2-isopropyl thioxanthone, 2-chloro thioxanthone, 2-dodecyl thioxanthone, 2,4-diethyl thioxanthone, 2,4-dimethyl thioxanthone, 1-methoxycarbonyl thioxanthone, 2-ethoxycarbonyl thioxanthone, 3-(2-methoxyethoxycarbonyl) thioxanthone, 4-butoxycarbonyl thioxanthone, 3-butoxycarbonyl-7-methyl thioxanthone, 1-cyano-3-chloro thioxanthone, 1-ethoxycarbonyl-3-chloro thioxanthone, 1-ethoxycarbonyl-3-ethoxy thioxanthone, 1-ethoxycarbonyl-3-amino thioxanthone, 1-ethoxycarbonyl-3-phenylsulfuryl thioxanthone, 3,4-di[2-(2-methoxyethoxy)ethoxycarbonyl] thioxanthone, 1-ethoxycarbonyl-3-(1-methyl-1-morpholinoethyl) thioxanthone, 2-methyl-6-dimethoxymethyl thioxanthone, 2-methyl-6-(1,1-dimethoxybenzyl) thioxanthone, 2-morpholinomethyl thioxanthone, 2-methyl-6-morpholinomethyl thioxanthone, N-allylthioxanthone-3,4-dicarboximide, N-octylthioxanthone-3,4-dicarboximide, N-(1,1,3,3-tetramethylbutyl)-thioxanthone-3,4-dicarboximide, 1-phenoxy thioxanthone, 6-ethoxycarbonyl-1-2-methoxythioxanthone, 6-ethoxycarbonyl-2-methylthioxanthone, thioxanthone-2-polyethylene glycol ester, 2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthon-2-yloxy)-N,N,N-trimethyl-1-propanaminium chloride, or those described in the patent application PCT/EP2011/069514, such as n-dodecyl-7-methyl-thioxanthone-3-carboxylate and N,N-disobutyl-7-methyl-thioxanthone-3-carbamide. Also suitable are polymeric thioxanthone derivatives (e.g. those presently marketed as Omnipol® TX from IGM Resins B.V., Genopol® TX-1 from Rahn A.G., Speedcure® 7010 from Lambson Limited).

Example of benzophenones are benzophenone, 4-phenyl benzophenone, 4-methoxy benzophenone, 4,4'-dimethoxybenzophenone, 4,4'-dimethyl benzophenone, 4,4'-dichloro benzophenone, 4,4'-dimethylamino benzophenone, 4,4'-diethylamino benzophenone, 4-methyl benzophenone, 2,4,6-trimethyl benzophenone, 4-(4-methylthiophenyl) benzophenone, 3,3'-dimethyl-4-methoxy benzophenone, methyl 2-benzoyl benzoate, 4-(2-hydroxyethylthio) benzophenone, 4-(4-tolylthio) benzophenone, 4-benzoyl-N,N,N-trimethylbenzene methanaminium chloride, 2-hydroxy-3-(4-benzoylphenoxy)-N,N,N-trimethyl-1-propanaminium chloride monohydrate, 4-(13-acryloyl-1,4,7,10,13-pentaoxatridecyl) benzophenone, 4-benzoyl-N,N-dimethyl-N-[2-(1-oxo-2-propenyl)oxylethyl-benzene methanaminium chloride, or those described in US9938231 (e.g. Omnirad® 991 from IGM Resins B.V.).

Also suitable are polymeric benzophenone derivatives (e.g. those presently marketed as Omnipol® BP, Omnipol® 2702 and Omnipol® 682 all from IGM Resins B.V., Genopol® BP-2 from Rahn A.G. and Speedcure® 7005 from Lambson Limited).

Examples of 3-acylcoumarin derivatives are 3-benzoyl coumarin, 3-benzoyl-7-methoxy coumarin, 3-benzoyl-5,7-di(propoxy) coumarin, 3-benzoyl-6,8-dichloro coumarin, 3-benzoyl-6-chloro coumarin, 3,3'-carbonyl-bis[5,7-di(propoxy) coumarin], 3,3'-carbonyl-bis(7-methoxy coumarin), 3,3'-carbonyl-bis(7-diethylamino coumarin), 3-isobutyroyl coumarin, 3-benzoyl-5,7-dimethoxy coumarin, 3-benzoyl-5,7-diethoxy coumarin, 3-benzoyl-5,7-dibutoxy coumarin, 3-benzoyl-5,7-di(methoxyethoxy) coumarin, 3-benzoyl-5,7-di(allyloxy) coumarin, 3-benzoyl-7-dimethylamino coumarin, 3-benzoyl-7-diethylamino coumarin, 3-isobutyroyl-1,7-dimethylamino coumarin, 5,7-dimethoxy-3-(1-benzoyl) coumarin, 5,7-dimethoxy-3(1-benzoyl)-coumarin, 3-benzoylbenzo [f]coumarin, 7-diethylamino-3-thienoyl coumarin, 3-(4-cyanobenzoyl)-5,7-dimethoxy coumarin, or those described in EP2909243 and WO2017216699.

