

## 1

## Backgrounds in Photopolymerization Reactions: A Short Overview

The goal of this chapter is to provide the reader with the backgrounds of the involved scientific and technical aspects in photopolymerization reactions (characteristics, processes, kinetics, light sources, polymerizable media, properties of the resulting materials, and different areas of applications) but not to detail the “polymer” point of view of this field. In the present case, we will only give a basic and rather brief description that should allow an easy understanding of the following chapters of this book.

Examples of general books dealing with this “polymer aspect” can be found in Refs. [1–40]. In the past 10 years, we observed a huge development of applications involving light in the different facets of the polymerization area (see Parts III and IV) such that a complete description would require in the writing of a single book on this subject! This is not the goal of the present monograph where the general concern is the photosensitive systems. Therefore, in the present chapter, we decided to only include the references of some typical (review) papers.

### 1.1 Photopolymerization and Photo-cross-linking

#### 1.1.1 Reactions

It is known that a polymerization reaction consists in adding many monomer units  $M$  to each other, thereby creating a macromolecule (1.1). The initiation step of this reaction corresponds to the decomposition of a molecule (an initiator  $I$ ) usually obtained through a thermal process (1.2). This produces an initiating species ( $X\cdot$ ) being able to attack the first monomer unit. Other units add further to form the macromolecule.



Instead of thermal activation of polymerization, other stimuli such as light, electron beam, X-rays,  $\gamma$ -rays, plasma, microwaves, or even pressure can be used (see Ref. [32]). Among them, the exposure of a resin (monomer/oligomer matrix) to a

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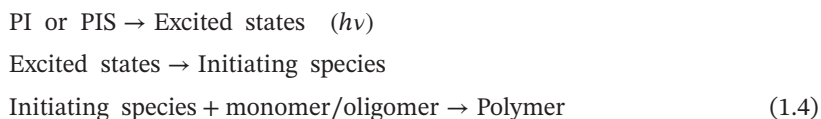
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suitable light is found to be a very convenient way for the initiation step: in that case, the reaction is called a photopolymerization (1.3).



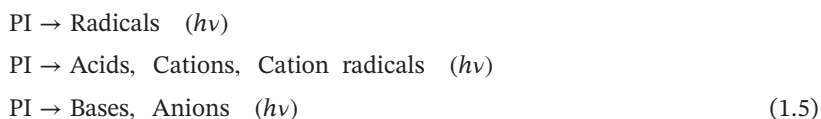
### 1.1.2 Photoinitiation Step

Because of their absorption properties, monomers or oligomers are usually not sensitive to the available lights (except a few cases involving specifically designed light-absorbing structures). The addition of a photoinitiator (PI) or a photoinitiating system containing a PI and other compounds (PIS) is necessary (1.4). Excited states are generated under the light exposure of PI (see Chapters 2–4). Then, an initiating species is produced. Its nature – radical ( $R\cdot$ ), cationic ( $C^+$ ), and anionic ( $A^-$ ) – is dependent on the starting molecule.



### 1.1.3 Different Kinds of Photopolymerization Reactions

Accordingly, the usual types of photopolymerization reactions – free radical polymerization (FRP), cationic polymerization (CP), anionic photopolymerization (AP), or acid- and base-catalyzed photo-cross-linking reactions – can be encountered, e.g. (1.5), in suitable resins.

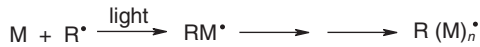


The term “photopolymerization” is very general and relates to two different concepts (Scheme 1.1). A photoinduced polymerization reaction is a chain reaction where one photon yields one initiating species and induces the incorporation of a large number of monomer units. A photo-cross-linking reaction refers to a process involving a prepolymer or a polymer backbone in which a cross-link is formed between two macromolecular chains: each chain propagation requires the absorption of a photon. This kind of polymer can be designed in such a way that it contains pendent (e.g. in polyvinyl cinnamates) or in-chain photo-cross-linkable moieties (e.g. in chalcone-type chromophore-based polymers).

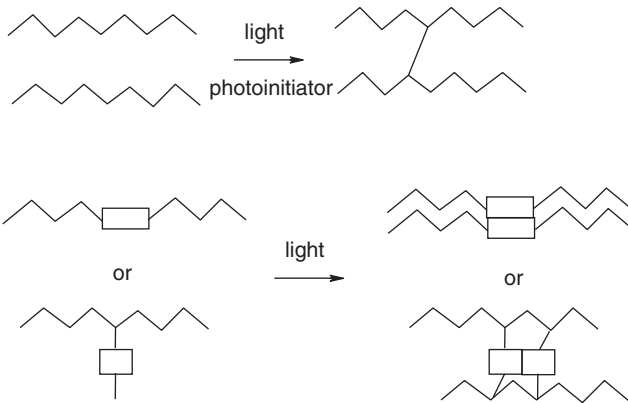
### 1.1.4 Monomers and Oligomers

A monomer is a rather small molecule having usually one or several chemical reactive functions (e.g. acrylates), whereas an oligomer is a large molecular structure consisting of repetitive units of a given chemical structure, which constitutes the

Photoinduced radical polymerization

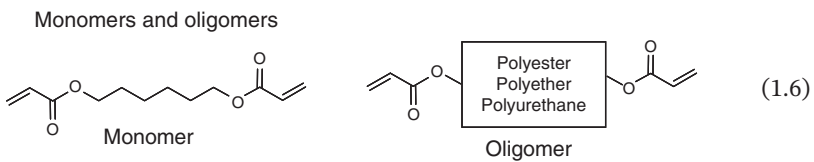


Photocrosslinking reaction

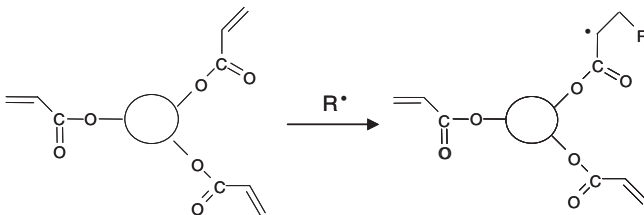


**Scheme 1.1** Crosslinking mechanisms.

backbone and contains one or more reactive chemical functions (1.6). The oligomer skeleton governs the final physical and chemical properties of cured coating.



When using multifunctional monomers or oligomers, the photoinduced polymerization reaction does not obviously proceed to form a linear polymer. As it develops in the three directions of space, it also leads to a cross-linking reaction, thereby creating a polymer network (see Scheme 1.2 for a free radical reaction). Sometimes, the reaction is depicted as a cross-linking photopolymerization.



**Scheme 1.2** Multifunctional monomer.

### 1.1.5 Photopolymerizable Formulations

A photopolymerizable formulation consists in (i) a monomer/oligomer matrix (the monomer plays the role of a reactive diluent to adjust the viscosity of the formulation; it readily copolymerizes), (ii) a PI or a PIS, and (iii) various additives, e.g. flow, slip, mist, wetting, dispersion agents, inhibitors for handling and fillers, plasticizers, matting or gloss agents, pigments, and light stabilizers according to the applications.

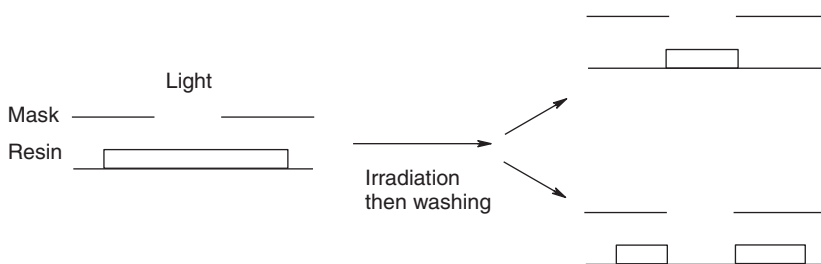
#### 1.1.6 UV Curing

Originally, UV curing is a word that designs an ever-expanding industrial field [7, 11, 21, 41–45] where light is used to transform a liquid photosensitive formulation into an insoluble solid film for coating applications through a photopolymerization reaction. Although it also includes electron beam curing, the term “radiation curing” is often used instead of “UV curing.” “Photocuring” is a practical word that refers to the use of light to induce this rapid conversion of the resin into a cured and dried solid film. Film thicknesses typically range from a few micrometers to a few 100  $\mu\text{m}$  (and even more; high thicknesses can now be photopolymerized) depending on the applications. In 3D printing technologies, the idea consists in building up a solid object through a layer-by-layer photopolymerization procedure. Today, many novel applications are found in other areas.

#### 1.1.7 Imaging

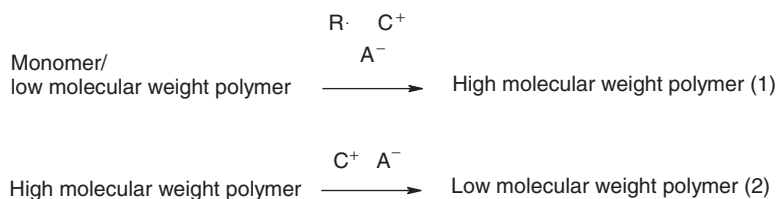
In the imaging area, an image is obtained according to a process largely described in the literature, e.g. [9, 10, 35]. The resin layer is irradiated through a mask. A reaction takes place in the irradiated areas. Two basically different reactions can occur (Scheme 1.3): (i) a photopolymerization or a photo-cross-linking reaction that renders the film insoluble (using a suitable solvent allows to dissolve the monomer present in the shadow areas; after etching of the unprotected surface and bake-out of the polymerized film, a negative image is thus formed), and (ii) a depolymerization or a hydrophobicity/hydrophilicity change (that leads to solubilization of the illuminated areas, thereby forming a positive image).

