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(72) KIPKE, Cary A., US
(72) OXMAN, Joe D., US
(71) MINNESOTA MINING AND MANUFACTURING COMPANY, US

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(54) **REACTIONS DE PHOTOPOLYMERISATION INDUITES PAR CHEMILUMINESCENCE**

(54) **PHOTOPOLYMERIZATION REACTIONS INDUCED BY CHEMILUMINESCENCE**

(57) L'invention se rapporte à la photopolymérisation d'une matière photopolymérisable effectuée au moyen d'une réaction chémiluminesc ente. L'invention se rapporte également aux produits fabriqués selon ce procédé.

(57) Photopolymerization of a photopolymerizable material is carried out using a chemiluminescent reaction. Products made by this process are also described.

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(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: KIPKE, Cary, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). OXMAN, Joel, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: BJORKMAN, Dale, A. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

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(57) Abstract

Photopolymerization of a photopolymerizable material is carried out using a chemiluminescent reaction. Products made by this process are also described.

PHOTOPOLYMERIZATION REACTIONS INDUCED BY CHEMILUMINESCENCE

Field of the Invention

This invention relates to photopolymerization reactions. More specifically, this invention relates to photopolymerization reactions that are initiated by electromagnetic radiation emitted from a chemiluminescent reaction.

Background

Applications of chemiluminescence as a light source are known in the art. Examples include optical display devices (US 5,222,797), as a light source for endoscopic examination (US 5,179,938), as a lighting device for emergencies or in the absence of electricity (US 5,043,851), and in fishing lures (US 5,190,366).

U.S. Patent No. 3,698,391 to Ulman describes a method for chemically initiating photochemical reactions in the absence of an external light source. Chemiluminescent reactions and electrochemiluminescent reactions are described for carrying out various reactions including cycloadditions, isomerizations, and rearrangements. Yields are described in the single digits, and no disclosure is provided related to the preparation of polymers.

Summary of the Invention

The present invention relates to a method for carrying out a polymerization reaction. In this method, a photopolymerizable material is exposed to electromagnetic radiation emitted by a chemiluminescent reaction, thereby photopolymerizing the photopolymerizable material.

Detailed Description

For purposes of the present invention, chemiluminescence is the emission of electromagnetic radiation of wavelength between about 250-1400 nanometers by means of a chemical reaction. Chemiluminescence is defined as the emission of light, from at least one molecule, by means of a chemical reaction. A chemiluminescent reaction results in the formation of an excited state molecule that is capable of direct light emission or capable of energy transfer to at least one other molecule that emits light or generates a photoinitiator. Preferred wavelength ranges for light emission are in the UV range (250-400 nm), the visible range (400-800), the near IR range (700-1400).

Chemiluminescent light sources have significant advantages over traditional electric light sources that are used for photoinitiated reactions. For example, chemiluminescent sources may have low cost, are portable, and are safe to use in specific environments such as under water or in places where flammable materials make other light sources dangerous. Additionally, chemiluminescent light sources may be provided in a flexible specified shape or configuration that provides light in environments that are difficult to access using traditional light sources. When provided as a liquid, gel, or paste, the chemiluminescent material will conform to any geometry.

The polymerization reaction of the present invention is carried out by first providing a photopolymerizable composition, so that upon exposure of the composition to an appropriate electromagnetic radiation source, the chemical species of the composition will undergo a polymerization reaction to form a high (e.g. greater than about 10,000 molecular weight) molecular weight compound. Preferably, the resulting polymer is crosslinked or crosslinkable.

Under the present invention, the electromagnetic radiation source is provided by a chemiluminescent reaction. Typical chemiluminescence systems involve the reaction of two reactive species, such as the reaction of hydrogen peroxide with oxalate compounds. These reactive species are generally provided as two separate reaction components that are mixed together at the time of use. The reaction components may optionally be added directly to the polymerizable

composition, but more preferably is provided as a distinct article or solution that is physically separate from the polymerizable composition.