Examples of 3-(aroylmethylene) thiazolines are 3-methy-1,2-benzoylmethylene-β-benzo thiazoline, 3-methyl-2-benzoylmethylene-benzo thiazoline, 3-ethyl-2-propionylmethylene–β–benzo thiazoline.

Examples of other aromatic carbonyl compounds are acetophenone, 3-methoxyacetophenone, 4-phenylacetophenone, benzil, such as that described in WO 2013/164394, 2-acetylnaphthalene, 2-naphthaldehyde, 9,10-anthraquinone, 9-fluorenone, dibenzosuberone, xanthone, 2,5-bis(4-diethylaminobenzylidene) cyclopentanone, α-(para-dimethylamino benzylidene), ketones, such as 2-(4-dimethylamino-benzylidene)-indan-1-one or 3-(4-dimethylaminophenyl)-1-indan-5-yl-propenone, 3-phenylthiophthalimide, N-methyl-3,5-di(ethylthio) phthalimide.

Particularly preferred are thioxanthones, coumarins and 3-acylcoumarins.

It was observed that the above components (d) increase the activity of photoinitiators (b) without shortening the shelf life of the compositions. Moreover, such compositions have the special advantage that an appropriate choice of the photosensitizer (d) allows the spectral sensitivity of photoinitioator (b) to be shifted to any desired wavelength region. The skilled in the art is able to select the suitable photosensitizer (d) to make the photoinitiator(s) (b) work at any desired wavelength region.

The further possible photoinitiators (e) can be present in an amount comprised between 0.5 and 15 % by weight, of the total content of the composition, preferably between 1 and 10% by weight of the composition.

Examples of other suitable photoinitiators (e) are camphorquinone, benzophenone, benzophenone derivatives, acetophenone, acetophenone derivatives, dialkoxyacetophenones, α-hydroxyketones, α-aminoketones, 4-aroyl-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, e.g. benzil dimethyl ketal, ketosulfones, e.g 1-[4-[(4-benzoyl-phenyl)-thio]-phenyl]-2-methyl-2-[(4-methyl-phenyl)-sulfonyl]-propan-1-one (Esacure® 1001, from IGM Resins B.V.), 3-ketocoumarins, for example as described in EP2909243 and WO2017216699, phenylglyoxylates and derivatives thereof, dimeric phenyl glyoxylates, peresters, e.g. benzophenonetetracarboxylic acid peresters, for example as described in EP 126 541, acylphosphine photoinitiators (which can be selected from mono-acylphosphine oxides, bis-acylphosphine oxides, tris-acylphosphine oxides and multifunctional mono- or bisacylphosphine oxides), halomethyltriazines, hexaaryl bisimidazole/coinitiator systems, e.g. ortho-chlorohexaphenylbisimidazole in combination with 2-mercaptobenzothiazole, ferrocenium compounds or titanocenes, for example dicyclopentadienyl-bis(2,6-difluoro-3-pyrrolo-phenyl)titanium, O-acyloxime ester photoinitiators.

Examples of α-hydroxyketones and α–aminoketones are 1-hydroxy cyclohexylphenyl ketone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one, 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]phenyl}-2-methyl-propane-1-one), 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl}-2-methyl-propan-1-one, 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropane-1-one), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one, and (2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl) phenyl]-1-butanone).

Examples of O-acyloxime ester photoinitiators are 1,2-octanedione,1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime), ethanone 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazole-3-yl] 1-(O-acetyloxime) or those described in GB 2339571.

Examples of acylphosphine photoinitiators include, but are not limited to, bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide, bis(2,4,6-trimethylbenzoyl)-(2,4-dipentyloxyphenyl), 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide, ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate, and phenyl(2,4,6-trimethylbenzoyl)phosphinic acid glycerol ethoxylated triester (Omnipol TP from IGM Resins B.V.).

Examples of the halomethyltriazines based photoinitiators are 2-[2-(4-methoxy-phenyl)-vinyl]-4,6-bis-trichloromethyl [1,3,5]triazine, 2-(4-methoxy-phenyl)-4,6-bis-trichloromethyl [1,3,5]triazine, 2-(3,4-

dimethoxyphenyl)-4,6-bis-trichloromethyl [1,3,5]triazine, 2-methyl-4,6-bis-trichloromethyl [1,3,5] triazine.