Photopolymerizable formulations



**Scheme 1.3** Different processes in imaging area.

Free radical photopolymerization (FRP) and photo-cross-linking (Scheme 1.4) lead to a negative image through (1). The acid- or base-catalyzed reaction (Scheme 1.4) leads to either a negative image (1) or a positive image (2). FRP and photo-cross-linking lead to a negative image through (1). The acid- or base-catalyzed reaction leads to either a negative image (1) or a positive image (2).

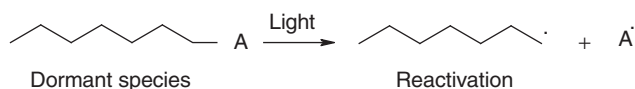


**Scheme 1.4** Chemical mechanisms.

In microelectronics, such a monomer/oligomer or polymer matrix sensitive to a light source is named a photoresist. In the imaging technology, the organic matrix is called a photopolymer. Strictly speaking, a photopolymer refers to a polymer sensitive to light, but this word is often used to design a monomer/oligomer matrix that polymerizes under light exposure. The term “photomaterial” refers to an organic photosensitive matrix that leads, upon irradiation, to a polymer material exhibiting specific properties useful in the nanotechnology field; it could also design the final material formed through this photochemical route.

### 1.1.8 Controlled Photopolymerization

Conventional photopolymerization reactions lead to a dead polymer. On the opposite, a controlled photopolymerization is a living reaction where a formed polymer chain (considered as a dormant species) can be reactivated upon light exposure in order to start a novel polymerization (Scheme 1.5).



**Scheme 1.5** Light activation of dormant species.

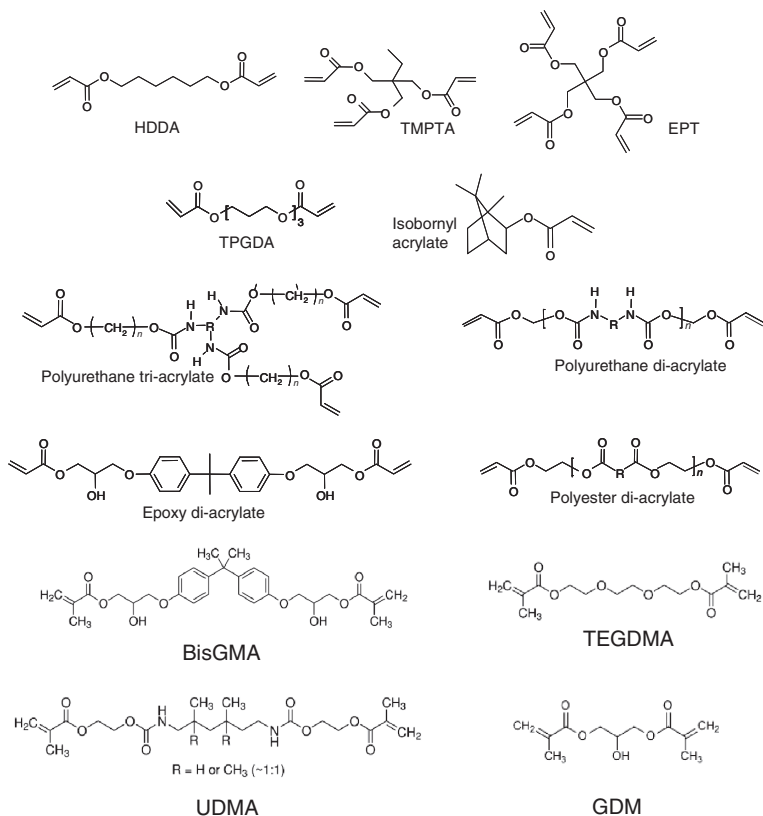
## 1.2 Photopolymerization Reactions

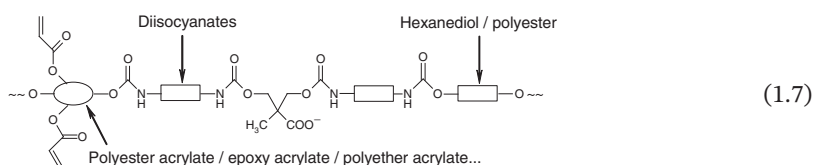
### 1.2.1 Monomers and Oligomers in Photopolymerization Reactions

Details can be found in Refs. [1–40]. The following sections only focus on the examples of usual and representative monomers/oligomers used in the photopolymerization area as well as some considerations on the reactions where they are involved.

### 1.2.1.1 Monomers/Oligomers in Radical Photopolymerization

Typical monomers and oligomers are based on acrylates and methacrylates such as trimethylolpropane triacrylate (TMPTA), 2-hydroxy ethyl methacrylate (HEMA), 2-hydroxyethyl acrylate (HEA), hexanediol diacrylate (HDDA), tetrapropylene glycol diacrylate (TPGDA), 2-(dimethyl-amino)ethyl methacrylate (DMAEMA), poly(ethylene glycol)methyl ether methacrylate (PEGMA), poly(ethylene glycol)diacrylate (PEGDA), triethyleneglycol dimethacrylate (TEGDMA), epoxy diacrylate oligomer diluted with 25% of tripropyleneglycol diacrylate monomer (EpAc), bisphenol A-glycidyl methacrylate (Bis-GMA), TEGDMA, and so on (see e.g. (1.7)). They possess sometimes a strong odor and exhibit skin irritating properties. Unsaturated polyester resins dissolved in styrene were well known in the curing of glass-reinforced materials. Owing to the current pressure of new environmental regulations, the interest for solventless systems, e.g. water-soluble media, emulsions, dispersions, and increases; reactive monomer/oligomer cross-linkers can be added (Chapter 17). Many novel matrices are continuously proposed. A growing interest is noted in the use of new starting monomer structures for getting novel end use properties, low-toxicity monomers, renewable monomers, and reworkable materials.



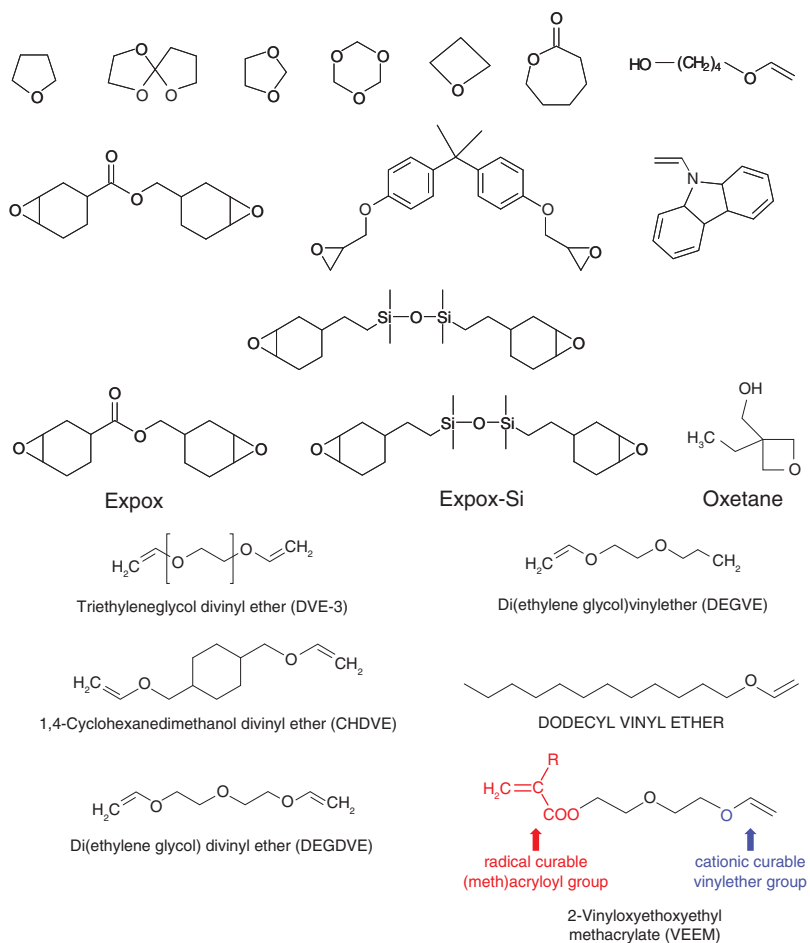


The FRP of multifunctional monomers and oligomers in film is very fast (in the one second time range under high-power lamps in industrial conditions) and generally sensitive to the presence of oxygen. It presents a relatively slow post-effect. Under continuous laser sources, the exposure time can drop down to 1 ms or less. The role of the photoinitiator is important for getting a suitable photosensitivity of the formulations under UV to NIR lights, LED exposures, and air (Chapters 3, 7, 10, 11, 13, and 15). Oxygen inhibition significantly affects the top surface layer and the network structure in terms of physical properties. Photopolymerization of thick clear coatings (centimeter range or several tens of centimeter as can be seen in Chapter 18) can be achieved, provided a suitable photoinitiating system is used.

These radical polymerizations can be carried out not only in traditional reactions in film as mentioned above but also in many other experimental conditions such as in the following examples. Polymerization reactions of acrylates under red/NIR lights are accompanied by the production of heat that likely ensures an acceleration of the monomer conversion and gives the opportunity to get an efficient in-depth curing (see Chapter 18). Using a photochemical process, the polymerization of (meth)acrylate-based self-assembled systems allowing fast initiation rates at room temperature was developed (see Chapter 17). Acrylate-functionalized polyesters or unsaturated polyester/acrylic functional polyurethane have been considered attractive compared to liquid finishes in photopolymerization of powder formulations. Cross-linked copolymers can be formed as interpenetrating polymer networks (IPNs) combining the properties of two polymer backbones (e.g. acrylate/epoxide and acrylate/vinylether) using the hybrid cure technique (see Chapter 17). Radical reactions involving acrylates or methacrylates are largely encountered in controlled or living radical photopolymerizations (Chapter 16) and are highly interesting as the activation and reactivation arise under exposure to a light source (on/off procedure) at room temperature. Acrylates are also involved in hybrid sol-gel photopolymerization (Chapter 17). Photoactivated redox polymerization of acrylate- or methacrylate-based monomer structures is emerging as an elegant solution to combine the top surface efficiency and temporal control of a photopolymerization process with the interstitial robustness of a redox polymerization (Chapter 17). Radical matrices (based on acrylates) are also largely used in two-photon absorption-induced polymerization (Chapters 13 and 19) as well as in dual-cure photopolymerization reactions (pregelification followed by complete curing, surface cure followed by body cure, UV irradiation, and thermal drying or UV curing followed by air drying).

