Jean-Pierre Fouassier, Jacques Lalevée

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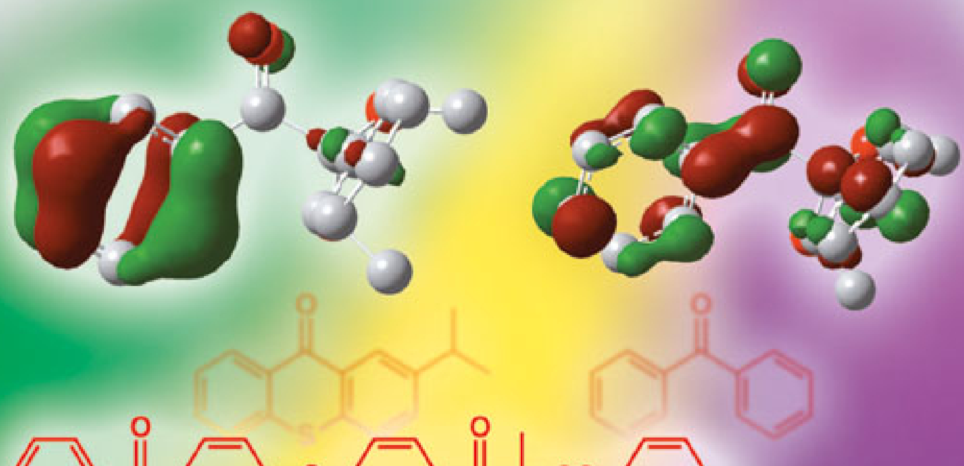
# Photoinitiators for Polymer Synthesis

## Scope, Reactivity, and Efficiency



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*Jean Pierre Fouassier and Jacques Lalevée*

# Photoinitiators for Polymer Synthesis

Scope, Reactivity and Efficiency

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*To Geneviève F., Gaëlle, Hugo and Emilie L.*

*for their patience and understanding*

*To our colleagues over the world for the marvellous time we spent together during all these years.*

# Contents

## Abbreviations

| | |
|---|---|
| AA | acrylamide |
| ABE | allylbutylether |
| ABP | aminobenzophenone |
| ADD | acridinediones |
| AH | electron/proton donor |
| AIBN | azo bis-isobutyro nitrile |
| ALD | Aldehydes |
| ALK | Alkoxyamines |
| AN | acrylonitrile |
| AOT | bis-2 ethyl hexyl sodium sulfosuccinate |
| APG | alkylphenylglyoxylates |
| AQ | anthraquinone |
| ATR | Attenuated reflectance |
| ATRP | atom transfer radical polymerization |
| BA | butylacrylate |
| BAc | [2-oxo-1,2-di(pheny)ethyl]acetate |
| BAPO | Bis-acyl phosphine oxide |
| BBD | Benzoyl benzodioxolane |
| BBDOM | bisbenzo-[1,3]dioxol-5-yl methanone |
| BC | borane complexes |
| BD | Benzodioxinone |
| BDE | bond dissociation energy |
| BE | benzoin esters |
| BIP-T | bis-(4-tert-butylphenyl) iodonium triflate |
| BMA | butylmethacrylate |
| BME | benzoin methyl ether |
| BMS | benzophenone phenyl sulfide |
| BP | benzophenone |
| BPO | benzoyl peroxide |
| BPSK | 1-Propanone,1-[4-[(4-benzoylphenyl)thio]phenyl]-2-methyl-2-[(4-methylphenyl)sulfonyl] |
| BTTB | 4-Benzoyl(4′-tert-butylperoxycarboxyl) tert-butylperbenzoate |
| BVE | butylvinylether |