Cationic photoinitiators can be also used as the further photoinitiators (e), when the photocurable compositions according to the invention are used in hybrid systems (which in this connection mean mixtures of free- radically and cationically curing systems). Examples of suitable cationic photoinitiators are aromatic sulfonium, phosphonium or iodonium salts, as described e.g. in US4,950,581, or cyclopentadienylarene-iron(II) complex salts, e.g. (η^6-isopropylbenzene)(η^5-cyclopentadienyl) iron(II) hexafluorophosphate or photolatent acids based on oximes, as described, for example, in GB 2 348 644, US4,450,598, US4,136,055, WO 00/10972 and WO 00/26219.

The photocuring composition according to the invention may also comprise conventional additives, from 0 to 10% based on the total content of the composition. Additives (f) can be, for example, thermal initiators, binders, stabilizers, and mixture thereof.

The choice of additives is governed by the field of use in question and the properties desired for that field. The additives (f) described above are known in the art and are accordingly used in the amounts conventionally used in the art.

For instance, especially in the case of pigmented compositions, the composition may also comprise, as additional additive (f), a thermal initiator, a compound that forms free radicals when heated, e.g. an azo compounds, such as 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), a triazene, diazosulfide, pentazadiene or a peroxy compound, for example a hydroperoxide or peroxycarbonate, e.g. tert-butyl hydroperoxide, as described e.g. in EP 245 639.

Binders may also be added to the photocurable composition of the invention. The addition of binders is particularly advantageous when the photocurable compounds are liquid or viscous substances. The amount of binder may be, for example, from 5 to 60% by weight, preferably from 10 to 50% by weight, based on the total content of the composition, excluding possible water and solvents. The choice of binder is made in accordance with the field of use and the properties required therefor, such as developability in aqueous and organic solvent systems, adhesion to substrates and sensitivity to oxygen.

Suitable binders are, for example, polymers having a weight average molecular weight (Mw) of approximately from 5,000 Da to 2,000,000 Da, preferably from 10,000 Da to 1,000,000 Da. Illustrative examples are: homo- and copolymers of acrylates and methacrylates, e.g. copolymers of methyl methacrylate/ethyl acrylate/methacrylic acid, poly(methacrylic acid alkyl esters), poly(acrylic acid alkyl esters); cellulose esters and ethers, such as cellulose acetate, cellulose acetate butyrate, methylcellulose, ethylcellulose, polyvinylbutyral, polyvinylformal, cyclised rubber, polyethers such as polyethylene oxide, polypropylene oxide, polytetrahydrofuran, polystyrene, polycarbonates, polyurethanes, chlorinated polyolefins, e.g. polyvinyl chloride, co-polymers of vinyl chloride/vinylidene chloride, co-polymers of vinylidene chloride with acrylonitrile, methyl methacrylate and vinyl acetate, polyvinyl acetate, co-poly (ethylene/vinyl acetate), polymers such as polycaprolactam and poly(hexamethylene adipamide), polyesters such as poly(ethylene glycol terephthalate) and poly(hexamethylene glycol succinate).

Suitable stabilizers are, for example, thermal inhibitors, such as hydroquinone, hydroquinone derivatives, p-methoxyphenol, β-benzol or sterically hindered phenols, e.g. 2,6-di(tert-butyl)-p-cresol, which prevent premature polymerization. In order to increase dark storage stability it is possible to use, for example, copper compounds, such as copper naphthenate, stearate or octoate, phosphorus compounds, for example triphenylphosphine, tributylphosphine, triethyl phosphite, triphenyl phosphite or tribenzyl phosphite, quaternary ammonium compounds, e.g. tetramethylammonium chloride or trimethylbenzylammonium chloride, or hydroxylamine derivatives, e.g. N,N-diethylhydroxylamine. For the purpose of excluding atmospheric oxygen during polymerization it is possible to add paraffin or similar wax-like substances which, being insoluble in the polymer, migrate to the surface at the beginning of the polymerization and form a transparent surface layer which prevents air from entering.

It is also possible to add a light stabilizer, such as UV absorbers, e.g. hydroxyphenylbenzotriazole, hydroxyphenylbenzophenone, oxalic acid amide or hydroxyphenyl-s-triazine type. Such components can be used on their own or in the form of mixtures, with or without the use of sterically hindered amines (HALS).

The photocurable compositions according to the invention may also comprise, as further additives (f), photoreducible dyes, e.g. a xanthene, benzoxanthene, benzothioxanthene, thiazine, pyronin, porphyrin or acridine dye, and/or radiation cleavable trihalomethyl compounds. These compounds are described, for example, in EP445624.

