

## Invited Review

# High-Performance Photoinitiating Systems for Free Radical Photopolymerization. Application to Holographic Recording<sup>†</sup>

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## ABSTRACT

The photoinitiating systems (PIS) usable in free radical photopolymerization are briefly reviewed. Apart conventional Type I and Type II photoinitiators, three-component PIS exhibiting a photocyclic behavior are discussed. The mechanisms of photo-reaction are presented, highlighting the role of a redox additive which reacts with the photoinitiator photoproduct. Recent applications in holography recording are described showing that the selection of a PIS plays a crucial role in this application.

## INTRODUCTION

Photopolymerization is basically described as a chemical reaction whereby organic materials exposed to electromagnetic radiation combine to form high-molecular-weight polymer molecules (1,2). Historically, photopolymerization was first used over 4000 years ago during the time of ancient Egypt in the mummification process (3). During the last decades, there was a rapid increase in the number of commercial applications of photopolymerization. In brief, the general categories of photopolymer applications are electronic materials (1), printing materials (4), optical and electro-optical materials (5,6), fabrication of devices and materials (7), adhesives and sealants (8), coatings (9) and surface modifications (10,11).

Photopolymer resins usually contain a photoinitiator or a more complex photoinitiating system (PIS), a mixture of monomers and oligomers, some additives and fillers (12). The most versatile process is the free radical photopolymerization which offers the most important choice of monomers and oligomers as well as a large number of potential PIS. The efficiency of the PIS is determined by the absorption properties, the quantum yield of initiating radicals and the reactivity of these radicals toward the monomer (13). It is well recognized that the PIS is the corner stone of photopolymerization process and numerous works have been devoted to the development of PIS for specific applications ranging from metal coating to laser direct imaging.

Holography also represents an interesting and growing field due to an increasing demand in security or data storage (14–16). The development of applications in holography is directly governed

by the photosensitivity of the photopolymer and the diffraction efficiency which could be obtained. Therefore, there is a need for highly efficient PIS capable to initiate the photopolymerization reaction at relatively low dose. Surprisingly, the field of holography recording did not take advantage of the research performed recently in the field of PIS. Indeed, a recent review shows that there is not a strong focus on the efficiency of the PIS in holography recording (16). The photosensitivity of photopolymers being one of the major issue in this field, it is of importance to discuss the last developments in PIS for evaluating their potential use in holography applications.

Different polymer chemistries have been studied as reactive medium to produce holograms. Due to intrinsic drawbacks for most of them, it turns out the free radical photopolymerization is the best chemical reaction which allows the recording of holograms with a good efficiency and a good durability (16). Therefore, the major interest focuses on the PIS usable for free radical photopolymerization.

In this study, the conventional Type I and Type II PIS are briefly described. A particular attention is paid to three-component PIS that have emerged as an improvement over Type I and Type II initiating systems. The spectroscopic studies of some of these systems outline the possible presence of a photocyclic reaction. Such behavior allows the recovery of the dye after photoreaction, leading to higher probability of radical production. The efficiency of these systems is higher than conventional systems, a fact which places these systems as good candidates for holographic recording.