| | |
|---|---|
| Bz | benzil |
| BZ | benzoin |
| C1 | 7-diethylamino-4-methyl coumarin |
| C6 | 3-(2′-benzothiazoryl)-7-diethylaminocoumarin |
| CA | cyanoacrylates |
| CD | cyclodextrin |
| CIDEP | chemically induced electron polarization |
| CIDNP | chemically induced nuclear polarization |
| CL | caprolactone |
| CNT | photopolymerized lipidic assemblies |
| co-I | co-initiator |
| CPG | cyano N-phenylglycine |
| CQ | camphorquinone |
| CT | charge transfer |
| CTC | charge transfer complex |
| CTP | computer-to-plate |
| CTX | chlorothioxanthone |
| CumOOH | cumene hydroperoxide |
| CW | continuous-wave |
| DB | deoxybenzoin |
| DCPA | dicylopentenyl acrylates |
| DDT | diphenyldithienothiophene |
| DEAP | 2,2-dietoxyacetophenone |
| DEDMSA | *N*,*N*-diethyl-1,1-dimethylsilylamine |
| DEEA | 2-(2-ethoxy-ethoxy) ethyl acrylate |
| DFT | density functional theory |
| DH | hydrogen donor |
| DMAEB | dimethylamino ethyl benzoate |
| DMPA | 2,2-dimethoxy -2 phenyl-acetophenone |
| DMPO | 5,5′-dimethyl-1-pyrroline N-oxide |
| DPA | diphenyl acetylene |
| dPI | difunctional photoinitiators |
| DSC | differential scanning calorimetry |
| DTAC | dodecyl trimethylammonium chloride |
| DUV | deep UV |
| DVE | divinylether |
| EA | electronic affinity |
| EAB | diethyl amino benzophenone |
| EDB | ethyl dimethylaminobenzoate |
| EHA | 2-ethyl hexyl ester |
| EL | ethyl linoleate |
| EMP | *N*-ethoxy-2-methylpyridinium |
| EMS | epoxy-modified silicone |
| Eo | Eosin Y |
| EP | epoxy acrylate |

| | |
|---|---|
| EpAc | epoxy acrylate; see Section 16 p359 |
| EPDM | ethylene-propylene-diene monomers |
| EPHT | electron/proton hydrogen transfer |
| EPOX | 3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate |
| EPT | ethoxylated pentaerythritol tetraacrylate |
| ERL | exposure reciprocity law |
| ESO | epoxidized soybean oil |
| ESR | electron spin resonance |
| ESR-ST | Electron spin resonance spin trapping |
| ET | energy transfer |
| eT | electron transfer |
| EtBz | ethylbenzene |
| EUV | extreme UV |
| EVE | ethylvinylether |
| FBs | fluorescent bulbs |
| Fc(+) | ferrocenium salt derivative |
| FRP | free radical photopolymerization |
| FRPCP | free-radical-promoted cationic polymerization |
| FTIR | Fourier transform infrared |
| FU | fumarate |
| GRIN | gradient index |
| HABI | 2,2',4,4',5,5'-hexaarylbiimidazole |
| HALS | Hindered amine light stabilizer |
| HAP | 2-hydroxy-2- methyl-1- phenyl-1- propanone |
| HCAP | 1-hydroxy- cyclohexyl-1- phenyl ketone |
| HCs | hydrocarbons |
| HDDA | hexane diol diacrylate |
| hfc | hyprefine splitting |
| HFS | hyperfine splitting |
| HOMO | highest occupied molecular orbital |
| HQME | hydroquinone methyl ether |
| HRAM | Highly reactive acrylate monomers |
| HSG | hybrid sol–gel |
| HT | hydrogen transfer |
| IP | ionization potential |
| IPNs | Interpenetrating polymer networks |
| IR | infrared |
| ISC | intersystem crossing |
| ITX | isopropylthioxanthone |
| JAW | julolidine derivative |
| K-ESR | kinetic electron spin resonance |
| KC | ketocoumarin |
| 2K-PUR | two-component polyurethane |
| LAT | light absorbing transients |
| LCAO | linear combination of atomic orbitals |

| | |
|---|---|
| LCD | liquid crystal display |
| LDI | Laser direct imaging |
| LDO | limonene dioxide |
| LED | light-emitting diode |
| LFP | laser flash photolysis |
| LIPAC | laser-induced photoacoustic calorimetry |
| LS | light stabilizers |
| LUMO | lowest unoccupied molecular orbital |
| MA | methylacrylate |
| MA | monomer acceptor |
| MAL | maleate |
| MB | methylene blue |
| MBI | mercaptobenzimidazole |
| MBO | mercaptobenzoxazole |
| MBT | mercaptobenzothiazole |
| MD | monomer donor |
| MDEA | methyldiethanolamine |
| MDF | medium-density fiber |
| MEK | methyl ethyl ketone |
| MIR | multiple internal reflectance |
| MK | Mischler's ketone |
| MMA | methylmethacrylate |
| MO | molecular orbitals |
| mPI | Multifunctional photoinitiators |
| MPPK | 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone |
| MWD | molecular weight distribution |
| NAS | 2-[p-(diethyl-amino)styryl]naphtho[1,2-d]thiazole |
| NHC | N-heterocyclic carbene |
| NIOTf | *N*-(trifluoromethanesulfonyloxy)-1,8-naphthalimide |
| NIR | near-IR reflectance |
| NMP2 | nitroxide-mediated photopolymerization |
| NMP | nitroxide-mediated photopolymerization |
| NMR | Nuclear magnetic resonance |
| NOR | norbornenes |
| NP | nanoparticles |
| NPG | *N*-phenyl glycine |
| NQ | naphthoquinone |
| NVET | nonvertical energy transfer |
| NVP | *N*-vinylpyrolidone |
| OD | optical density |
| OLED | organic light-emitting diode |
| OMC | organometallic compounds |
| $On^+$ | onium salt derivative |
| OrM | organic matrixes |
| $P^+$ | pyrilium salt derivative |