Further customary additives (f) are, depending upon the intended use, optical brighteners, fillers, pigments, both white and colored pigments, colorants, antistatics, wetting agents or flow improvers. Additives conventionally used in the art, e.g. antistatics, flow improvers and adhesion enhancers, can also be used.

In addition to the above components, other components may be present in the composition of the invention.

It is also possible for chain-transfer reagents conventionally used in the art to be added to the compositions according to the invention. Examples are mercaptans, amines and benzothiazole.

The composition of the invention may also comprise colorants and/or colored pigments. Depending upon the intended use, both inorganic and organic pigments may be used. Such additives are well known to the person skilled in the art; some examples are carbon black, iron oxides, such as iron oxide yellow, iron oxide red, chromium yellow, chromium green, nickel titanium yellow, ultramarine blue, cobalt blue, bismuth vanadate, cadmium yellow and cadmium red. Examples of organic pigments are mono- or bis-azo pigments, and also metal complexes thereof, phthalocyanine pigments, polycyclic pigments, e.g. perylene, anthraquinone, thioindigo, quinacridone or triphenylmethane pigments, and also diketo-pyrrolo-pyrrole, isoindolinone, e.g. tetrachloroisoindolinone, isoindoline, dioxazine, benzimidazolone and quinophthalone pigments. The pigments may be used in the formulations on their own or in admixture.

Depending upon the intended use, the pigments can be added to the formulations in amounts conventionally used in the art, for example in an amount from 0.1 to 30% by weight or from 10 to 25% by weight, based on the total weight of the composition.

The composition may also comprise, for example, organic colorants of an extremely wide variety of classes. Examples are azo dyes, methine dyes, anthraquinone dyes and metal complex dyes. Usual concentrations are, for example, from 0.1 to 20% wt, especially from 1 to 5% wt, based on the total weight of the composition.

The photocurable compositions of the invention may comprise water.

The photocurable compositions of the invention are suitable for various purposes, for example as a printing ink, such as screen printing inks, flexographic printing inks, offset printing inks and inkjet printing inks, as clearcoats, as colored coats, for example for wood or metal, as powder coatings, as coating materials inter alia for paper, wood, metal or plastics, as daylight-curable paints for marking structures and roads, for photographic reproduction processes, for holographic recording materials, for image-recording processes or in the production of printing plates that can be developed using organic solvents or using aqueous-alkaline media, for the production of masks for screen printing, as dental filling compounds, as adhesives, as pressure-sensitive adhesives, as laminating resins, as photoresists, e.g. galvanoresists, as etch resists or permanent resists, both liquid and dry films, as photostructurable dielectrics, and as solder masks for electronic circuits, as resists in the production of color filters for any type of display screen or in the creation of structures during the manufacture of plasma displays and electroluminescent displays, in the production of optical switches, optical gratings (interference gratings), in the manufacture of three-dimensional articles by bulk curing (UV curing in transparent moulds) or according to the stereolithography process, as described, for example, in US4,575,330, in the manufacture of composite materials (e.g. styrene polyesters which may include glass fibers and/or other fibers and other adjuvants) and other methods of printing in three dimensions well-known to one skilled in the art, in the coating or sealing of electronic components or as coatings for optical fibers.

The photocurable compositions of the invention are also suitable for the production of optical lenses, e.g. contact lenses or Fresnel lenses, in the manufacture of medical apparatus, aids or implants, in dry film paints.

The photocurable compositions of the invention are also suitable for the preparation of gels having thermotropic properties. Such gels are described for example in DE 19700064 and EP 678534.

An article comprising a compound of formula (I) or comprising a photocurable composition of the invention, represents a further subject-matter of the invention.

The compounds and compositions according to the invention may also be used as free-radical photoinitiators or photoinitiating systems for radiation-curable powder coatings.

The photocurable compositions according to the invention are suitable, for example, as coating materials for all kinds of substrate, for example wood, textiles, paper, ceramics, glass, plastics, such as polyesters, polyethylene terephthalate, polyolefins and cellulose acetate, especially in the form of films, and also metals, such as Al, Cu, Ni, Fe, Zn, Mg or Co and GaAs, Si or SiO_2, to which a protective layer is to be applied or an image is to be applied e.g. by imagewise exposure.

A large number of the most varied kinds of light source may be used in the process according to the invention, the light source emitting at wavelengths from approximately 200 nm to approximately 800 nm. Both point sources and planiform radiators (lamp carpets) are suitable. Examples are: carbon arc lamps, xenon arc lamps, medium pressure, high pressure and low pressure mercury arc radiators, doped, where appropriate, with metal halides (metal halide lamps), microwave-excited metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon incandescent lamps, flash lamps, photographic floodlight lamps, light-emitting diodes (LED), electron beams, X-rays and lasers.