## CONVENTIONAL TYPE I AND TYPE II PHOTINIATING SYSTEMS

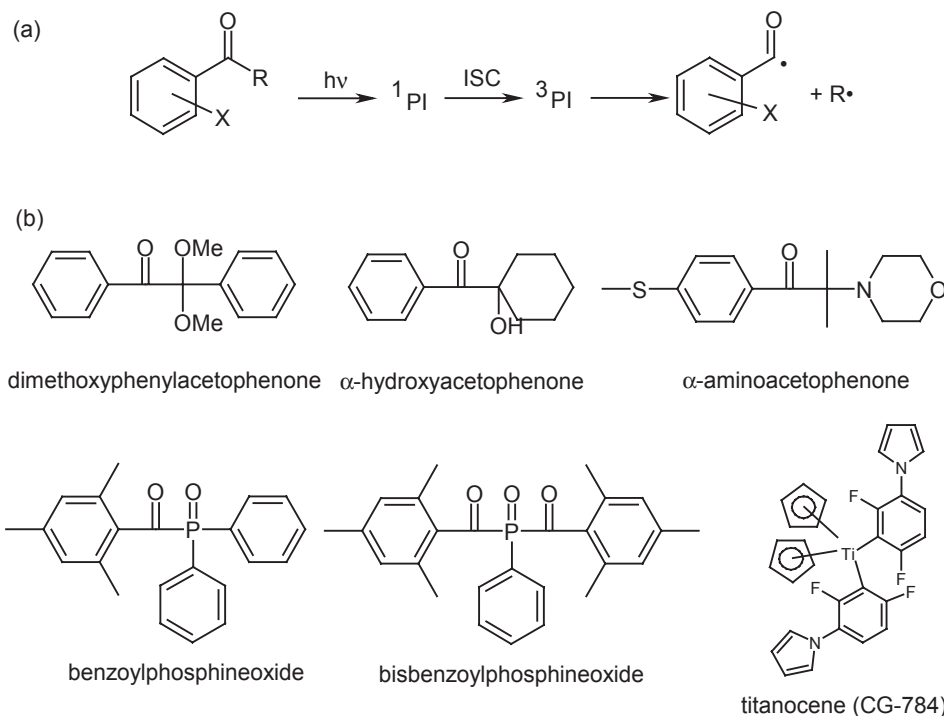
With respect to the formation of initiating radicals, the photoinitiation mechanism can proceed through two essential mechanisms. In the first one, the PIS excited state undergoes a homolytic cleavage through a Norrish I photoreaction (Type I). This produces two radicals that could be both reactive toward double bonds (Scheme 1) (17–19).

The most efficient Type I photoinitiators are benzoin ether derivatives, benzylketals, hydroxylalkylphenones,  $\alpha$ -aminoketones and acylphosphine oxides. The high rate of cleavage and quantum yield of radicals explain the efficiency of type I PIS (13,20). Most of the Type I photoinitiators are only active under UV irradiation (20,21). Only a limited set of available Type I PIS absorbs in the blue or green region: a bisbenzoylphosphine

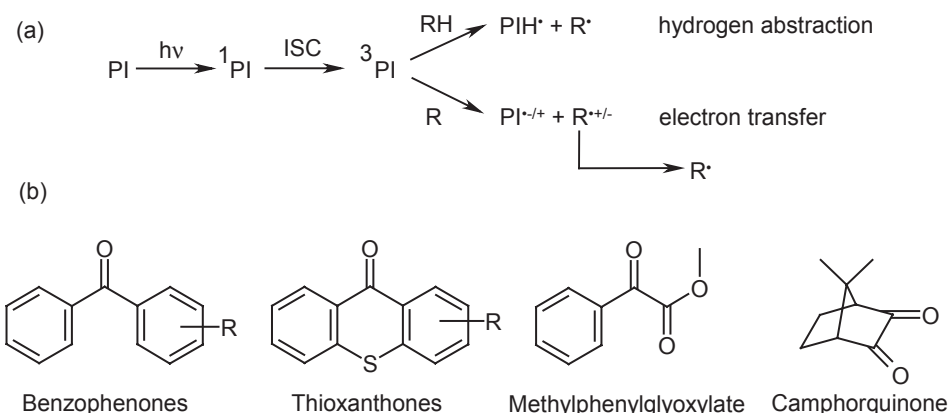
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**Scheme 1.** a) Photocleavage reaction from triplet state of Type I photoinitiators. b) Examples of commercially available Type I PIS.