| | |
|---|---|
| PAG | Photoacid generators |
| PBG | photobase generator |
| PBN | phenyl-*N*-tertbutyl nitrone |
| PC | photocatalyst |
| PCBs | printed circuit boards |
| PCL | polycaprolactone |
| PDO | 1-phenyl 2-propanedione-2 (ethoxycarbonyl) oxime |
| PEG | polyethyleneglycol |
| PES | potential energy surface |
| PETA | pentaerythritol tetraacrylate |
| PHS | Poly(hydrosilane)s |
| PHT | pure hydrogen transfer |
| PI | photoinitiator |
| PIS | photoinitiating system |
| PLA | Polylactic acid |
| PLP | pulsed laser polymerization |
| PLP | Pulsed laser-induced polymerization |
| PMK | 2-methyl-1-(benzoyl)-2-morpholino-propan-1-one |
| PMMA | polymethylmethacrylate |
| POH | phenolic compounds |
| PPD | 1-phenyl-1,2-propanedione |
| PPK | 2-benzyl-2-dimethylamino-1-(phenyl)-1-butanone |
| PS | photosensitizer |
| PS/PI | photosensitizer/photoinitiator |
| PSAs | Pressure-sensitive adhesives |
| PVC | polyvinylchloride |
| PWBs | printed wiring boards |
| PYR | pyrromethene |
| RAFT | reversible addition-fragmentation transfer |
| RB | Rose Bengal |
| RFID | radiofrequency identification |
| ROMP | Ring-opening metathesis photopolymerization |
| ROOH | peroxide derivative |
| ROOH | hydroperoxide derivative |
| ROP | ring-opening polymerization |
| RP | radical pair |
| RPM | radical pair mechanism |
| RSH | mercaptan |
| RT-FTIR | real-time Fourier transform infrared |
| SCM | solvatochromic comparison method |
| SCRP | spin-correlated radical pair |
| SDS | sodium dodecyl sulfate |
| SG1 | N-(2-methylpropyl)-N-(1-diethylphosphono-2, 2-dimethylpropyl)-N-oxyl |
| SHOMO | singly highest occupied molecular orbital |

| | |
|---|---|
| SOMO | singly occupied molecular orbital |
| STY | styrene |
| SU | suberone |
| SWNT | single-wall carbon nanotube |
| TEA | triethyl amine |
| TEMPO | 2,2,6,6, tetramethylpiperidine N-oxyl radical |
| THF | tetrahydrofuran |
| ThP | thiophene |
| TI | titanocene derivative |
| TIPNO | 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide |
| TLS | thermal lens spectroscopy |
| TM | triplet mechanism |
| TMP | 2,2,6,6-tetramethylpiperidine |
| TMPTA | trimethylolpropane triacrylate |
| $TP^+$ | thiopyrilium salt derivative |
| TPA | two-photon absorption |
| TPGDA | tetrapropyleneglycol diacrylate |
| TPK | 1-[4-(methylthio) phenyl]-ethanone |
| TPMK | 2-methyl-1-(4-methylthiobenzoyl)-2-morpholino-propan-1-one |
| TPO | 2,4,6-trimethyl benzoyl-diphenylphosphine oxide |
| TPP | triphenylphosphine |
| TR-ESR | time resolved electron spin resonance |
| TR-FTIR | time-resolved Fourier transform infra red |
| TR-S2FTIR | Laser-induced step-scan FTIR spectroscopy |
| TS | transition state |
| TST | transition state theory |
| TTMSS | tris(trimethyl)silylsilane |
| TX | thioxanthone |
| TX-SH | 2-mercaptothioxanthone |
| Tz | triazine derivative |
| ULSI | ultra large scale integration |
| UV | ultraviolet |
| UVA | UV absorbers |
| VA | vinyl acetate |
| VC | vinylcarbazole |
| VE | vinyl ethers |
| VE | vinylacetate |
| VET | vertical energy transfer |
| Vi | violanthrone |
| VIE | vitamin E |
| VLSI | very large scale integration |
| VOC | volatile organic compounds |
| VP | vinylpyrrolidone |
| VUV | vacuum ultraviolet |
| XT | xanthones |