According to one embodiment, said light source comprises UV light in at least one of the UVA, UVB and UVC ranges.

According to a preferred embodiment, said light source is a LED source, particularly preferred are LED light source emitting at wavelengths comprised between 365 nm and 420 nm, more preferably at 365 nm, 385 nm and 395 nm.

According to the invention the distance between the lamp and the substrate to be exposed may vary according to the intended use and the type and strength of the lamp, e.g. from 0.1 cm to 150 cm, preferably from 1 cm to 50 cm.

Said photopolymerizable composition may also be applied over a substrate already comprising a coated or printed layer. Said photopolymerizable composition may, after photopolymerization with said light source, be overprinted or overcoated with one or more compositions suitable for printing or coating.

The article obtained by applying said photopolymerizable composition to said substrate by said means of coating or printing, and photopolymerizing by said light source, with or without further elaboration of the article by further coating or printing, represents a further subject-matter of this invention.

As it could be seen in the Experimental Section which follows, n-octyl-BAPO in a solid form according to the invention is more reactive than the corresponding compound in a liquid form, which represents an unexpected outcome.

The invention is illustrated in detail below by the following examples, which are illustrative and not limiting.

EXPERIMENTAL SECTION

In case of inconsistencies between the chemical name and the chemical structures herein indicated, the chemical structures prevail.

^{1}H NMR and ^{31}P-NMR spectra were recorded with a Bruker Ascend 300 MHz NMR Spectrometer.

DSC diagrams were recorded with a Mettler-Toledo DSC1.

Heptane mixture was purchased from VWR International.

EXAMPLE 1

Synthesis of bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide (n-octyl-BAPO)

At 88-90°C, under nitrogen flow, to a stirred dispersion of bis(2,4,6-trimethylbenzoyl)-phosphine (262 g, 0.79 moles), n-octyl chloride (124 g, 0.82 moles) and tetrabutylammonium bromide (25 g, 0.08 moles) in water 541g an aqueous solution of potassium carbonate (60 g in 60 g of water) is added over 2 hours. The reaction is kept under stirring form 3 further hours at 88-90°C, then overnight at room temperature. The completeness of the reaction is checked by 31P-NMR. The reactor is heated at 65°C and the aqueous reaction mixture is extracted with a heptane mixture (514 g) by stirring for 15 minutes. The aqueous phase is discharged, the temperature is lowered to 55°C and an aqueous solution of hydrogen peroxide 33% (124 g, 1.20 moles) diluted in 550 g of water is added to the organic phase over 3 hours keeping the temperature between 55-60°C. The completeness of the reaction is checked by ^{31}P-NMR. Stirring is stopped and the phases are separated. The organic phase is washed at 55°C with water, then with a sodium bicarbonate 5% solution and again with water. The organic phase is filtered on a 10-20 micron paper filter and concentrated under reduced pressure and then cooled at 3°C and kept at this temperature for 6 hours. The title compound precipitates and is filtered on Buchner and washed with cold heptane mixture to give a white/light yellow solid (242 g, 0.53 moles, 67% yield).

^{31}P-NMR (Toluene-d_8, δ ppm): 27.6.

^{1}H-NMR ($CDCl_3$, δ ppm):0.85-0.95 (3H), 1.20-1.70 (12H), 2.20-2.10 (2H), 2.30(18H), 6.87 (4H).

EXAMPLE 2

The activity of n-octyl-BAPO in a solid form of the invention HPLC (area%) 99.36 was evaluated with respect to n-octyl-BAPO of the prior art in a viscous liquid form HPLC (area%) 95.69.

Test Example

Tack-free in clear formulation

The photopolymerizable compositions for the test were prepared by dissolving the PIs at the concentration of 4% by weight in a solution of Photomer 3016 (Bisphenol A epoxy diacrylate) 50%, Photomer 4335 (PETIA) 15%, Photomer 4600 (DPHA) 15%, Photomer 4172 (PPTTA) 20%.

The PIs were tested with:

- UV-Hg bulb lamp at 120 m/min and
- a UV LED lamp 365 nm 16 W/cm^2 power.

The photopolymerizable composition is spread with a thickness of 12 g/m^2 on a BYK coated cardboard.

The results are expressed in meters per minutes as the maximum speed at which the tack-free is reached in the table below. The higher the value obtained the better the reactivity of the PIs.