The components used to provide chemiluminescent light may be comprised of those chemicals known in the art to create light chemically upon mixing. Preferred systems are the two-component chemistries comprising an oxalate component, a peroxide component together with a fluorescer and a catalyst. Examples of such systems include those disclosed in US Patent No. 5,281,347 and 3,689,391, the disclosures of which are incorporated by reference. These systems may include additional fluorescent species, catalysts, solvents, accelerators and additive systems.

Chemiluminescent light can be "tuned" to provide light at distinct wavelength regions via an excited state energy transfer reaction to specific acceptor molecules. A donor molecule is defined as an excited state molecule that is formed from a chemiluminescence reaction. This molecule may directly emit light or transfer energy to an acceptor molecule. Acceptor molecules may be molecules that accept energy from a donor molecule and then emit light or generate photoinitiators. Examples of acceptor molecules that emit light throughout the visible region are described in, e.g. US 3,597,362 and US 3,749,677, and examples of acceptor molecules that emit light throughout the near infrared region are described in , e.g.US 3,630,941 and US 3,590,003, the disclosures of which are incorporated herein by reference. Light emission from a chemiluminescent reaction may provide advantages, in comparison to solid state light sources, for photopolymerization reactions. Light emission from a chemiluminescent reaction can be controlled through use of an acceptor molecule or a mixture of acceptor molecules to provide light that overlaps with the absorption region of a photoreactive molecule that is capable of initiating photopolymerization. Although solid-state light sources such as lasers, laser diodes, and light-emitting diodes provide light in the UV, visible, and near infrared energy regions, there are regions within this wavelength range (250-1400 nm) that cannot readily or currently be accessed using these solid-state light sources.

Other light sources (e.g. tungsten, mercury vapor, xenon lamps, etc.) provide a broad light emission in the UV, visible, and near infrared regions, but may be inefficient for photopolymerization reactions because only a small wavelength region of the emitted light is utilized by the light absorbing photoinitiator. With such light sources, filters may be used to select the desired wavelength while eliminating the ineffective wavelength of light. Chemiluminescent light sources, on the other hand, may be selected that have single, multiple, broad, or narrow light emission spectra, so that more of the emitted light is utilized in the photopolymerization process. A narrow emission spectrum is a region of light that is comparable to the absorption spectrum region of the photoinitiator molecule. Typical photoinitiator molecules have an absorption spectrum range of about 100 nm. Suitable acceptor molecules that emit light in a chemiluminescent reaction have an emission spectrum range of about 100 nm. Preferably, the chemiluminescent emission spectrum is substantially, equal to or encompassed by the photoinitiator absorbance spectrum. Thus, preferably most of the radiation emitted by the chemiluminescent reaction is absorbed by the photoinitiator molecule.

The use of at least two different molecules in a chemiluminescent system (that emits light in two distinct spectral regions) provides the opportunity to utilize at least two different photoinitiator molecules that absorb light in the desired spectral regions. This system may be advantageous to provide "staged" curing during the photopolymerization process. Compositions of this nature can utilize one or more curing mechanisms each of which could be initiated via a distinct photoinitiator. Each material could be initiated at distinct wavelength of light affording materials that could be polymerized independently for obtaining unique material properties. For example, adhesives that could be applied as liquid, photopolymerized to tacky stage, and further photopolymerized with a second wavelength of light to a structured cross-linked state.

In the fluid state, chemiluminescence provides a unique light source for many photopolymerization applications. While the use of chemiluminescent light sources for photopolymerization is contemplated in all environments, the present

invention finds particular advantage for uses in which electrically generated light is undesirable or unsafe. Such as aqueous environments, the oral cavity, areas of potential explosion, and for applications that are physically restricting for the relatively bulky lamps. Because the chemiluminescent material may be provided as a liquid, the light source may be placed in locations that electric light sources cannot readily reach, such as in cracks, fissures, in enclosed areas, or underwater.