# Introduction

Light-induced polymerization reactions are largely encountered in many industrial daily life applications or in promising laboratory developments. The basic idea is to readily transform a liquid monomer (or a soft film) into a solid material (or a solid film) on light exposure. The huge sectors of applications, both in traditional and high-tech areas, are found in UV curing (this area corresponds to the largest part of radiation curing that includes UV and electron beam curing), laser imaging, microlithography, stereolithography, microelectronics, optics, holography, medicine, and nanotechnology.

UV curing represents a green technology (environmentally friendly, nearly no release of volatile organic compounds (VOCs), room temperature operation, possible use of renewable materials, use of convenient light sources (light-emitting diodes (LEDs), household lamps, LED bulbs, and the sun) that continues its rapid development. The applications concern, for example, the use of varnishes and paints (for a lot of applications on a large variety of substrates, e.g., wood, plastics, metal, and papers), the design of coatings having specific properties (for flooring, packaging, release papers, wood and medium-density fiber (MDF) panels, automotive, pipe lining, and optical fibers), the development of adhesives (laminating, pressure sensitive, and hot melt), and the graphic arts area (drying of inks, inkjets, overprint varnishes, protective and decorative coatings, and the manufacture of conventional printing plates).

Other applications of photopolymerization reactions concern medicine (restorative and preventative denture relining, wound dressing, ophthalmic lenses, glasses, artificial eye lens, and drug microencapsulation), microelectronics (soldering resists, mask repairs, encapsulants, conductive screen inks, metal conductor layers, and photoresists), microlithography (writing of complex relief structures for the manufacture of microcircuits or the patterning of selective areas in microelectronic packaging using the laser direct imaging (LDI) technology; direct writing on a printing plate in the computer-to-plate technology), 3D machining (or three-dimensional photopolymerization or stereolithography) that gives the possibility of making objects for prototyping applications, optics (holographic recording and information storage, computer-generated and embossed holograms, manufacture of optical elements, e.g., diffraction grating, mirrors, lenses, waveguides, array illuminators, and display devices), and structured materials on the nanoscale size.

Photopolymerization reactions are currently encountered in various experimental conditions, for example, in film, gas phase, aerosols, multilayers, (micro)heterogeneous media or solid state, on surface, in ionic liquids, *in situ* for the manufacture of microfluidic devices, *in vivo*, and under magnetic field. Very different aspects can be concerned with gradient, template, frontal, controlled, sol–gel, two-photon, laser-induced or spatially controlled, and pulsed laser photopolymerization.

As a photopolymerization reaction involves a photoinitiating system, a polymerizable medium, and a light source, a strong interplay should exist between them. The photoinitiator has a crucial role as it absorbs the light, converts the energy into reactive species (excited states, free radicals, cations, acids, and bases) and starts the reaction. Its reactivity governs the efficiency of the polymerization. A look at the literature shows that a considerable number of works are devoted to the design of photosensitive systems being able to operate in many various (and sometimes exotic) experimental conditions. This research field is particularly rich. Fantastic developments have appeared all along the past three decades. Significant achievements have been made since the early works on photopolymerization in the 1960s and the traditional developments of the UV-curing area. At present, high-tech applications are continuously emerging. Tailor-made photochemistry and chemistry have appeared in this area. The search for a safe and green technology has been launched. Interesting items relate not only to the polymer science and technology field but also to the photochemistry, physical chemistry, and organic chemistry areas.

We believe that the proposed book focused on this exciting topic related to the photosensitive systems encountered in photopolymerization reactions will be helpful for many readers. Why a new book? Indeed, in the past 20 years, many aspects of light-induced polymerization reactions have been obviously already discussed in books and review papers. Each of these books, however, usually covers more deeply selected aspects depending first on the origin (university, industry) and the activity sector of the author (photochemistry, polymer chemistry, and applications) and second on the goals of the book (general presentation of the technology, guide for end users, and academic scope). Our previous general book published more than 15 years ago (1995) and devoted to the three photoinitiation-photopolymerization-photocuring complementary aspects already provided a first account on the photosensitive systems.