Results

Compound	UV Hg 120 W/cm Tack-free m/min
n-octyl-BAPO solid	50
n-octyl-BAPO liquid	45

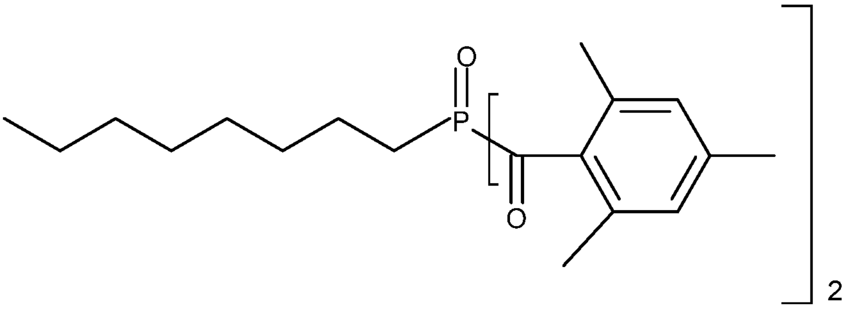
Compound	UV LED365 nm 16 W/cm^2 Tack-free m/min
n-octyl-BAPO solid	40
n-octyl-BAPO liquid	32

The above tack-free test shows that the solid n-octyl-BAPO is incredibly more reactive than the liquid n-octyl-BAPO.

Even taking into account the difference in purity, which is less than 4%, the reactivity surprisingly is increased, as it is more than 10% higher under Hg lamp and 25% higher under LED lamp.

Claims

1. A compound which is bis(2,4,6-trimethylbenzoyl)-n-octyl-phosphine oxide of formula (I)



(I)

characterized in that is it in a solid form.

2. The compound of formula (I) according to claim 1 which has a melting point higher than 38°C.
3. The compound of formula (I) according to claim 1 or 2, which shows a Differential Scanning Calorimetry onset from 38 to 50°C, more preferably from 38 to 48°C, for instance from 39 to 45°C.
4. The compound of formula (I) according to any of claims 1 to 3, which shows a Differential Scanning Calorimetry peak from 40 to 50°C, more preferably from 41 to 48°C, for example at about 41°C, about 42°C, about 43°C, about 44°C, about 45°C, about 46°C, about 47°C or about 48°C, wherein about" means that the mentioned values may vary of 1-1.2%
5. Use of compound of formula (I) according to any of claims 1 to 4, as a photoinitiator.
6. A photopolymerizable composition comprising:
   a) from 50 to 99.7%, preferably from 70 to 98.9% by weight, based on the total content of the composition, of at least one ethylenically unsaturated compound;
   b) from 0.1 to 35%, preferably from 0.1 to 20%, and more preferably from 0.2 to 15% by weight, based on the total content of the composition, of compound of formula (I) according to any of claims 1 to 5; and

c) from 0 to 20% by weight, preferably from 0 to 15%, and more preferably from 0.2 to 15% by weight, based on the total content of the composition, of an accelerator and/or of a coinitiator.

7. The photocurable composition according to claim 6, further comprising one or more of the following components:

d) from 0.01 to 15% by weight based on the total content of the composition, of one or more photosensitizer; and/or

e) from 0.5 to 15% by weight based on the total content of the composition, one or more further photoinitiators.

8. The photocurable composition according to claim 6 or 7, characterized in that said accelerator and/or coinitiator is an amine, preferably a tertiary amine.

9. A process for photocuring photopolymerizable compositions, coatings, adhesives and inks, which process comprises:

(i) providing a photopolymerizable composition according to any one of claims 6 to 8;

(ii) coating or printing said photopolymerizable composition onto a substrate; and

(iii) photopolymerizing said coated or printed composition on said substrate with a light source.

10. A process for three-dimensional printing which comprises providing a photopolymerizable composition according to any one of claims 6 to 8 and photocuring said composition with a light source.

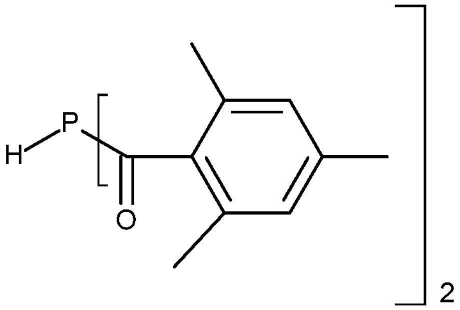
11. The process according to claims 9 or 10, characterized in that said light source comprises UV light in at least one of the UVA, UVB and UVC wavelength range.

12. The process according to any one of claims 9 to 11, characterized in that said light source is a LED source emitting in the range from 350 to 420 nm.

13. An article of manufacture obtained according to the process of any one of claims 9 to 12 or by three-dimensional printing of a composition of any one of claims 6 to 8.