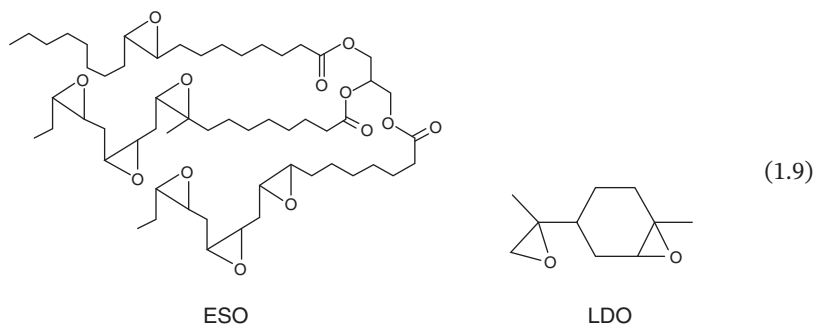
### 1.2.1.2 Monomers/Oligomers in Cationic Photopolymerization

The range of available cationic monomers and oligomers, e.g. (1.8), has been largely expanded. THF, lactones, acetals, and cyclohexene oxide (CHO) are examples of monofunctional monomers. Epoxides, e.g. 3,4-epoxycyclohexane methyl 3,4-epoxycyclohexyl carboxylate (EPOX), bisphenol A diglycidyl ether (DEGMA), and vinyl ethers, e.g. triethylene glycol divinyl ether (DVE-3) and *N*-vinylcarbazole (NVC), are very widely used and are known to give coatings with high thermal capability, excellent adhesion, good chemical resistance, and environmentally friendly characteristic. Vinyl ethers polymerize faster than epoxides (e.g. cycloaliphatic diepoxide). Cyclic ethers such as oxetanes can be alternatives to epoxides for getting faster curing speeds in industrial lines. A proper selection of novel cationic monomers, organic-inorganic hybrid resins, modified usual cationic monomers, renewable monomers (e.g. (1.9)), or dual-cure formulations helps in the design of high-performance systems (see Chapters 5 and 19).



(1.8)



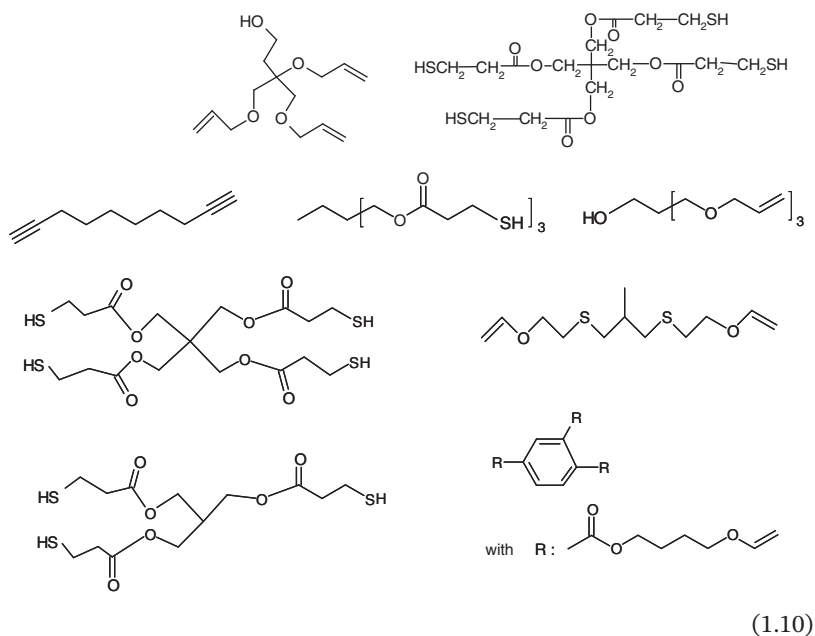


The cationic photopolymerization (CP) in a film is fast, usually insensitive to oxygen (except in free radical promoted cationic photopolymerization (FRPCP) where novel photoinitiating systems have to be used to overcome this drawback; see Chapter 12), and sensitive to moisture and water. An important dark post-effect is noted (see Chapter 5). The molecular origin of the induction period is discussed in Ref. [46].

Cationic monomers are also used in living/controlled polymerizations, IPN synthesis, sol-gel polymerizations, and two-photon polymerizations (Chapters 16, 17, and 19). UV deblockable acid releasing systems (known as photolabile systems) allow to start a cross-linking reaction (of epoxide groups) on demand as the generation of the acid is triggered by light exposure (Chapter 6).

### 1.2.1.3 Monomers in Thiol-ene Photopolymerization

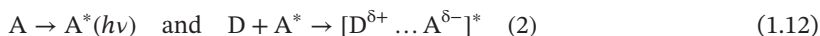
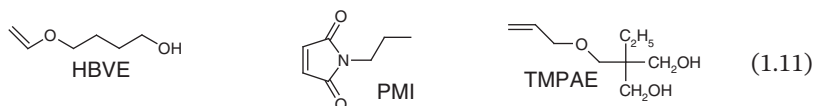
A lot of olefins (allyl ethers, vinyl ethers, allylic urethanes, ureas and phosphazenes, vinyl-functionalized silicones, norbornenes, etc.) and di-, tri-, and tetra-functional thiols have been proposed. Examples are shown in (1.10).



Thiol-ene photopolymerization shows some interesting features: very fast process, low or even no oxygen inhibition effect, and formation of highly cross-linked networks with good adhesion, reduced shrinkage and stress, and improved physical and mechanical properties. The reaction refers to a step-growth addition of a thiol to the double bond (vinyl, allyl, acrylate, methacrylate, etc.). The recent huge developments in thiol-ene and related thiol-ene chemistries are presented in Chapter 17.

#### 1.2.1.4 Monomers in Charge Transfer Photopolymerization

Maleimides (absorption around 300–350) and vinyl ethers (absorption below 250 nm) are representative monomers (1.11). A photoinitiator-free charge transfer polymerization (1.12) refers to a reaction between a monomer containing an electron-poor moiety A and a monomer bearing an electron-rich moiety D that forms a charge transfer complex CTC whose absorption is red shifted (Chapters 4 and 17). Such CTCs absorb above 350 nm. A photoinitiator can also be added (homopolymerization and cross-propagation occur).



#### 1.2.1.5 Monomers in Anionic Photopolymerization

Cyanoacrylates are suitable anionic monomers. UV deblockable base releasing systems are known for an anionic ring opening of epoxides (see also Chapter 6). The use of AP is rather limited in industrial applications as it should be carried out in the absence of impurities and compounds sensitive to nucleophiles.

#### 1.2.1.6 Monomers in Photoinduced Copper-Catalyzed Azide-Alkyne Cycloaddition

Multifunctional azide and alkyne monomers having triazole linkage are used (Chapter 17). Photoinduced copper-catalyzed azide-alkyne cycloaddition (photo-CuAAC reaction) represents an important new photopolymerization strategy where the significant interest of the thermal process is improved by the addition of a spatial and temporal control brought out by the light.

#### 1.2.1.7 Monomers in Photoactivated Hydrosilylation Reactions

Hydrosilylation reactions use silicone polymers containing Si-H/Si-vinyl and Si-H/Si-epoxide or silanes and triple bonds (see Chapter 17).

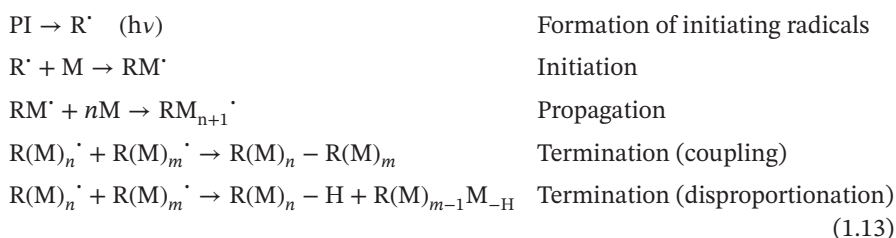
## 1.2.2 Monitoring the Photopolymerization Reaction

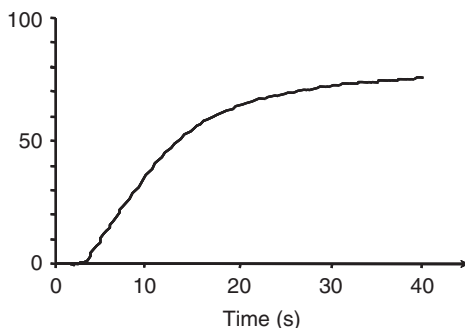
The investigation of the photopolymerization reactions is based on different kinds of analytical methods extensively reported in the past in the relevant literature or in books (see in Refs. [11, 21, 27, 30, 39, 42]). The most popular methods are (i) FTIR and real-time FTIR analysis (measurement of the monomer conversion from an IR band as a function of light exposure time, (ii) photocalorimetry (photo-DSC; measurement of the total amount of evolved heat that is related to the conversion), (iii) photorheology, and to a lesser extent (iv) optical pyrometry (measurement of the sample temperature rise that reflects the monomer conversion). Other miscellaneous less traditional methods have been cited, in particular infrared spectroscopy in attenuated reflection geometry with variable angle of incidence (VA-ATR-FTIR) [47], Raman confocal microscopy where the main interest is the analysis of the side surface of the sample at different distances from the irradiated surface (e.g. [48, 49]), thermal imaging for the analysis of thick (filled) curable coatings (see examples in Chapter 18) [50], magnetic levitation for the FRP of low molecular weight monomers exhibiting a large change in density upon polymerization [51], rheometric quartz crystal microbalance measurements at a frequency of 15 MHz for the direct evaluation of the rheological properties of the film [52], positron annihilation technique and NIR photorheology for the investigation of the microstructural free volume evolution during a photopolymerization [53], and real-time near-infrared photorheometer analysis for evaluating the conversion of a cured layer at a constant cure depth of vinyl ester-based biophotopolymers [54].