For obvious reasons, all these three fascinating aspects that continuously appear in the literature cannot be unfortunately developed now (in 2011) in detail in a single monograph because of the rapid growth of the research. A book that mostly concentrates on the photosensitive systems that are used to initiate the photopolymerization reaction, their adaptation to the light sources, their excited state processes, the reactivity of the generated initiating species (free radicals, acids, and bases), their interaction with the different available monomers, their working out mechanisms, and the approach for a complete understanding of the (photo)chemical reactivity was missing. This prompted us to write the present book. It aims at providing an original and up-to-date presentation of these points together with a discussion of the structure/reactivity/efficiency relationships observed in photoinitiating systems usable in radical, cationic, and anionic photopolymerization as well as in acid and base catalyzed photocrosslinking reactions. We wish to focus on the necessary role of the basic research toward the progress of the applied research through the large part we have devoted to the involved mechanisms. In fact, everybody is aware that there is no real technical future development without a present high-quality scientific research. In our opinion, such an extensive and complete book within this philosophy has never been written before.

Science is changing very fast. During the preparation of a book, any author has the feeling of walking behind the developments that unceasingly appear. It is rather difficult to have the latest photography of the situation by the end of the manuscript; this is also reinforced by the necessary delay to print and deliver the book. Therefore, we decided here to give not only the best up-to-date situation of the subject but also to take time to define a lot of basic principles and concepts, mechanistic reaction schemes, and examples of reactivity/efficiency studies that remain true and are not submitted to a significant aging on a 10-year timescale.

The book is divided into four parts. In Part I, we deliver a general presentation of the basic principles and applications of the involved photopolymerization reactions with a description of the available light sources, the different monomers and the properties of the cured materials, the various aspects and characteristics of the reactions, and the role of the photosensitive systems and the typical examples of applications in different areas. The part especially concerned with the polymer science point of view (as other books have already dealt in detail with this aspect) focuses on general considerations and latest developments and to what is necessary to clearly understand the following parts. Then, we enter into the heart of the book.

In Parts II and III, we give (i) the most exhaustive presentation of the commercially and academically used or potentially interesting photoinitiating systems developed in the literature (photoinitiators, co-initiators, photosensitizers, macrophotoinitiators, multicomponent combinations, and tailor-made compounds for specific properties), (ii) the characteristics of the excited states, and (iii) the involved reaction mechanisms. We provide an overview of all the available systems but we focus our attention on newly developed photoinitiators, recently reported studies, and novel data on previous well-known systems. All this information is provided for radical photopolymerization (Part II) and cationic and anionic photopolymerization and photoacid and photobase catalyzed photocrosslinking (Part III).

In Part IV, we gather and discuss (i) a large set of data, mostly derived from time-resolved laser spectroscopy and electron spin resonance (ESR) experiments, related to both the photoinitiating system excited states and the initiating radicals (e.g., a complete presentation of the experimental and theoretical reactivity of more than 15 kinds of radicals is provided); (ii) the most recent results of quantum mechanical calculations that allow probing of the photophysical/photochemical properties as well as the chemical reactivity of a given photoinitiating system; and (iii) the reactivity in solution, in micelle, in bulk, in film, under air, in low viscosity media, or under low light intensities.

The book also outlines the latest developments and trends for the design of novel molecules. This concerns first the elaboration of smart systems exhibiting well-designed functional properties or/and suitable for processes in the nanotechnology area. A second direction refers to the development of an evergreen (photo)chemistry elaborating, for example, safe, renewable, reworkable, or biocompatible materials. A third trend is related to the use of soft irradiation conditions for particular applications, which requires the design of low oxygen sensitivity compounds under exposure to low-intensity visible light sources, sun, LEDs, laser diodes, or household lamps (e.g., fluorescence or LED bulbs).

When questioning the Chemical Abstract database, many references appear. We have not intended to give here an exhaustive list of references or a survey of the patent literature. We used, however, more than 2000 references. Pioneer works are cited but our present list of references mainly refers to papers dispatched during the past 15 years. The selection of the articles is most of the time a rather hard and sensitive task. We have done our best and beg forgiveness for possible omissions.

This research field has known a fantastic evolution. We would like now to share the real pleasure we had (and still have) in participating and contributing to this area. Writing this book was really a great pleasure. We hope that our readers, R and D researchers, engineers, technicians, University people, and students involved in various scientific or/and technical areas such as photochemistry, polymer chemistry, organic chemistry, radical chemistry, physical chemistry, radiation curing, imaging, physics, optics, medicine, nanotechnology will appreciate this book and enjoy its content.

And now, it is time to dive into the magic of the photoinitiator/photosensitizer world!