Jean-Pierre Fouassier, Jacques Lalevée

WILEY-VCH

Photoinitiators for Polymer Synthesis

Scope, Reactivity, and Efficiency

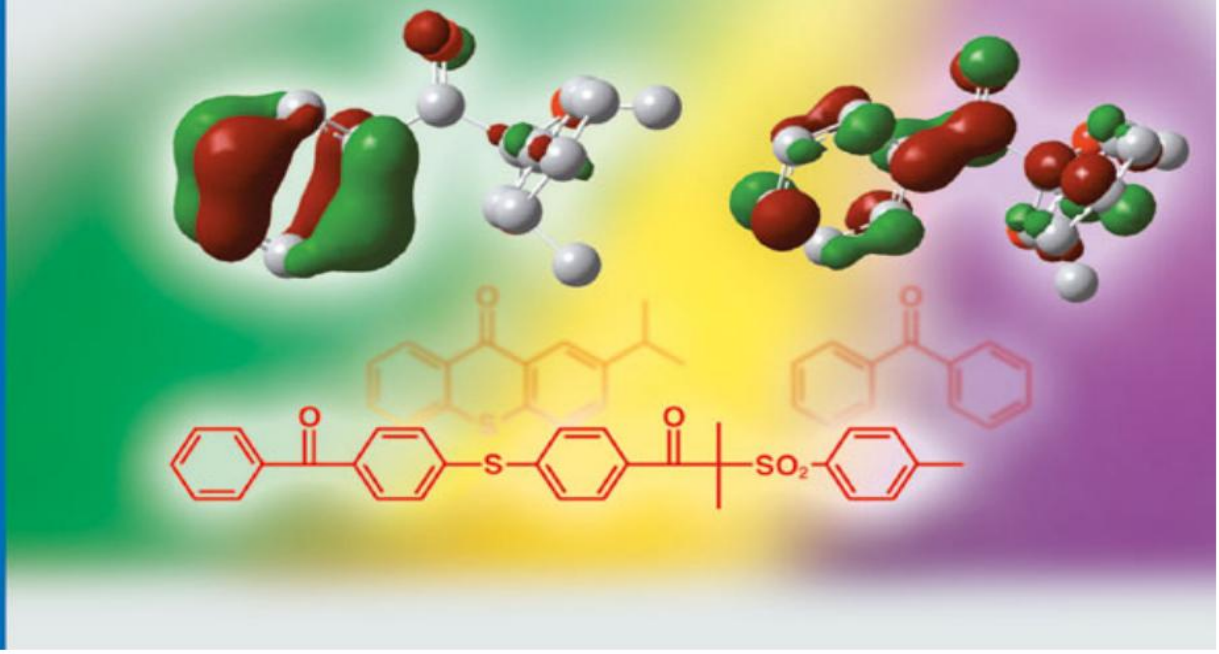

Table of Contents

Index

Related Titles

Ramamurthy, V.
Supramolecular Photochemistry
Controlling Photochemical Processes
2011
ISBN: 978-0-470-23053-4
Allen, N. S. (ed.)
Handbook of Photochemistry and Photophysics of Polymeric Materials
2010
ISBN: 978-0-470-13796-3
Albini, A., Fagnoni, M. (eds.)
Handbook of Synthetic Photochemistry
2010
ISBN: 978-3-527-32391-3
Wardle, B.
Principles and Applications of Photochemistry
2010
ISBN: 978-0-470-01493-6
Stochel, G., Stasicka, Z., Brindell, M., Macyk, W., Szacilowski, K.
Bioinorganic Photochemistry
2009
ISBN: 978-1-4051-6172-5

Jean Pierre Fouassier and Jacques Lalevée

Photoinitiators for Polymer Synthesis

Scope, Reactivity and Efficiency

WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Jean Pierre Fouassier

formerly University of Haute Alsace

Ecole Nationale Supérieure de Chimie

3 rue Alfred Werner

68093 Mulhouse Cedex

France

Prof. Jacques Lalevée}

University of Haute Alsace

Institut Science des Matériaux

IS2M-LRC 7228, CNRS

15 rue Jean Starcky

68057 Mulhouse Cedex

France

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-33210-6

ePDF ISBN: 978-3-527-64827-6

ePub ISBN: 978-3-527-64826-9

mobi ISBN: 978-3-527-64825-2

oBook ISBN: 978-3-527-64824-5

Dedication

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.

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