**Scheme 2.** a) General reaction mechanism of a Type II PIS containing the photoinitiator (PI) and a coinitiator working through hydrogen abstraction (HR) or electron transfer (ET). b) Examples of commercially available Type II PI.

oxide derivative (Irgacure 819) exhibits an absorption spectrum extending up to around 410–420 nm. One of the main features of this class of acylphosphine is the high photobleaching ability that increases the photoinitiation efficiency. This is especially useful when curing films and coatings with high thickness. However, this class of acylphosphine oxide is known to suffer from oxygen inhibition, a fact which limits their applications (17). A titanocene derivative (CG-784) is known to absorb in the green region and was used with several high-index organic monomers and incorporated into acrylate oligomer-based formulations, irradiating at 546 nm (23). However, it seems that only a small part of the active species acts as initiating radicals and are not sufficient to achieve the appropriate monomer conversion (12). Recently, a visible light photoinitiator based on acylgermanium structure was developed. This compound absorbs visible light at wavelengths up to 550 nm, and exhibits high reactivity.

The main drawback relies on the availability of the molecule (proprietary structure) and the high price due to synthesis (24).

The formation of initiating radical from Type II PIS requires a photoinitiator which reacts from its triplet state with a coinitiator (Scheme 2). Typical Type II PIS with good absorption features in the UV–blue region are benzophenones (25–32), thioxanthenes (33–38), camphorquinone (39–41), benzyls (26, 42) and keto-coumarins derivatives (43–45). For visible light PIS, many dyes were reported as photoinitiators such as coumarins (45), xanthenic dyes (46–48), cyanine dyes, thiazine dyes (46) and pyrromethene dyes (49–51). The coinitiator is generally a hydrogen donor which forms an initiating radical after photoreaction. By contrast, the ketyl radical formed on the photoinitiator moiety is generally inactive with respect to the double bonds, or even acts as a terminating agent toward the polymerization reaction (12,52–54). In addition, amines (40,54–59), ethers (60–62), sulfides (62–66)

and thiols (66–68) have also been used as hydrogen donors. Coinitiators reacting through electron transfer are borate salts (69,70), iodonium salts (52–73) or triazine derivatives (50) which lead to the production of radical after a photodissociative electron transfer reaction.

Although Type I PIS can exhibit high quantum yields of radicals, their main drawback is due to the spectral limitation in the UV to blue region. By contrast, Type II PIS are versatile initiators for UV curing systems and visible light photopolymerization. The combination of different dyes and coinitiators provides tremendous flexibility in the selection of irradiation wavelength from the UV to the red region. However, these systems show limited efficiency compared with Type I systems.

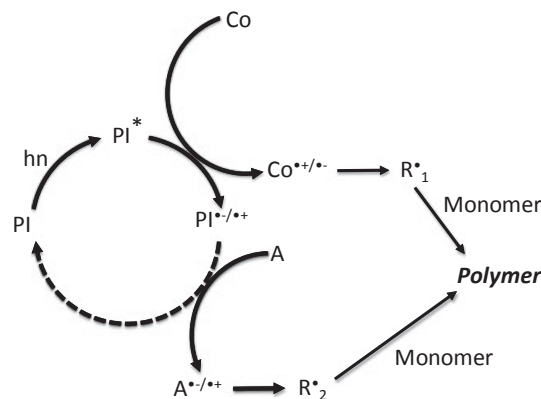
## PHOTOCYCLIC INITIATING SYSTEMS

To overcome the lack of reactivity of conventional systems under visible light, many groups have developed more complex PIS in which not only the intrinsic problem of reactivity of the Type II system is circumvented but also the dye is recovered after reaction, leading to so-called three-component PIS or photocyclic initiating systems (PCIS). Indeed, the photopolymerization efficiency of Type II PIS can be greatly improved by addition of a third additive, which yields to an additional formation of initiating radicals by reaction with one photoproduct arising from the photochemical reaction (74–78). The use of PIS based on three components offers tremendous flexibility in the selection of the light sources and the determination of the actinic wavelength because a wide variety of dyes may be used. Three different kinds of additives can be used: (1) latent species that create reactive centers after reaction, (2) molecules that are oxidized and (3) molecules that are reduced. Many works have shown that these PIS lead to increased rate of polymerization and final monomer conversion than the corresponding Type II PIS (50,51,78,79).