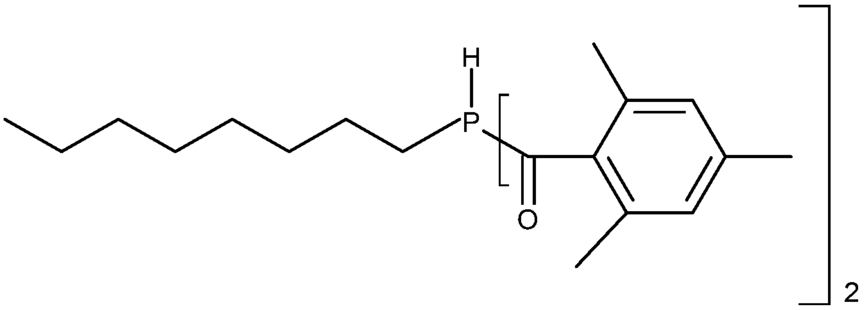
14. A process for the manufacture of compound of formula (I) according to any of claims 1 to 5, which comprises the following steps:

    1. reacting compound of formula (II)



(II)

with a n-octyl-Hal, wherein Hal represents a halogen atom, preferably bromine or chlorine, in a suitable solvent, thus obtaining compound of formula (III)



(III)

    2. oxidating compound of formula (III) in a suitable solvent, thus providing compound of formula (I) in a solid form.

15. Use of compound of formula (II) as defined in claim 14 for the preparation of compound of formula (I), preferably for the preparation of compound of formula (I) in a solid form according to any of claims 1 to 4.