Some photopolymerization applications may require a chemiluminescent reaction in a different physical form, such as described in U.S. Patent number 3,590,003. For example, the chemiluminescent source may be provided as a stick or in tubular form; as described in US Patent Nos. 4,508,642; 5,043,851; and 5,190,366; in pouches as described in US 3,539,794; in a parallel or helically woven pattern as described in US 5,222,797; in a thin sheet as describe in US 5,226,710, US 4,814,949; or in a spray as described in US 3,697,434. The disclosures of the above cited patents describing delivery systems are incorporated herein by reference.

An alternative method of delivering chemiluminescent materials to a desired surface is by use of a dispensing instrument containing one or all components of the chemiluminescent reaction. For example, one or more components may be delivered throughout a marker, pen, paint brush, spray or crayon. One component may be separated from the other component by microencapsulation. Crayons may particularly be an appropriate delivery vehicle for microencapsulated components, because the microcapsule will rupture on marking of the substrate with the crayon. Such crayons may be manufactured generally as described in US Patent No. 5,039,243 (the disclosure of which is incorporated herein by reference) by substituting the fragrance described therein with components of the chemiluminescent reaction. When using a dispensing apparatus to deliver a component of the chemiluminescent reaction, the second component may optionally be pre-placed on the substrate, or may be delivered by a second dispensing apparatus or sprayed onto the substrate in an alternative delivery mode as will be apparent to the artisan.

Another alternative delivery system is by providing the components in a dual barrel cartridge with a mixing element or alternative shapes that contain the separated chemistry that can be activated with a mixing element.

The chemiluminescent effect may be optionally enhanced by use of one or more mechanical apparatuses, such as a reflective coating on hardware for directional light (e.g. US 5,121,302, incorporated herein by reference), or by focusing of the chemiluminescent light using lenses (microstructured plastic or glass).

A particularly preferred delivery system for chemiluminescent materials is to provide the components in the form of a liquid, gel or paste. This material is mixed together (for example, on site) to initiate the chemiluminescent reaction, and the system is placed adjacent the photopolymerizable material, thereby exposing the photopolymerizable system to polymerization radiation. It will be understood that "adjacent" for purposes of the present invention means in direct physical contact or physically spaced from the photopolymerizable material at a location close enough for effective transmission of radiation to the material.

For curing dental impression materials, a chemiluminescent reaction may be carried out in a tray designed for holding such materials, as described in co-pending U.S. patent application entitled "Dental Impression Tray with Chemiluminescent Light Source" attorney docket number 52326USA2A filed on even date herewith.

In one aspect of the present invention, the chemiluminescent material is selected such that the photopolymerizable material is insoluble in the chemiluminescent solution/gel/paste, and the chemiluminescent material is applied directly to the photopolymerizable material without substantial mixing between the chemiluminescent material and the photopolymerizable material.

In another aspect of the present invention, the reactants for the chemiluminescent reaction are mixed together on site to initiate the chemiluminescent reaction, and the system is applied adjacent to a radiation-transmissive barrier layer system, thereby exposing the photopolymerizable material to polymerization radiation.

In yet another aspect of the present invention, the chemiluminescent material is dispersed or dissolved directly in the photopolymerizable material. The photopolymerizable material is cured by the light or energy emitted by the intimately mixed chemiluminescent material. The nature of the resulting polymer is determined by the concentration and degree of agitation of the reaction solution. Thus, the polymer may polymerize to a solid form, with chemiluminescent reaction products entrained within the polymer. Optionally, the chemiluminescent reaction components may be provided with polymerizable functionalities so that the chemiluminescent reaction components, in addition to providing light, also participate directly in the polymerization reaction. It is also contemplated that the polymerization reaction may be carried out in a dilute solution, so that particles of polymerized material are formed. With agitation of the solution and the use of multiple phases of solutions (e.g. oil and water), spherical particles, hollow particles and particles having alternative geometries may be formed by following the principles of encapsulation technology, such as described for example in U.S. Pat. No. 3,516,941, the disclosure of which is incorporated herein by reference.