The first class of molecules, latent species that leads to the formation of reactive centers after reaction, contains chain transfer agents such as S–H, P–H, Si–H or Ge–H based molecules. They have found only limited applications and will not be discussed further (80).

Molecules that are oxidized during the process are electron donors. Amine derivatives such as *N*-methyldiethanolamine (27,28), or triethylamine (78) are the common electron donor reported to date for the PIS in the literature. The aromatic amines such as *N*-phenylglycine are used to avoid the toxicity of alkyl amines (40). Triarylalkyl borates, sulfur- or tin-containing compounds, sulfonates (80) have also been reported as well as, although to a lower extent, amides, ethers, ferrocene, metallocenes, ureas, salts of xanthanates, salts of tetraphenylboronic acid, ... As can be expected, the oxidation potential of the donor plays a key role in the mechanism of electron transfer.

Among the additives that are reduced during the process, the most commonly used are iodonium salts which exhibit a low reduction potential (12,20,81–84). Such iodonium salts can be replaced by bromo compounds (28,85). Triazine derivatives are also quite popular candidates, and are one of the most common electron acceptors used as third component for the systems based on dye/borate salts (91). Alcoxypyridinium derivatives were also used as coinitiators to improve the efficiency of two-component PIS based on borate salts (90). In the past, peroxides, sulfonium and pyridinium salts, iron arene complexes and hexaarylbi-



**Scheme 3.** General reaction mechanism occurring in three-component photocyclic initiating system (PCIS).

dazole have been found to be interesting alternatives to iodoniums or triazines. In that case, the reduction potential of third component is an important criterion to select the compound and the third component plays extremely important roles in initiation kinetic steps (49,50).

A wide variety of dyes was reported in the literature as photosensitizers for three-component PIS. The selection of dye is the key criteria with respect to the irradiation wavelength and excited-state properties. Many dyes used in Type II PIS may also be used in three-component PIS: coumarin dyes, xanthene dyes, acridine dyes, thiazole dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, aminothiaryl methanes, merocyanines dyes, squarylium dyes, pyridinium dyes, etc... Many studies reported the photopolymerization efficiency, kinetics and mechanistic reactivity of this type of systems (45,49–52,74–78,85–92). The mechanisms which have been proposed for three-component systems can be summarized into two general classes: (1) Parallel reactions in which two coinitiators react with the excited dye independently; (2) Sequential reactions in which two of the three components first react together followed by the reaction of the third component with one of the photoproducts (Scheme 3). In all the proposed mechanisms, the dye absorbs the light and prompts the photoreaction either through the excited singlet state or through the triplet state. In the case of parallel reactions, the total yield of radicals depends on the reactivity of each coinitiator with the excited state, an obvious fact which do not deserve further discussion. More interesting are the sequential reactions in which the photoreaction could be an electron transfer or a hydrogen transfer with the coinitiator (Co) (Scheme 3). An initiating radical is formed from the coinitiator and the dye turns into its reduced or oxidized form. In the presence of the third component (A), a redox reaction takes place between the additive and the reduced or oxidized form of the dye. This reaction yields two advantages: the additive (A) leads to the formation of supplementary initiating radical, and the ground-state dye is recovered and can be involved in further photoreaction. Therefore, a real cyclic photoreaction occurs until complete depletion of reactants.