## 1.2.3 Kinetic Laws in Photopolymerization Reactions

### 1.2.3.1 Radical Photopolymerization

The different steps of a radical photopolymerization reaction are recalled in Eqn. (1.13). Under light irradiation of the PI, initiating radicals  $R\cdot$  are created. Then, they react with the monomer  $M$  to give the first monomer radical. The propagation of the reaction takes place through the subsequent addition of monomer units to the growing macroradical. Finally, the last step is the mono- or bimolecular termination reaction, depending on the experimental conditions. The bimolecular termination occurs through the recombination of two polymer chains (coupling is preferred for radicals presenting a small steric effect) and disproportionation (that is more important with disubstituted radicals). The monomolecular termination (radical occlusion) arises when the photopolymerizable resin becomes so viscous or rigid that the diffusion of the remaining monomer close to the reactive centers is prevented.





**Figure 1.1** Typical time evolution of the radical photopolymerization reaction of an acrylate monomer.

During the reaction, consumption of the monomer double bonds occurs. The photopolymerization profile (or the conversion–time curve) has a characteristic S-shape (Figure 1.1) and can be divided into three different regimes: (i) in the early stages after the light illumination, the excited states and the reactive species react with the inhibitors such as oxygen, stabilizers (see below) leading to an induction period during which the polymerization hardly starts; (ii) when all the inhibitors are consumed, the reactive species react with the monomer and lead to the formation of macroradicals that propagate (at low conversion, change of refractive index already occurs); thus, the polymerization rate rapidly increases to reach a maximum value  $R_p^{\max}$  (the medium becomes tack-free); and (iii) the medium becomes more and more solid and the polymerization reaction slows down until a plateau is reached for conversion. An important problem encountered in FRPs is the volume shrinkage that is attributable to the contraction of the material following the single- to double-bond conversion.

Once the light irradiation that has induced the photopolymerization has been turned off, a dark polymerization (also referred as post-effect) can take place and contributes to the further consumption of the residual monomer. A radical photopolymerization exhibits a relatively low post-effect [55]. For example, after switching off the light at 50% conversion obtained in 0.3 second for a polyurethane acrylate, the increased conversion is  $\sim 10/15\%$  (after 1 second in the dark). This post-effect is due to the presence of long-lived radicals trapped in the polymer network that can be recorded by ESR after a few hours of storage of the cured film in air and room temperature. The final conversion of the monomer remains lower than 100%.

In the quasi-linear part of the % conversion vs. time plot of a radical photopolymerization in a film where the termination occurs through a bimolecular reaction, the rate of polymerization  $R_p$  and the initiation rate  $R_i$  are given, as in solution, by the usual relationship Eq. (1.14), where  $k_p$  is the propagation rate constant,  $k_t$  is the termination rate constant,  $[M]$  is the monomer concentration,  $I_{\text{abs}}$  is the amount of energy absorbed at the considered wavelength, and  $\varphi_i$  is the initiation quantum yield (the number of starting chains per photon absorbed). The polymerization quantum yield  $\varphi_m$  relates to the number of monomer units polymerized per photon absorbed.

The kinetic chain length  $l$  depends on  $\varphi_m$  and  $\varphi_i$ :

$$R_p = (k_p/k_t^{0.5}) R_i^{0.5} [M] \quad \text{with : } R_i = \varphi_i I_{\text{abs}} = \varphi_i I_0 (\lambda_m) [1 - \exp(-2.3\epsilon_m l c)]$$

$$\text{and } \varphi_m = R_p / I_{\text{abs}} \quad \text{and } l = \varphi_m / \varphi_i \quad (1.14)$$

The polymerization quantum yield  $\varphi_m$  observed with multifunctional acrylates in film can be very high (e.g. in the range of 200–13 000 under air or 20 000 in laminated conditions) [56]. The kinetic chain length is typically in the range of 10 000–50 000 for the most reactive formulations.

In the photoresist and imaging technology fields, the photosensitivity of a formulation ( $S = t_{1/2} I_{\text{abs}} h\nu$ ) corresponds to the amount of energy (often expressed in  $\text{mJ cm}^{-2}$ ) required to polymerize half of the reactive functions (50% conversion in the time  $t_{1/2}$ ). Photosensitivities in the imaging area can be as low as  $0.1 \text{ mJ cm}^{-2}$ .

### 1.2.3.2 Cationic Photopolymerization

The kinetic scheme for a CP is more complicated [32]. The Brønsted  $\text{H}^+$  or the Lewis acid  $\text{LA}^+$  created upon light exposure of the cationic PI reacts with a monomer unit. The propagation is ensured by the further reaction of the macrocation with the monomer. The termination of the CP is generally due to the presence of nucleophilic species such as water, amino- or hydroxyl-containing compounds, etc. In the case of polymerization of epoxides or vinyl ethers, the polymerization proceeds by a ring opening or a double bond addition, respectively, resulting in a linear polyether.

The polymerization rates are generally lower than those obtained for acrylate monomers because of the low propagation rate constants: e.g. the rates of the polymerization reaction (carried out under a laser beam) of a cycloaliphatic epoxide and a polyurethane acrylate are in a 1 : 1.6 ratio. The nucleophilic character of the counteranion is of prime importance (Chapter 5). Indeed, a strongly nucleophilic anion prevents an efficient reaction of the cationic center with the monomer. The initiation rate  $R_i$  is defined as in Eq. (1.14). Kinetic rate constants of epoxides are accessible. The polymerization quantum yield of a diethyleneglycol divinylether (DVE) is high. The post-effect is important.

### 1.2.3.3 Dependence of Photopolymerization Rate

The rates of polymerization  $R_p$  of a photopolymerizable formulation (e.g. a few tens of micrometer thick) are a function of both

- (i) the intrinsic parameters that depend on the properties of the monomer (propagation and termination rate constants and chain transfer) and the photoinitiator (its chemical structure as seen along the following chapters governs the photochemical and chemical reactivity ( $\varphi_i$ ) and the absorption properties ( $\lambda$ ,  $\epsilon$ )).
- (ii) the experimental conditions (photoinitiator and monomer concentrations, sample thickness, light intensity  $I_0$ , temperature, spectral and time distribution of light, and presence of air).

All the  $R_p$ s dependences were originally studied in many papers (see Chapters 8 and 9) dealing with radical and cationic photopolymerization reactions in solutions

and in films. The observed conversion depends on film thickness. For example, in a polyurethane acrylate matrix, the double bond conversions after 1.5 seconds of exposure under air were evaluated, in a given system, as 5%, 20%, 40%, 60%, and 70% for thicknesses 3, 6, 10, 24, and 30  $\mu\text{m}$ , respectively. This phenomenon is due to the fast diffusion of oxygen into the film (see below and Chapters 2 and 13). Moreover, the penetration profile of the light in a film depends on the optical density, i.e. on the PI concentration and the wavelength (through  $\epsilon$ ). For example, the fraction of light absorbed by a 30  $\mu\text{m}$  film in a given condition can change from  $\sim 10\%$  to 60% upon a 10-fold increase of the concentration or  $\epsilon$ . Upon a 100-fold increase,  $\sim 100\%$  of the light is absorbed within 10  $\mu\text{m}$  (see also Chapter 18).

In the fast photopolymerization reactions for coating applications, less than 10–15% of the photoinitiator is consumed during the light exposure. When the photolysis of PI leads to colored products, an inner filter effect appears: photons are absorbed by these photolysis products and a less amount of photons is absorbed by PI. Interesting PIs might be those that bleach under irradiation (see Chapters 3, 4, 7, 11, and 14). When increasing the concentration, the PI absorption properties might be modified (e.g. in a dye where aggregation processes can occur: both the concentration and the  $\epsilon$  values are changed at the same time).

In a radical film polymerization,  $R_p$  is very often proportional to  $I_0^{0.5}$ . Other dependences occur (i) in a matrix exhibiting unimolecular termination when a tight network is formed and decreases the chain mobility or (ii) when a more complicated kinetic scheme is involved in the system, for example, in biphotonic processes (see below) where the consecutive absorption of two photons is required can sometimes arise in photoinitiators in conventional curing.

#### 1.2.3.4 Laser-Induced Photopolymerization

The laser-induced polymerization with extremely high power densities exhibits some particular features with respect to the conventional irradiation by usual lamps. The polymerization develops very rapidly, e.g. within the 10  $\mu\text{s}$  range when using 800  $\text{W cm}^{-2}$  delivered by a focused CW  $\text{Ar}^+$  laser compared to the 0.5, 5, and 50 ms time range for a 400  $\text{W cm}^{-2}$  CW  $\text{Ar}^+$  laser, a 10  $\text{W cm}^{-2}$  UV source, and a 1  $\text{W cm}^{-2}$  UV source, respectively) [57]. After an intense laser irradiation, dark polymerization can take place even for a radical polymerization. The ultrafast photopolymerization reaction is particularly effective in applications such as laser direct imaging or stereolithography and allows the formation of a solid polymer by a short and intense pulse after which the material is expanded within few seconds. The intense laser pulse creates a high concentration of initiating species that affects the polymerization in two different ways. First, it drastically increases  $R_p$ . Second, the dissolved oxygen is completely consumed at the early stage after the light exposure. The corresponding time  $t_{\text{th}}$  (gel point) is used to define a threshold energy  $E_{\text{th}}$  to have an insoluble polymer ( $E_{\text{th}} = I_{\text{abs}} t_{\text{th}}$ ).