An alternative format for delivery of chemiluminescent light utilizes adhesive tape. In this embodiment, one or more components of the chemiluminescent reaction is microencapsulated, and the capsules are provided on the adhesive-side of a tape. The cohesive strength of the capsules is selected to be less than the adhesive strength of the adhesive, so that as the tape is unrolled, microcapsules are ruptured, thereby releasing the capsule fill and initiating the chemiluminescent reaction. This tape is adhered to a surface and the chemiluminescent light cures a photopolymerizable material.

Microcapsules used in any delivery system of the present invention may be made by processes known in the microencapsulation art. For example, microcapsules may be prepared by in situ processes such as aminoplast polymerization. The techniques disclosed, generally referred to as an in situ polymerization reaction, yield for example, an aminoplast photopolymerizable material capsule wall material. In the process, a hydrophobic oil phase is dispersed in an aqueous phase containing the aminoplast photopolymerizable material

precursors by applying high shear agitation. Addition of an acid catalyst initiates the polycondensation of the aminoplast precursors, resulting in the deposition of the aminoplast photopolymerizable material about the dispersed droplets of the oil phase, producing the microcapsules.

The hydrophobic inner phase for the capsule may be any in situ aminoplast encapsulatable composition as discussed in U.S. Pat. No. 3,516,941, provided that the inner phase meets the criteria for acting as a solvent to the binder.

When the microcapsule is prepared by interfacial polycondensation, the capsule skin may be composed of any condensation polymer or addition polymer, e.g., polyamide, polyurethane, polysulfonamide, polyurea, polyester, polycarbonate, etc. Polyamides prepared by interfacial polycondensation of an amine with an acid chloride or polymers formed by reaction of isocyanate prepolymer with polyamines are preferred. Microcapsules formed by coacervation processes are also useful in forming microcapsule shells that may be used in the present invention. Coacervation is the well known process of forming higher molecular weight gelatin polymers as taught in U.S. Pat. Nos. 5,800,458 and 2,800,457.

The material to be polymerized may be any suitable photopolymerization material, such as free-radically reactive materials, cationic polymerization materials, charge transfer polymerization reactive materials, hydrosilation reactive materials or photocyloaddition reactive polymerization materials. Typically, many of these materials incorporate a separate chemical initiator that is activated by the light emitted from the chemiluminescent light source.

The polymerizable material may be selected from one or more photopolymerizable materials, including photopolymerizable materials that cure through different cure mechanisms. Such mixtures of photopolymerizable materials are sometimes referred to as hybrid curing photopolymerizable materials. The photopolymerizable material may additionally utilize multiple cure mechanisms for the complete curing of the photopolymerizable material system. For example, heat may be utilized to cure a free radical curable component, while the chemiluminescent light source may be used for the cationic curable component of a

hybrid system. Additionally, multiple wavelengths of light may be utilized for curing different aspects of a multi-component photopolymerizable material system.

The nature of the ultimate polymerized material is of course dependent on the properties of the backbone polymer and grafted functionalities. Thus, polymers of all natures may be prepared using the present invention, from brittle polymers or hard polymers to elastomeric polymers. The present invention therefore contemplates the preparation of a wide variety of materials having very different uses, all of which have in common that they may be prepared by a photopolymerization process using a chemiluminescent reaction as the radiation source.

Representative examples of free radically polymerizable materials are those compounds that contain at least one ethylenically unsaturated double bond and can be monomers, oligomers, or prepolymers.

A wide variety of free-radically polymerizable monomers can be photopolymerized using chemiluminescent reaction as a light source. Suitable monomers contain at least one ethylenically-unsaturated double bond, can be oligomers, and are capable of undergoing addition polymerization. Preferred monomers include mono-, di- or poly- acrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-hexyl acrylate, stearyl acrylate, allyl acrylate, glycerol diacrylate, glycerol triacrylate, ethyleneglycol diacrylate, diethyleneglycol diacrylate, triethyleneglycol dimethacrylate, 1,3-propanediol diacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol trimethacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol hexacrylate, bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane, bis[1-(3-acryloxy-2-hydroxy)]-p-propoxyphenyl-dimethylemethane, trishydroxyethyl-isocyanurate trimethacrylate; the bis-acrylates and bis-methacrylates of polyethylene glycols of molecular weight 200-500, copolymerizable mixtures of acrylated monomers such as those of U.S. Patent No. 4,652,274, and acrylated oligomers such as those of U.S. Patent No. 4,642,126; unsaturated amides such as methylene bis-acrylamide, methylene bis-

methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamine tris-acrylamide and beta-methacrylaminoethyl methacrylate; and vinyl compounds such as styrene, diallyl phthalate, divinyl succinate, divinyl adipate and divinylphthalate. Mixtures of two or more monomers can be used if desired.

Other suitable free radically polymerizable compositions include the combination of ethylenically unsaturated compounds and polythiol compounds such as those disclosed in *Radiation Curing of Polymeric Materials*, Chapter 13, pp. 160-175, American Chemical Society, 1990, and references therein. Further examples are disclosed in U.S. Patent No. 4,808,638 and references therein.

A further class of free radically polymerizable materials include donor/acceptor charge complexes comprised of the combination of at least one unsaturated compound having an electron donor group and one compound having an electron withdrawing group such as those described in EPA 0 618 237 A1. Compositions disclosed therein can be photopolymerized in the absence or presence of conventional free radical initiators.

Numerous examples of free radical photoinitiators for the polymerization of unsaturated compound have been disclosed. Representative examples are described in the *Handbook of Organic Photochemistry*, Vol. II, pp. 330-335, CRC Press Inc., 1989, and references therein. Other examples are disclosed in US Patent Application Serial No. 08/365,494 filed December 28, 1994, the disclosure of which is hereby incorporated by reference.

Representative cationically polymerizable materials include epoxies, epoxy/polyols vinyl ethers and a variety of other compounds as disclosed in WO95/14716 and references therein. Other cationically polymerizable compositions are disclosed in the *Journal of Polymer Science*, Vol. A, pp. 977-999, and U.S. Patent No. 4,264,703.

Examples of organic materials polymerizable by cationic polymerization and suitable for the hardenable compositions according to the invention are of the following types, it being possible for these to be used by themselves or as mixtures of at least two components:

I. Ethylenically unsaturated compounds polymerizable by a cationic mechanism. These include:

1. Monoolefins and diolefins, for example isobutylene, butadiene, isoprene, styrene, α-methylstyrene, divinylbenzenes, N-vinylpyrrolidone, N-vinylcarbazole and acrolein.

2. Vinyl ethers, for example methyl vinyl ether, isobutyl vinyl ether, trimethylopropane trivinyl ether and ethylene glycol divinyl ether; and cyclic vinyl ethers, for example 3,4-dihydro-2-formyl-2H-pyran (acrolein dimer) and the 3,4-dihydro-2H-pyran-2-carboxylic acid ester of 2-hydroxymethyl-3,4-dihydro-2H-pyran.

3. Vinyl esters, for example vinyl acetate and vinyl stearate.

II. Heterocyclic compounds polymerizable by cationic polymerization, for example ethylene oxide, propylene oxide, epichlorohydrin, glycidyl ethers of monohydric alcohols or phenols, for example n-butyl glycidyl ether, n-octyl glycidyl ether, phenyl glycidyl ether and cresyl glycidyl ether; glycidyl acrylate, glycidyl methacrylate, styrene oxide and cyclohexene oxide; oxetanes such as 3,3-dimethyloxetane and 3,3-di(chloromethyl)oxetane; tetrahydrofuran; dioxolanes, trioxane and 1,3,6-trioxacyclooctane; lactones such as β-propiolactone, γ-valerolactone and ε-caprolactone; thiiranes such as ethylene sulfide and propylene sulfide; azetidines such as N-acylazetidines, for example N-benzoylazetidine, as well as the adducts of azetidine with diisocyanates, for example toluylene-2,4-diisocyanate and toluylene-2,6-diisocyanate and 4,4'-diaminodiphenylmethane diisocyanate; epoxy resins; and linear and branched polymers with glycidyl groups in the side-chains, for example homopolymers and copolymers of polyacrylate and polymethacrylate glycidyl esters.