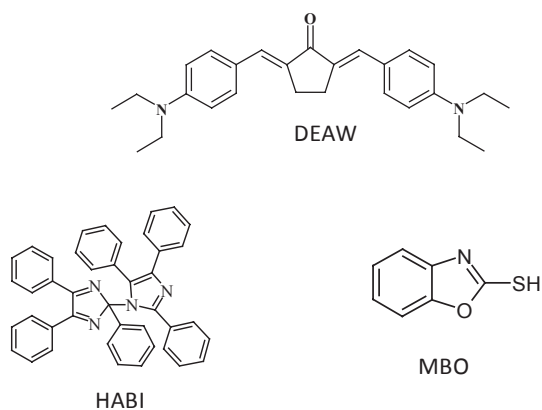
## APPLICATIONS IN HOLOGRAPHY RECORDING

An optical application of photopolymerization is holographic devices, whereby a three-dimensional image is built when light

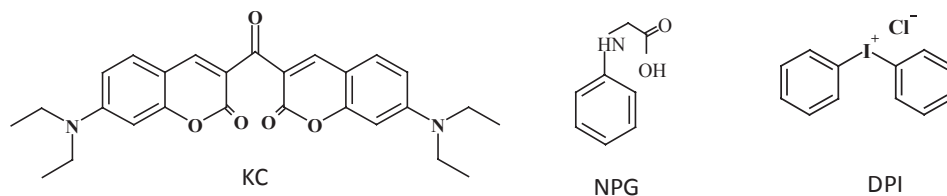
is shined on a two-dimensional structure (1,2,15). Photopolymerization is ideally suited for such application as the reaction is spatially and temporally controlled. Holographic elements, reversible holograms and switchable holographic gratings have been prepared by this method (5,15,93–95). Different PIS have been used for holographic recording applications.

Among the Type II PIS, the ion pair formed by methylene blue and rose bengal has been tested as photoinitiator in dry films made of acrylamide and polyvinylalcohol (46). Under irradiation with 633 or 514 nm light, diffraction efficiencies of 65% and 35% and sensitivities of 30 and 100 mJ cm<sup>-2</sup> have been, respectively, reached with a spatial resolution of *ca.* 1000 lines mm<sup>-1</sup>. The inhibition time depended on the recording intensity, and decreased at higher intensities for both wavelengths of irradiation.

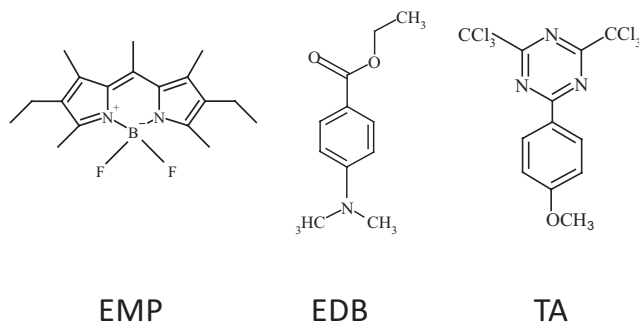
The influence of irradiation intensity, dye concentration on the photochemical bleaching process and holographic recording capabilities of a series of xanthene dyes such as erythrosin B (ErB), eosin Y (EY), rose bengal (RB), rhodamine B (RoB) and fluorescein (F), has been investigated in the presence of triethanolamine (TEA) as electron donor (96,97). The bleaching kinetics followed the order ErB > EY > RB > RoB > F. The diffraction efficiency obtained with ErB is significantly larger than that with EY, RB, RoB and F under the same experimental conditions as a consequence of the highest photobleaching rate constant of this initiating system. A different resin using oligourethane acrylates has been used for holographic applications such as interferometry and pattern recognition systems (98). Using EY, F, MB and thionine (TH) as photosensitizers with dimethylaminoethanol, morpholine and piperidine as electron donors, a sufficiently high speed of recording in the 460–540 nm range has been noticed. Holographic experiment in the red light with the MB systems outlined low reactivity and slow recording rates. However, after a modification in the monomer system, it



**Scheme 4.** Structures of compounds used in (22).



**Scheme 5.** Structures of compounds used in (86).



**Scheme 6.** Structures of compounds used in (103).

was possible to decrease the recording time from 2400 to 1500–1800 s with irradiation intensity around 3 mW cm<sup>-2</sup> (98).