With pulsed repetitive lasers, a single UV pulse is sufficient to produce a tack-free surface or to allow a complete insolubilization of oxygen-free resins. The repetition rate has a marked effect on both the polymer yield and the molecular weight distribution, presumably because the polymerization develops to a high extent in the

dark period between two consecutive pulses separated by a few seconds or more. With femtosecond lasers, very high power densities are reached in each pulse of light, which enables two-photon absorption processes (Chapters 2, 13, and 19) [58].

When the polymerization process requires the same energy regardless of the light intensity, it obeys to the reciprocity law (Chapter 2). Interestingly, the formation of the polymeric network was found to linearly depend on the light intensity. Indeed, increasing the laser intensity leads to the generation of more radicals, and therefore, the kinetic chain length decreases. This could affect the final properties of the materials.

### 1.2.3.5 Kinetics of the Photopolymerization in Bulk

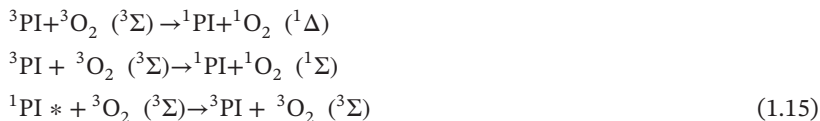
The kinetics of a polymerization reaction corresponds to the analysis of the evolution of the monomer conversion as a function of time. This evolution is accompanied by a change of the physical properties of the medium. The complete investigation of the overall kinetics of the fast film photopolymerization of multifunctional monomers is rather a hard and complex task (see Refs. [59, 60]). In a quasi-stationary regime, the usual  $R_p$  expression recalled above (Eq. (1.34)) for a free radical chain process is successfully applied only at the early stages of such a polymerization. A network is rapidly formed, even at low conversion, and the viscosity increases: as a consequence, the propagation  $k_p$  and the termination  $k_t$  rate constants change as a function of the conversion as well as the initial quantum yield, which is dependent on the cage-escape reactions of the radicals. Relationships have been proposed. The network formation of a diacrylate polymer network from the low-viscous initial state to the polymer gel has been modeled [61]. Cage effects and magnetic field effects are treated in Ref. [62].

Termination, transfer, and propagation kinetics [63, 64]; chain initiation and termination [65]; chain length-dependent termination [66]; and  $\beta$ -scission rate coefficient in acrylate radical polymerization [67] are continuously investigated using pulsed laser polymerization (PLP), PLP size exclusion chromatography (PLP-SEC) [68], SEC-ESI (electrospray ionization) MS (mass spectrometry) [69], or single pulse pulsed laser polymerization electron paramagnetic resonance (SP-PLP-EPR) connected with theoretical calculations (ab initio-based kinetic Monte Carlo analysis [70]). The inhibition and termination reactions in the FRP of a diacrylic monomer-ethoxylated bisphenol A diacrylate initiated by an aryl phosphine oxide as well as the effect of the incident light intensity and the initial photoinitiator concentration were studied by kinetic modeling; an excellent agreement between the experimental and calculated conversion vs. time curves was observed [71].

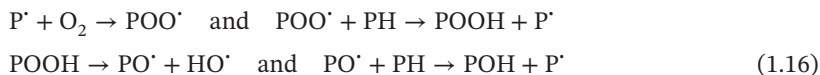
The fast photoinitiated FRP of semicrystalline acrylated oligomers in the solid and liquid state using a semiempirical scaling model is described in Ref. [72]. The well-known gel effect observed in liquid-state photopolymerization cannot be invoked to account for the reaction acceleration in the crystallized resin, the acceleration resulting from the buildup of the radical concentration in a diffusion-controlled process. The closed-form analytical expression of the conversion fits the experimental data.

### 1.2.4 Oxygen Inhibition

Oxygen is a paramagnetic species that possesses two unpaired electrons (each of them is located in the degenerate antibonding  $\pi^*$  orbitals). It is highly reactive toward triplet states and singlet oxygen is generated (see in (1.15) where  $^1\text{PI}$  stands here for the PI ground state and  $^1\text{PI}^*$  or  $^3\text{PI}$  for the excited states; see Chapter 2). It also increases the intersystem crossing pathway ( $^1\text{PI}^* \rightarrow ^3\text{PI}$ ). A  $\text{PI}/\text{O}_2$  electron transfer yielding an oxygen radical anion (the superoxide anion) as well as an addition biradical might also occur.



As known (see Ref. [73]), oxygen is also an efficient radical scavenger as exemplified by the usual photooxidation sequence leading to peroxy and oxy radicals (1.16). Oxygen leads to a number of detrimental effects in radical or radical-sensitized cationic photopolymerization, e.g. (i) the presence of an induction period, (ii) the decrease of the polymerization rate and the final conversion, (iii) the reduction of the polymer chain length, and (iv) the formation of a tacky surface on the coating. In photoinitiated polymerization, the excited  $\text{PI}/\text{O}_2$  interactions obviously decrease the yield in initiating species. Both the initiating and propagating radicals ( $\text{P}^{\cdot}$ ) are scavenged by  $\text{O}_2$  and yield highly stable and useless peroxy radicals (Chapter 8).

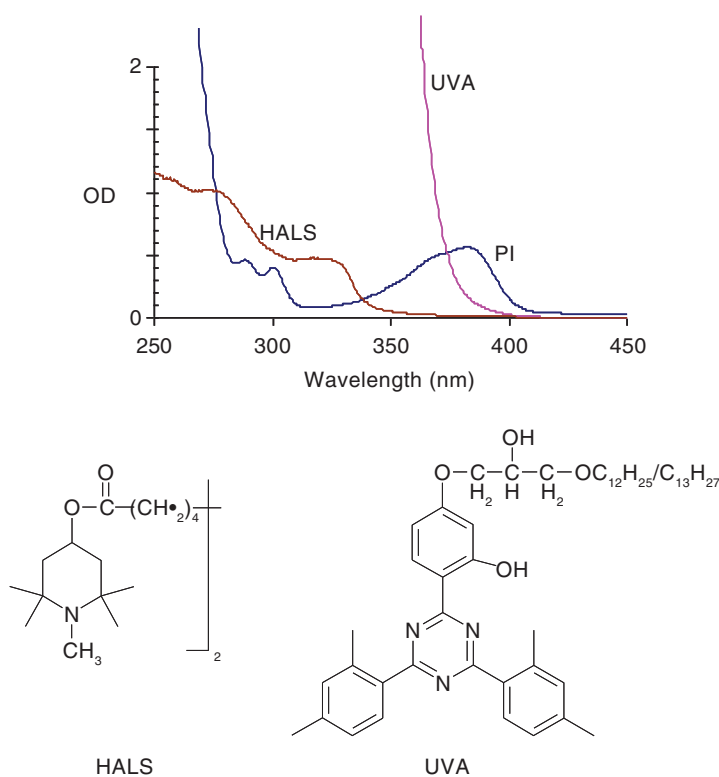


To overcome the inhibition effects of oxygen, several methods have been proposed (see Ref. [73] and Chapters 8, 9, and 13): (i) the purge with an inert gas; (ii) the use of high light intensities; (iii) the consumption of the dissolved oxygen in the film (using additives containing easily extractable hydrogen atoms such as amines, thiols, boranes, and particular monomers (e.g. *N*-vinylamides)); (iv) the use of trivalent phosphorus compounds (e.g. triphenylphosphine [TPP], 2-diphenylphosphinobenzoic acid [2dppba], and phosphates), organozirconiums that scavenge the peroxy and alkoxy radicals (Chapters 13 and 17) or 2-[2-(2-methoxyethoxy)ethoxy] acetic acid reported for the photo-FRP of acrylate-based and ceramic-filled inks [74]; (v) the incorporation of specific photoinitiators, oxygen scavengers, singlet oxygen traps, and photosensitizers (see Chapters 13 and 17); and (vi) the use of a physical barrier such as paraffin waxes or a protective film (polyethylene, polyol, etc.).

### 1.2.5 Role of Light Stabilizers

Upon the further exposure of a cured coating to light, a photooxidation of the polymer matrix occurs as a consequence of the influence of the UV/visible light, oxygen, humidity, and toxic agents of the atmosphere. This leads to a damage of the cured material (aging), which results in loss of gloss, cracking, color changes,





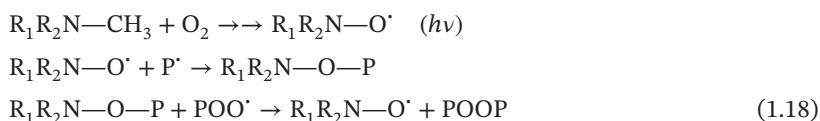
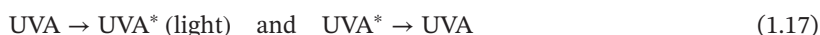
**Figure 1.2** Typical ground-state absorption spectra of a UVA, a HALS, and a given photoinitiator (a thioxanthone).

yellowing, blistering, and loss of adhesion (e.g. Refs. [75–78]). Photostabilizers or light stabilizers (LSs) incorporated in the photopolymerizable formulation before the UV curing step are capable of limiting these detrimental effects. For practical use, LS have to exhibit many properties, especially the absence of interaction with the formulation. The most usual LS are the UV absorbers (UVA) (based on 2-(2-hydroxyphenyl)-benzotriazoles, 2-hydroxy-benzophenone, 2-hydroxyphenyl-triazines, etc.) and the sterically hindered amines HALS (e.g. derived from 2',2',6,6'-tetramethyl-piperidine) [79, 80].