Of particular importance among these above-mentioned polymerizable compounds are the epoxy resins and especially the diepoxides and polyepoxides and epoxy resin prepolymers of the type used to prepare crosslinked epoxy resins. The diepoxides and polyepoxides can be aliphatic, cycloaliphatic or aromatic

compounds. Examples of such compounds are the glycidyl ethers and β-methylglycidyl ethers of aliphatic or cycloaliphatic diols or polyols, for example those of ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, diethylene glycol, polyethylene glycol, polypropylene glycol, glycerol, trimethylopropane or 1,4-di-methylolcyclohexane or of 2,2-bis(4-hydroxycyclohexyl)propane and N,N-bis(2-hydroxyethyl)aniline; and the glycidyl ethers of diphenols and polyphenols, for example resorcinol, 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydiphenyl-2,2-propane, novolaks and 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane. Further examples are N-glycidyl compounds, for example the diglycidyl compounds of ethyleneurea, 1,3-propyleneurea, 5-dimethylhydantoin or 4,4'-methylene-5,5'-tetramethyldihydantoin, or those like triglycidyl isocyanurate.

Other glycidyl compounds of industrial importance are the glycidyl esters of carboxylic acids, especially dicarboxylic and polycarboxylic acids. Examples of these are the glycidyl esters of succinic acid, adipic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, tetrahydrophthalic and hexahydrophthalic acids, isophthalic acid or trimellitic acid, or of fatty acid dimers.

Examples of polyepoxides other than glycidyl compounds are the diepoxides of vinylcyclohexene and dicyclopentadiene, 3-(3', 4'-epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro[5,5]undecane, the 3',4'-epoxycyclohexylmethyl ester of 3,4-epoxycyclohexanecarboxylic acid, butadiene diepoxide or isoprene diepoxide, epoxidized linoleic acid derivatives or epoxidized polybutadiene.

Preferred epoxy resins are diglycidyl ethers (which may or may not have been lengthened beforehand) of dihydric phenols or dihydric aliphatic alcohols having 2 to 4 carbon atoms. Particular preference is given to the diglycidyl ethers (which may or may not have been lengthened beforehand) of 2,2-bis(4-hydroxyphenyl)-propane and bis(4-hydroxyphenyl)methane.

Numerous photoinitiators for cationic polymerization have been disclosed. Representative examples include onium salts and mixed ligand arene cyclopentadiene metal salts with complex metal halide ions, U.S. Patent No. 5,375,115. A variety of cationic photoinitiators are disclosed in the Handbook of

Organic Photochemistry, , Vol. II, pp. 335-337, CRC Press Inc., 1989 and references cited within. Additional cationic photoinitiators suitable for use with visible light are disclosed in U.S. Patent Application Serial No. 08/550,635, filed October 31, 1995 (the disclosure of which is incorporated herein by reference) and PCT WO 95/14716.

Representative examples of a hydrosilation reaction involving the reaction of a compound containing aliphatic unsaturation with a compound containing silicon bonded hydrogen are disclosed in U.S. Patent No. 5,145,886 and references therein.

Methods of inducing photohydrosilation utilizing photoactivated platinum catalysts are disclosed in U.S. Patent Nos. 5,145,886; 4,530,879; 4,510,094; and 4,916,169 and references therein.

Combinations of the above polymerizable compositions and initiators may be utilized to provide new compositions of matter.

The present method for polymerizing a polymerizable material by using a chemiluminescent light source finds specific advantage in applications such as custom gasket materials, auto-body filler, ceramic repair material, dental restorative, adhesive and impression materials, casting materials, and other medical and dental applications wherein polymerization reaction is carried out in-situ. Additional uses of the inventive system include multipurpose adhesives, structural adhesives, protective coatings, sealants, finishes, caulk, grout, custom molded shapes, repair kits for cable sheath, wire sealing in wet environments, marine products (underwater repair e.g. putty and adhesives) and the like. It is contemplated that the present system may provide significant advantage in custom photopolymerization applications requiring irregular shapes and sizes.