The performances of PIS based on synthetic derivatives of commercial dyes have been investigated with MDEA as coinitiator. A new eosin and rose bengal ester possessing a *o*-benzoyl- $\alpha$ -oxoimine group in the C-2' carboxylate has been synthesized (EO-AO and RB-AO) and the photopolymerization efficiency of 2-hydroxyethyl methacrylate (HEMA) has been studied at 525 nm (48,99). The dyes EO-AO and RB-AO are clearly better photoinitiators, with higher polymerization rate values, than the corresponding physical mixtures dye/acyloxime, or than the corresponding pure dyes. The addition of amine induces an increase in the polymerization rate.

In the research of new efficient systems for holographic recording at 546 nm, the efficiency of three-component PIS was also studied. One system (Scheme 4) was based on hexaarylbi-simidazole derivative (HABI), a chain transfer agent 2-mercaptobenzoxazole (MBO), and 2,5-bis[[4-(diethylamino)phenyl]methylene] cyclopentanone (DEAW) as a dye (22). Several high-index organic monomers have been incorporated into high optical quality acrylate oligomer-based formulations. A six-fold increase in the refractive index  $\Delta n$  was achieved compared with an all-acrylate formulation. Samples prepared from these formulations have been used to write and read more than 200 high-quality holograms in a given volume of material.

Another photosensitive organic material, based on a three-component PIS (Scheme 5) formed by 3-3'-carbonyl-bis-7-diethylaminocoumarin (KC), N-phenylglycine (NPG) and diphenyl iodonium chloride (DPI), has been used to polymerize an acrylic monomer (phenoxydiethyleneglycolacrylate). This three-component system has led to a better performance than the corresponding two component systems KC/NPG or KC/DPI (86). Reflection holograms have been recorded with this system at 488 nm (Ar<sup>+</sup> laser) with diffraction efficiency around 51% and refractive index modulation of 0.013 (86,100).

Moreover, the performance of new systems based on original synthesized dyes (NK-529, NK-3960, MCD and ECD) that could

be sensitive to He–Ne (632.8 nm) laser, 2-chlorohexaarylbiimidazole(o-cl-HABI) and 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA), was examined (101). More than 80% of reflection grating diffraction efficiency can be obtained. The holographic gratings have a good physical and chemical stability under ambient conditions.

Bipyromethene-BF<sub>2</sub> complexes (also known as BODIPY) have been also studied in photopolymers based on a hydrophobic binder as an alternative to redox initiation system based on xanthene dyes (102). In this way, the authors avoided the use of triethanolamine as the redox initiator, typical in hydrophilic binder photopolymers, which is related to the existence of diffusion phenomena in the recorded hologram. Using a pyromethene-derived dye and 4,4'-azobis(4-cyanovaleric acid) as initiator, photopolymer layers with high thickness, good optical quality have been obtained.

Recently, holographic recording of PIS based on pyromethene dyes (103) has been studied by real-time FTIR, time-resolved spectroscopic experiments with the aim to relate the photochemistry of PIS to the hologram formation. An optimized acrylate photopolymerizable resin was used to probe the reactivity of the PCIS based on the pyromethene dye (2,6-diethyl-1,3,5,7,8-pentamethylpyromethene BF<sub>2</sub> complex) with an amine as electron donor a triazine and iodonium salt as an electron acceptor (Scheme 6).