The typical absorption spectra of a UVA and a HALS compound are shown in Figure 1.2. Although the PI/HALS interactions that have been discussed (see Chapter 4) are not negligible, the polymerization efficiency is generally weakly affected by the presence of UVA and HALS.

The deactivation of the electronically excited UVA where the H atom of the OH group has moved from oxygen to nitrogen occurs according to a non-radiative mechanism (associated with a back movement of the H atom) without any generation of radical species (1.17). A HALS predominantly behaves (1.18) as a chain breaking electron acceptor. The generated nitroxyl forms a nitroxide upon combination with

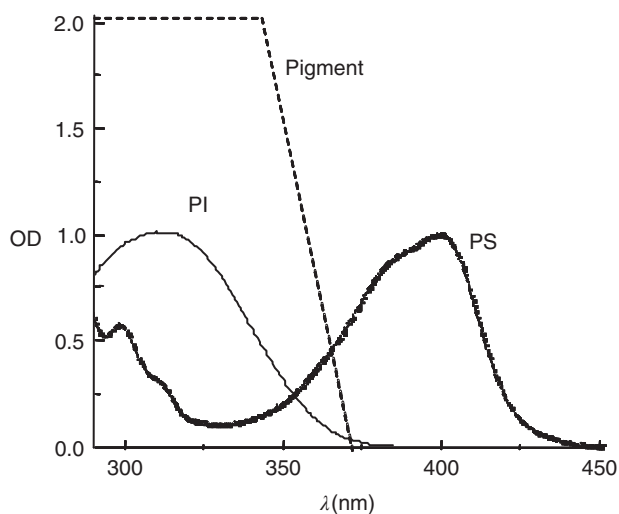
a radical. This nitroxide further reacts with peroxy radicals, forms a peroxide, and regenerate the nitroxide.



### 1.2.6 Competitive Absorption of Light by a Pigment

Pigments are colored chemical compounds, e.g.  $\text{TiO}_2$  (rutile or anatase), oxides sulfates, titanates, Fe oxides, sulfides, chromates, silico aluminates, mixed metallic oxides, carbon black, and organic structures. When incorporated into a photocurable coating, a pigment has several effects: (i) a direct light absorption that decreases the amount of light absorbed by the photosensitive system, (ii) a light reflection or diffusion capability that affects the transmission of the light through the film, and (iii) a possible photocatalytic or photosensitizing effect. The competitive light absorption by a pigment can be detrimental to that of the photoinitiator (PI). As a consequence, the design of a system containing a photosensitizer (PS) that absorbs in the spectral window offered by the pigment (Figure 1.3) or the proposal of PIs with suitable absorptions is obviously necessary (Chapter 2).

The UV curing efficiency of pigmented media (in terms of polymerized thickness) depends on the color and the nature of the pigment (transparent platelet-shaped



**Figure 1.3** Typical absorption of a white pigment, a photoinitiator PI, and a photosensitizer PS.

pigments, pearl luster pigments, metallic pigments, etc.). The photopolymerization of inks (that can be considered as thin pigmented coatings) under air require to use a high PI optical density and a highly reactive PI to ensure a complete curing of the aerated surface. In the case of thick pigmented coatings (e.g. paints), one strategy consisted in using a blend of two PIs: one for the surface cure and one for the body cure, the concentrations being adjusted to ensure both a fast surface polymerization and a good penetration of the light into the coating. Another one used multicomponent photoinitiating systems where additional thermal reactions occur. Novel efficient strategies are discussed in Chapter 18.

### 1.2.7 Role of Environment in the Polymerization Reaction

The environment (which is considered here as anything not related to the photoinitiating system itself and the monomer/oligomer medium) plays a role during the initiation step as well as the course of the polymerization reaction through the various compounds that can be present in the formulation and lead to different possible interactions with the monomer/oligomer and the photoinitiating system, e.g.:

- (i) *UVA and HALS as indicated above.* They exhibit a weakly inner filter effect. HALS can react with the photoinitiator.
- (ii) *Phenolic-type radical inhibitors.* They are present in the starting monomer (for ensuring a good shell life), e.g. hydroquinone methyl ether (HQME). As far as the initiation step is concerned, the excited states of a photoinitiator and the produced initiating radicals usually react with phenolic compounds through hydrogen transfer processes.
- (iii) *Phenols.* Tannins and phenolic species specially encountered in exotic woods are known as strong inhibitors in the polymerization of coatings in the wood finishing industry. Colored phenols can directly absorb the light, thus leading to a more or less important inner filter effect and react with the excited photoinitiator or the produced initiating radicals. In addition, as in thermal polymerization, the presence of phenols obviously affects the propagation and termination steps of the reaction.
- (iv) Oxy and peroxy radicals formed during the photopolymerization in aerated media. They usually react (see Chapter 7) with a lot of substrates, especially with the polymer chains (in chain branching or chain termination reactions).
- (v) Moisture and water in cationic photopolymerization reactions (Chapter 5).
- (vi) Surfactants in the photopolymerization reactions in heterogeneous media. The localization of the photoinitiator in the surfactant assembly, the effect of ionic vs. nonionic photoinitiators, the exit efficiency of the initiating radicals from the micelle, and the relative efficiency of the monomolecular vs. bimolecular reactions are some of the interesting topics to be considered (see Chapters 8 and 9).
- (vii) *Nanoparticles.* For example, the polymerization rates and monomer conversions increase in a UV-curable coating containing silicon nitride nanoparticles that scatter the light [81].

### 1.3 Implementation of Photopolymerization Reactions and Brief Overview of the Applications

As in thermally initiated polymerization, the light-induced photopolymerization reactions can be encountered in a lot of experimental conditions (in thin or thick films, solid state, multilayers, gas phase, aerosols, in vivo, organic or waterborne media, ionic liquids, self-assembled systems, under high or low intensity, monochromatic, or polychromatic sources, etc.) and/or with many different monomers, oligomers, or polymer media allowing large possibilities of applications or potential developments.

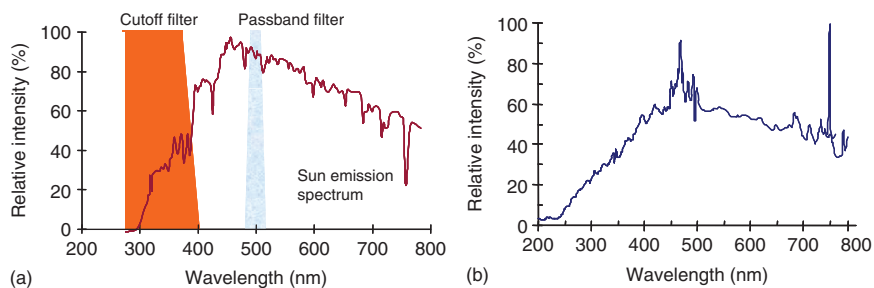
It is clear that the experimental conditions and devices are very different when going from one process to another or from a laboratory scale or a pilot scale to an industrial production line. The different devices will not be detailed here but they have in common to require a light source and well-adapted photoinitiating systems (see in the following chapters).

#### 1.3.1 Light Sources for Photopolymerization Reactions

##### 1.3.1.1 Electromagnetic Radiation

An electromagnetic radiation, usually referred as light, is characterized by a frequency  $\nu$  (in Hz) or a wavelength  $\lambda$  (in m) that are inversely proportional to one another  $\nu = c/\lambda$  ( $c = \sim 3 \times 10^8 \text{ m s}^{-1}$  is the speed of light in vacuum). The electromagnetic spectrum spans over a large frequency range that varies by many orders of magnitude. Because of the absorption properties of the photosensitive systems, the light used in photopolymerization reactions typically consists of (i) ultraviolet (UV) light (200–400 nm range classified as UVA: 320–400 nm, UVB: 290–320 nm, and UVC: 190–290 nm), (ii) visible light (400–700 nm), and (iii) near-infrared light (NIR; 700–1200 nm). Light has a dual wave–particle nature: it behaves like a wave in interference phenomena and as a particle (the photon) in the photoelectric effect.

A monochromatic radiation is considered as carrying an energy  $E = h\nu$  that corresponds to a photon ( $h = 6.62 \times 10^{-34} \text{ J s}$  is the Planck's constant). The energy of one mole of photons  $E_{\text{mole}}$  (called an Einstein) is defined by:  $E_{\text{mole}} = N_{\text{a}} E$ , where  $N_{\text{a}}$  is Avogadro's number ( $6.02 \times 10^{23}$ ). The intensity of radiation received by a sample at a given wavelength  $I_0(\lambda_0)$  is usually defined in photochemistry by the number of photons delivered by the source at this wavelength, in a defined wavelength interval, per surface unit and time unit. The amount of energy transported by the light beam (in  $\text{J cm}^{-2} \text{ s}^{-1}$ ) is expressed by  $E_{\text{beam}}(\lambda_0) = I_0(\lambda_0) h\nu_0$  where  $I_0(\lambda_0)$  and  $E_{\text{beam}}(\lambda_0)$  correspond to a photon density (number/ $\text{cm}^2 \text{ s}$ ) and a power density ( $\text{W cm}^{-2}$ ), respectively. In the case of a laser source,  $I_0(\lambda_0)$  usually refers to the number of photons per time unit, the irradiated area having the dimension of the laser spot;  $E_{\text{beam}}(\lambda_0)$  which is thus expressed in  $\text{J s}^{-1}$  corresponds to a power  $P$  (in W). The overall intensity  $I_0$  (or the total number of photons) delivered over a part of the electromagnetic spectrum is defined by an integral (Eq. (1.19)); the total energy  $E_{\text{beam}}$  is also an integral.