Figure 1

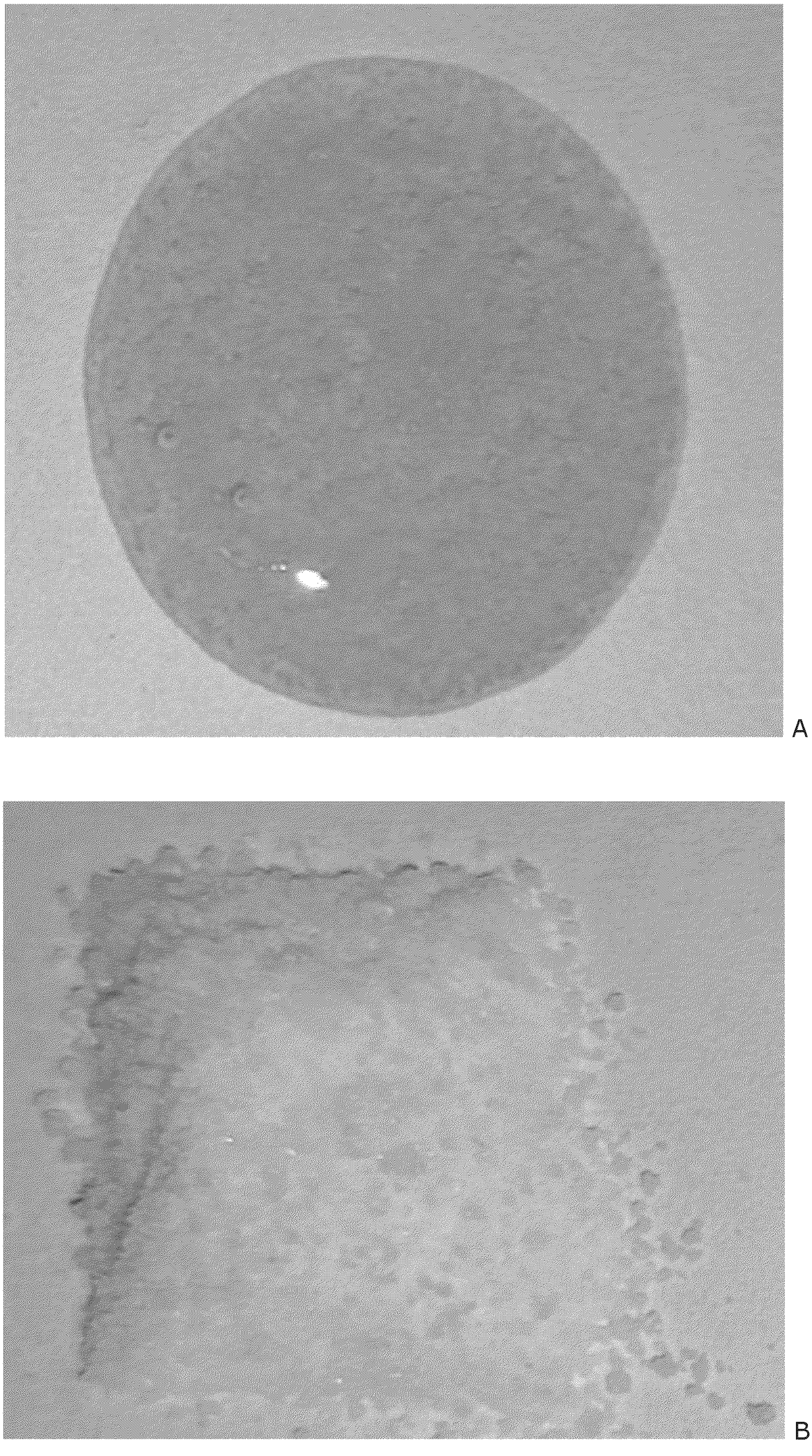
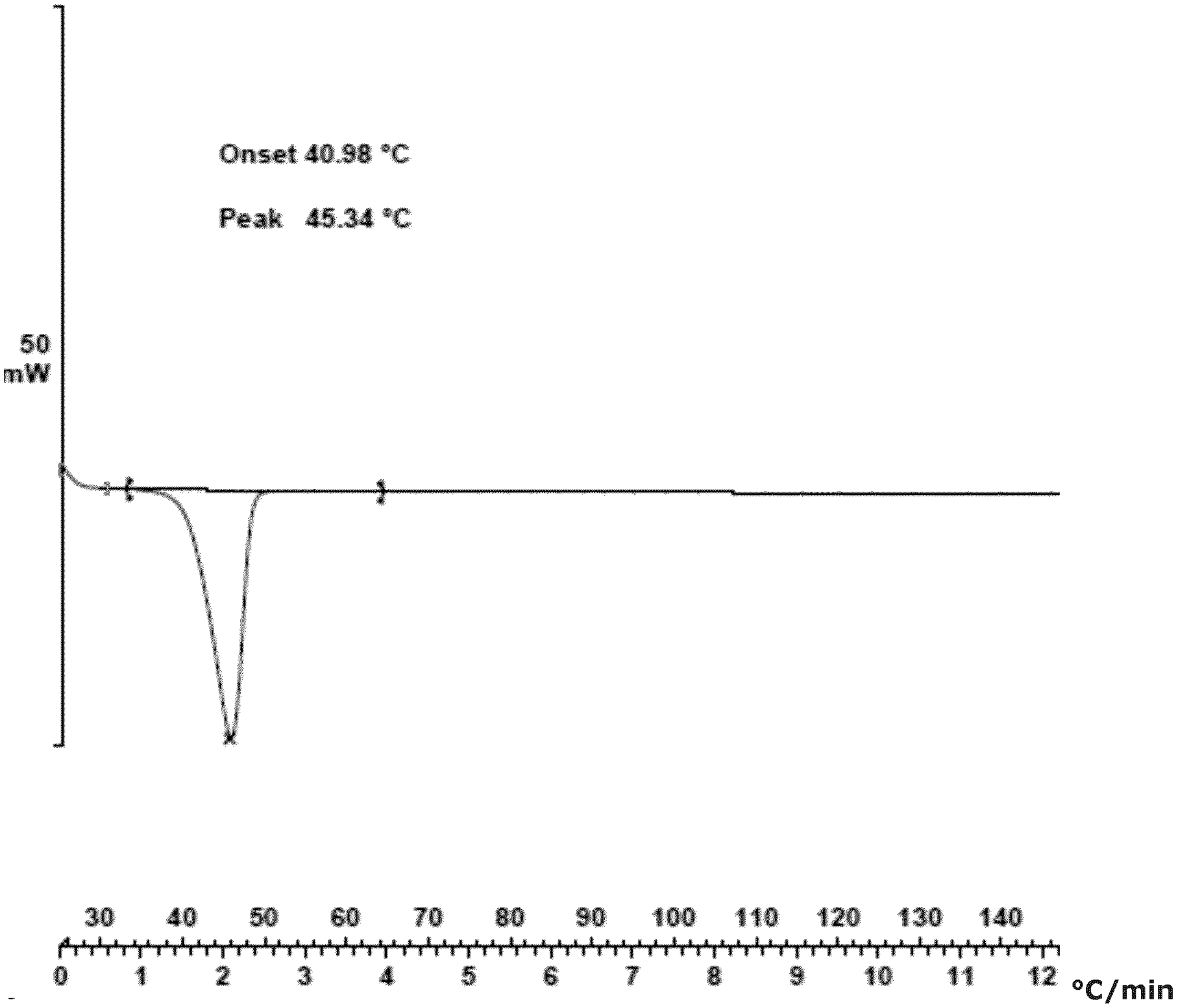


Figure 2



DSC diagram