It was shown that the efficiency of the PIS dye/coinitiator can be drastically increased when a redox additive is added due to a photocyclic behavior. Homogeneous irradiation of the sample leads to a photopolymerization reaction which was found to reach a fast vitrification, limiting the monomer conversion at about 55% for both dye/coinitiator and three-component systems. By contrast, holographic recording underlines the differences in PIS reactivity, allowing diffraction efficiencies close to 1 for the most reactive PIS. Therefore, the particular behavior of PCIS reveals marked differences between the PIS that are not detected with classical RT-FTIR measurements. The high diffraction efficiencies achieved promotes the use of the considered medium for WORM (write once read many) applications.

## CONCLUSION

In this short review, it is shown that recent works on PIS based on three components have led to high reactivity in photopolymerization reactions. Although these systems meet the requirement for holography recording, there was not great use of such systems in that field. The need to improve both the photosensitivity and the diffraction efficiency of holograms will be certainly the driving force to pay more attention on the development of PIS specifically designed for such application.

## AUTHOR BIOGRAPHIES



**Ahmad Ibrahim** is originally from the south of Lebanon. He earned his engineer degree from the Institute of textile and chemistry of Lyon (ITECH) in 2008. He received his PhD in 2011 at the Laboratory of Macromolecular Photochemistry and Engineering (LPIM, Mulhouse) on the development of three-component visible photoinitiating systems for holography recording. He spent 1 year (2011–2012)

as an assistant professor at the University of Haute-Alsace (Mulhouse, France). Currently, he started a postdoctoral fellow at the University of Haute-Alsace in December of 2012 under the supervision of X. Allonas for the development of composites materials using photochemical ways.



**Luciano Di Stefano** born in Argentina, Luciano H. Di Stefano worked in the Department of Organic Chemistry in the University of Buenos Aires, where he obtained his chemistry degree in 2012. He is now a first year PhD student at the LPIM.



**Olga Tarzi** received her Ph.D. in chemistry in 2006 from the University of Buenos Aires (Argentina) under the supervision of Prof. Rosa Erra-Balsells. For her Ph.D she studied the thermal stability and photochemistry of UV-MALDI-MS matrices. During 2007–2008 she was a postdoctoral fellow in Prof. Allonas laboratory, where she studied photoinitiating systems for free radical photopolymerization in the

visible. In 2008, she became member of the Argentinean Research Council (CONICET). Her research interests comprise the field of UV-MALDI-MS with focus on the study and development of new matrices for the analysis of synthetic polymers and carbohydrates.



**Haja Tar** studied Chemical Physics at the University of Haute Alsace, where she received her Master degree in 2010. Then, she started a PhD on the development of new photoinitiators for free radical polymerization, under the supervision of Prof. Xavier Allonas and Prof. Christian Ley.



**Christian Ley** obtained his PhD Thesis in 1999 on the photophysical properties and solvation dynamic of TX excited states. After 1-year postdoctoral position under the direction of Pr. J. Wirz (Basel) he became associate professor in the chemical department of ENS Ulm (Paris) in the group of Ultrafast Photochemistry directed by Dr. M.M. Martin. He was interested in the study of ultrafast processes in

photophysical and biological systems. In 2008 he joined the LPIM (UHA Mulhouse) directed by Pr. X. Allonas and got involved in photochemistry and primary processes in photopolymerization. Since 2013 he owned a full Professorship position.



**Xavier Allonas** PhD in 1995 on photoinduced electron transfer mechanism at the Department of Photochemistry in Mulhouse (France). Short postdoctoral training at the Institute of Physical Chemistry of Fribourg in Switzerland on picosecond transient grating spectroscopy. In 1996, Assistant Professor at the Chemistry Institute of Mulhouse. Full Professor at the University of Haute Alsace in Mulhouse in 2003. Since 2006, head of the Laboratory of Macromolecular Photo-

chemistry and Engineering. Current research interests are the processes involved in photopolymerization studied through time-resolved laser spectroscopies, real-time FTIR and molecular modeling. A particular interest is paid to the study of photoinitiating systems reactivity and photopolymerization kinetics for different applications such as laser imaging, paints and coatings, optics, microelectronics.

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