The following non-limiting example illustrates the ability to rapidly photopolymerize a liquid monomer composition utilizing a chemiluminescent light source.

Example 1

A photopolymerizable composition was prepared as described below.

Ingredient	Parts by Weight
trimethylolpropane triacrylate (TMPTA)	3.00
pentaerythritol tetrakis(3-mercaptopropionate) (PETMA)	1.00
(η^6-xylyl)(η^5-cyclopentadienyl)iron hexafluoroantimonate($CpXylFeSbF_6$)	0.04
butyrolactone	0.10

The $CpXylFeSbF_6$ compound was transferred to a 10cc glass vial and dissolved with the addition of butyrolactone. TMPTA and PETMA were then added to the vial and mixed thoroughly until homogeneous. The sample was capped and wrapped in foil to exclude extraneous light. Approximately 1 gm of the solution was transferred to each of two 1.5 dram clear glass vials. This represented an approximately a 1cm thick sample. Both vials were covered with foil to exclude light. A commercially available light stick ("Snaplight") 12 hour lightstick from Coghlan's LTD) was wrapped in foil with the exception of a cylindrical segment fitted to the base of the 1.5 dram glass vial. The foil was removed from one of the glass vials with photopolymer, the lightstick activated and the vial immediately placed into the light emitting reservoir. The photopolymer sample was probed with a stick as a function of time. After approximately 30 seconds, the sample had polymerized to a hard, tack-free solid whereas the sample protected from light remained fluid for an extended period of time.

< generated by mixing together two different reactive components >

In the Claims:

1. A process for carrying out a polymerization reaction initiated by electromagnetic radiation, comprising the step of exposing a photopolymerizable material to electromagnetic radiation that has been emitted by a chemiluminescent reaction <->, thereby polymerizing said photopolymerizable material.

2. The process of claim 1, wherein the photopolymerizable material comprises a free-radically photopolymerizable material.

3. The process of claim 1, wherein the photopolymerizable material comprises a cationically cured material.

4. The process of claim 1, wherein the photopolymerizable material comprises a material that is cured by a hydrosilation reaction.

5. The process according to claim 1, wherein the photopolymerizable material is selected from a mixture of at least two materials that cure through different cure mechanisms.

6. The process of claim 1, wherein the photopolymerizable material is a dental impression material.

7. The process of claim 1, wherein the photopolymerizable material is an orthopedic casting material.

8. The process of claim 1, wherein reactants for the chemiluminescent reaction are provided in the form of a liquid, gel or paste.

9. The process of claim 8, wherein reactants for the chemiluminescent reaction are mixed together to initiate the chemiluminescent reaction, and the mixed

chemiluminescent materials are placed adjacent the photopolymerizable material, thereby exposing the photopolymerizable material to polymerization radiation and polymerizing said photopolymerizable material.

10. The process of claim 9, wherein the chemiluminescent material is selected such that the photopolymerizable material is insoluble in the chemiluminescent solution/gel/paste, and the chemiluminescent material is applied directly to the photopolymerizable material without substantial mixing between the chemiluminescent material and the photopolymerizable material.

11. The process of claim 8, wherein reactants for the chemiluminescent reaction are mixed together to initiate the chemiluminescent reaction, and the mixed chemiluminescent materials are applied to a radiation-transmissive barrier layer adjacent the photopolymerizable material, thereby exposing the photopolymerizable material to polymerization radiation and polymerizing said photopolymerizable material.

12. The process of claim 1, wherein reactants for the chemiluminescent reaction are dispersed or dissolved directly in the photopolymerizable material, thereby exposing the photopolymerizable material to polymerization radiation and polymerizing said photopolymerizable material.

13. The process of claim 10, wherein at least one reactant of the chemiluminescent reaction contains photopolymerizable functionalities.

14. The product made by the process of any of the foregoing claims.