**Figure 1.4** (a) Example of an emission spectrum (of sun). Schematic transmission curves of typical filters (cutoff filter:  $T = 0\%$  for  $\lambda < 390\text{ nm}$  and passband filter:  $T = 100\%$  for  $500\text{ nm}$ ). (b) Emission spectrum of a xenon lamp.

$$I_0 = \int I_0(\lambda) d\lambda \quad \text{and} \quad E_{\text{beam}} = \int E_{\text{beam}}(\lambda) d\lambda \quad (1.19)$$

### 1.3.1.2 Characteristics of a Light Source

A light source [82, 83] is characterized by an emission spectrum (Figure 1.4) that represents the photon distribution as a function of wavelength, i.e.  $I_0(\lambda) = f(\lambda)$ . The ordinate of such a spectrum is often presented in arbitrary units or as a relative intensity. Some absolute irradiance measurements can also be available when using a calibrated spectrometer. According to the type of light source, (i) either a polychromatic light (such as what is called a white light) or a monochromatic light (e.g. a green light at  $532\text{ nm}$  using a Nd-Yag laser) is delivered, (ii) the intensity can vary over several orders of magnitude (e.g.  $1\text{--}10\,000\text{ mJ cm}^{-2}$ ), and (iii) the light can also be emitted either continuously in time or as a pulse or a series of pulses, thereby leading to a wide range of luminous power densities. This results in a large panel of situations for the energy absorbed by PI, the concentration of the initiating species, the presence of biphotonic effects, etc.

When using a polychromatic light, a careful selection of wavelengths (Figure 1.4) can be achieved through the use of various glass filters. Interference and passband filters transmit wavelengths in a given interval; they are narrow (a few  $\text{\AA}$  for the former) or broader (a few nanometers or a few  $10\text{ nm}$  for the latter). This allows to get a “quasi” monochromatic light source. Cutoff filters eliminate a part of the spectrum, e.g. the UV light (when a visible light exposure is only required) or the IR light (if a heating of the exposed sample has to be avoided).

The measurement of the light intensity is done in practice by radiometers that provide a calibrated flat output response in a given wavelength range in terms of the luminous energy per second and surface unit ( $\text{J s}^{-1}\text{ cm}^{-2}$  or  $\text{W cm}^{-2}$ ). As usually encountered in photochemistry [82, 84–88], chemical actinometers can also be used to calculate the number of photons.

### 1.3.1.3 Available Light Sources

The role of the light sources is crucial in a photochemical event [39, 42] so that a presentation of Hg or Xe lamps, laser beams, LEDs, or soft sources is necessary.

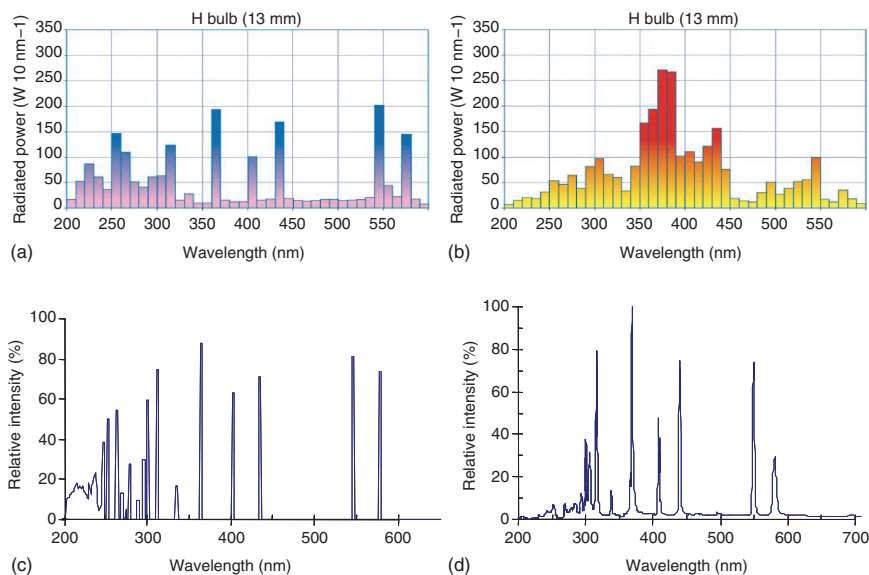
### 1.3.1.3.1 Xenon Lamps

The emission spectrum is continuous in wavelengths (Figure 1.4). Xenon Xe lamps emit a lot of heat but emit a high light intensity over a wide spectral range. In laboratory equipment, the light intensities of Xe and Hg–Xe lamps are typically  $\sim 60$  and  $200 \text{ mW cm}^{-2}$ , respectively.

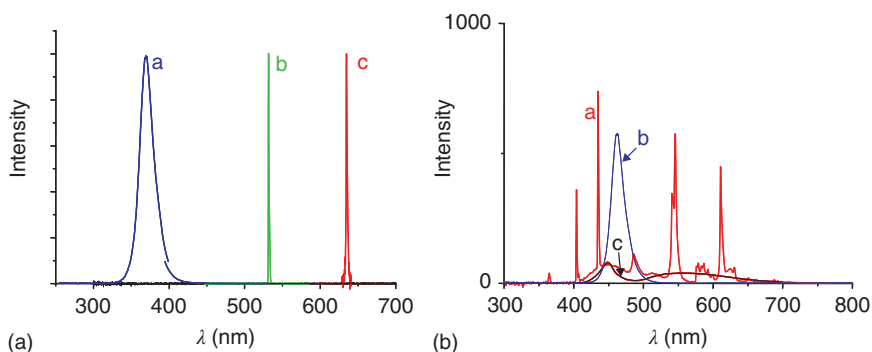
### 1.3.1.3.2 Mercury Lamps

Hg lamps emit a set of particular wavelengths with different intensities: 254, 313, 366, 405, 435, 546, and 579 nm. Commercial medium pressure Hg lamps for the UV curing technologies (electrical power  $\sim 60\text{--}240 \text{ W cm}^{-1}$ ; typical length of the lamp: 100–2300 mm) exhibit the spectrum shown in Figure 1.5c. High fluxes of photons (typically  $>1.2 \text{ W cm}^{-2}$  in the 280–445 nm range) are available. Hg lamps emit heat ( $>50\%$ ). Low-pressure Hg lamps mostly delivered photons around 254 nm. Among them, fluorescent lamps are Hg lamps that contain a fluorescent agent: the spectrum is changed and the intensity is very low. They are used as pregelification lamps to increase the core polymerization. Mercury lamps can be doped (e.g. by xenon, gallium, indium, lead, cobalt, and iron halides) in order to change the emission spectrum and generally to increase the light emission in the near UV/visible region around 410/420 nm, as can be seen in Figure 1.5a, b and d.

Contrary to usual Hg lamps where the Hg atoms are excited by an electric field, the excitation of Hg in the radio frequency-excited electrodeless lamps is provided by microwaves. Doped lamps are also available. These lamps have a high input power and emit a lower IR amount.



**Figure 1.5** (a,b) Typical emission spectra of different microwave powdered lamps. Source: reproduced with permission of Fusion Inc. (c) Typical emission spectrum of a mercury lamp. (d) Emission spectrum of a doped mercury lamp (Xe–Hg lamp) equipped with a 366 nm reflector.



**Figure 1.6** (A) Typical emission spectra of (a) 365 nm LED, (b) 532 nm diode laser, and (c) 635 nm diode laser. (B) Emission spectra (intensity in  $\mu\text{W cm}^{-2}$ ) of (a) a household fluorescent bulb, (b) a household blue LED bulb, and (c) a household white LED bulb.

#### 1.3.1.3.3 Light-Emitted Diodes LED

A light-emitted diode (LED) is based on a semiconductor material device. For example, LEDs can emit a light with an almost Gaussian distribution in a narrow wavelength range (FWHM), e.g. 40 nm for LEDs centered at 365 nm or 395 nm with an intensity about a few  $10\text{--}100 \text{ mW cm}^{-2}$  (Figure 1.6). The emission spectra exhibit a higher FWHM compared to that of a diode laser ( $<1.5 \text{ nm}$ ). Highly packed arrays of LED are possible (up to  $400 \text{ LED cm}^{-2}$ ). This allows light intensities up to 2 and  $20 \text{ W cm}^{-2}$  at 365 and 395 nm, respectively. As the light is delivered within a small wavelength interval, the output luminous power density per nanometer is 0.1 and  $0.5 \text{ W cm}^{-2} \text{ nm}^{-1}$  (at 365 and 395 nm) compared to  $0.2 \text{ W cm}^{-2} \text{ nm}^{-1}$  for a 100 W short arc lamp in the 365–440 nm range. Nowadays, the total power density (in  $\text{W cm}^{-2}$ ) over the whole emission spectrum can be much higher for a LED arrangement than for a mercury lamp. Today, LEDs are able to cover the whole wavelength range from the UV to the NIR, e.g. 365, 395, 405, 477, 525, and 850 nm.

The main benefits of LEDs are (i) low heat generation (no IR light); (ii) large range of color (no filter); (iii) low energy consumption; (iv) rugged and damage-resistant, no frequency interference, low operating costs, a little maintenance,  $\sim 50\,000$  hours of life, convenient portability; (v) safe and environmentally friendly (no mercury and cool to the touch); (vi) relatively low divergence of the light beam (their directional output can be exploited by clever designs such as light strips or concentrated arrays); and (vii) possible incorporation in programmed robots that can move the lamps to improve the curing of shadow areas. LEDs have gained a high potential. The adaptation of PIs and PISs to LED irradiations is discussed in Chapter 15.

#### 1.3.1.3.4 Laser Sources

Details on lasers [89] and laser applications in photopolymerization can be found in Refs. [5, 33]. Laser beams present specific characteristics: (i) a monochromatic light (this allows control of the light absorption and then the photochemical reactions; side reactions and local heating are reduced); (ii) large possibilities in wavelength selection; (iii) a high energy concentration onto a small surface (this ensures

a quasi-instantaneous curing and a reduced oxygen inhibition); (iv) a high spatial resolution, spectral selectivity, and narrow bandwidth of the emission (these properties are useful in holography); (v) an easy focalization (the photochemical event can be produced in a sample placed at a long distance from the light source); and (vi) a very short exposure time allowing a possible scanning of a surface by the laser spot, which behaves as a pencil of light (the direct imaging is affordable; high-resolution images can be obtained).

As in conventional sources, many lasers deliver the light continuously as a function of time. Some lasers can also emit the light as a (very) short pulse or a train of pulses. For example, a continuous-wave CW laser gives power values  $\sim 0.1$  kJ, a low intensity pulsed laser  $\sim 10$  kJ. This CW laser or this pulsed laser yields a higher power density compared to a conventional light source ( $\sim 10$  kW cm $^{-2}$  or  $\sim 1000$  kW cm $^{-2}$  vs.  $\sim 0.2$  kW cm $^{-2}$ ) because of their small beam diameters.

Many different lasers usable in the photopolymer area are available in the market. Examples of continuous-wave CW lasers are (i) argon ion lasers (emitting at 488 or 514 nm; the high power, up to a few watts, and the high quality of the beam were beneficial for the development of many fields such as holography, laser direct imaging [LDI] or computer-to-plate [CTP] technology), (ii) krypton ion lasers (various wavelengths from 406.7 to 676.4 nm), (iii) He–Ne lasers (at 633 nm), (iv) He–Cd lasers (325, 442 nm, etc.), and (v) pulsed excimer lasers (157, 193, and 248 nm) can be used in microelectronics for the manufacturing of integrated circuits. Repetitive pulsed lasers are used in PLP techniques. Femtosecond lasers (e.g. Ti:sapphire lasers) are used in two-photon polymerization. Semiconductor-based lasers or diode lasers operating at selected wavelengths (405, 457, 473, 532, 635, 830, 980, 1064 nm, etc.) with an output of  $\sim 0.01$ –4 W are now available and become an alternative to usual lasers (Figure 1.6). Their driving factors are (i) simple design (no complicated laser cavity), (ii) high power output, and (iii) easy stacking and arrangement (allowing the curing of complex forms). With laser diode arrays, the typical power density can average 10 kW cm $^{-2}$ .

#### 1.3.1.3.5 Sun and Soft Sources

Sun is a very convenient and inexpensive source of light but delivers a low intensity (typically  $< 5$  mW cm $^{-2}$  in the near-UV/visible wavelength range; see the emission spectrum in Figure 1.4), which is strongly affected by the weather, location, and year period. It might be of interest for particular outdoor or daylight indoor applications (Chapter 14). Visible light-induced polymerization is well documented as it will be seen later but works devoted to sunlight curing itself are rather scant.

With the actual need for green technologies, the development of new (photo) chemical systems and new soft irradiation conditions for photopolymerization reactions is ever required (Chapter 14). For example, the basic interests of household fluorescent bulbs FB (Figure 1.6), which already appeared in organic synthesis [90], might be the following: (i) the available higher luminous power in the 380–800 nm range ( $\sim 15$  mW cm $^{-2}$ ), (ii) the stability of this irradiation source, which is not affected by weather and location, (iii) the disposal of very safe light sources, and (iv) the use of commercial and cheap standard devices. In the same



way, compared to FBs, household LED bulbs (Figure 1.6) emit  $7\text{--}20\text{ mW cm}^{-2}$  in a selected quasi-monochromatic spectral range (e.g.  $\lambda_{\text{max}} \sim 462\text{ nm}$  for a blue LED bulb); white lights in a variety of color temperatures can also be delivered.

#### 1.3.1.3.6 Miscellaneous Sources

Whereas all the lamps described above emit a light whose intensity is constant as a function of time, flash lamps, and pulsed UV light sources deliver the photons in a single flash or a pulse of light (Chapter 15). Pulsed Xe lamps deliver lower heat. They are suited to specialty applications. Excimer lamps are discharge lamps. The emitted wavelength is a function of the gases which form the excimer. In particular, they can work at 308 nm or even at 222 or 172 nm in vacuum ultraviolet VUV devices (see Ref. [42] and references therein). It is known that UV lights can be generated from a plasma produced by a microwave excitation of suitable gases, and this was applied to the complete and regular curing of complicated objects (even a car body).

### 1.3.2 Brief Overview of the Application Areas

The various experimental constraints encountered in the applications (light source, matrix, and environment) play a significant role and explain why the design of suitable PISs is the subject of such intense research works. The very different areas where PIs and PISs are involved are detailed in Chapters 15–19. Polymerization reactions under light still open the way to a green technology in this twentieth century. Because of the government regulations toward health and environment, it continues to expand rapidly. Many practical aspects can be found in books (e.g. [1–40]), review papers (e.g. [91–93]), and in the Proceedings of the Radtech Conferences sponsored by the RadTech North America, RadTech Europe, or RadTech Asia Organizations and available in web sites (see also Chapter 19).

The largest part of the overall “photopolymer” market is found in the UV curing area (Chapter 19). The examples of applications in many fields of the day life include (see in Refs. [20–22, 38, 40, 44]) the following: (i) clear or pigmented coatings on a large variety of substrates (e.g. on wood, plastics, metal, papers, release papers, rubber, glass, textiles, optical fibers, inorganic oxides, magnetic media, displays, mobile phones, and game consoles) ensuring novel surface properties; (ii) the design of coatings having specific properties (e.g. for flooring, decorative, protecting, sound reduction, abrasion resistant coatings, antistatic, photoluminescent coatings, and antifogging films), packaging (with important safety considerations in food and beverage packaging), or pipe lining; (iii) the development of adhesives (laminating, pressure sensitive, structural, etc.) allowing strong bonds to glass, metal, plastics, and ceramics; (iv) the graphic arts area (printing plates, computer-to-plate systems, and UV drying of printing inks and ink-jets); (v) the rapid prototyping technologies (stereolithography, digital light processing, or 3D/4D printing); and (vi) the preparation of composites consisting of photocurable formulations where fillers and pigments are introduced. Various industrial areas (e.g. “coating industries,” medical sector, automotive area, and electronics) are concerned. Industrial PIs and PISs are shown in Chapter 14.

The market driving benefits of UV curing in operating lines of the coating industry remain: (i) rapid through-cure; (ii) low energy requirements; (iii) low-temperature treatments suitable for heat-sensitive substrates (pinewood, plastics, etc.), (iv) use of nonpolluting and solvent-free formulations (almost no volatile organic compounds (VOC)) or waterborne systems; (v) fast cure speeds; (vi) enhanced product durability; (vii) high surface quality for coatings; (viii) reduced throughput times in production, application versatility, small space requirements, relatively low investment, easy machine integration, and easy maintenance; (viii) low costs in material, production process, and waste management; and (ix) suitable adaptation for small series, high productivity, and very good price/performance ratio. The safety of the products and the light sources is seriously considered. Innovations are currently making headlines.

In addition to the coating area, other fields of applications are noticeably growing year after year (Chapter 19): e.g. (i) photoresists in microlithography, (ii) photocuring of polymer layers in organic electronics (organic solar cells, organic field effect transistors, organic light-emitting devices, etc.), (iii) laser direct imaging for the manufacturing of microcircuits, (iv) optics (holography, production of optical elements, etc.), (v) biosciences (e.g. biomaterials, 3D cell embedding, microencapsulation, lab-on-chip methodologies, dentistry, ophthalmology, etc.), and (vi) creation of micro- and nano-objects with a 3D resolution for various applications.

In high tech but also in more traditional sectors, many aspects that are relevant of the nanotechnology area (see Refs. [94, 95]) are explored for applications (e.g. elaboration of nanocomposites, micro- or nanostructured materials, nanoscale features, or incorporation of nanoscale metal particles having optical, electronic, magnetic, catalytic, or anti-aggregation properties). Academic and industrial interests are very important. Huge progresses have been done in the past ten years and a large growth is still expected.

The design of new photopolymerizable systems exhibiting novel properties, mechanical, physical, surface (e.g. hardness, adhesion, hydrophilicity, hydrophobicity, and low shrinkage), chemical (e.g. resistance to solvents), electrical, optical, magnetic, biocompatibility, and usage properties (e.g. low odor, low skin irritation, antibacterial, weatherability, and long-term stability), is continuously carried out. These properties are mainly obtained through a careful selection of the starting monomer/oligomer formulation: the photoinitiator has almost no influence except in the possible yellowing of the cured material, in the safe character of the final product, or, obviously, in the case of a bad curing. Many publications in the literature show the numerous perspectives that are now offered by the light-induced technologies and outline the dynamism of this research area (see in a recent book [39]). They also suggest that the PIs and PISs have to work in very specific and adapted conditions (see Part IV).

Several topics that receive a noticeable attention include (i) the development of safe light sources and soft conditions (Chapter 15); (ii) the preparation of well-defined polymers with a controlled chain length, functionality, and narrow molecular weight distribution for the preparation of a variety of novel polymer architectures (Chapter 16); (iii) the photopolymerization of thick coatings or dark

areas (e.g. in dentistry or in 3D printing), the key point being undoubtedly the photoinitiator as the penetration of the light is the decisive parameter (Chapter 18); (iv) the polymerization of waterborne coatings (Chapter 13); (v) the two-photon absorption-induced polymerization (Chapter 13); (vi) the development of efficient systems in aerated media (Chapter 13); (vii) the thiol-ene photopolymerization reactions (Chapter 17); (viii) the light-induced manufacturing of IPNs (Chapter 17); (ix) the photoactivated redox polymerization (Chapter 17); (x) the CuAAC photoreactions (Chapter 17); (xi) the photohydrosilylation reactions, the sol-gel photopolymerizations, the in situ incorporation of nanoparticles in films, the polymerization in ionic liquids and in organized media, and the hydrogel synthesis (Chapter 17); (xii) the NIR light-induced thermal polymerization (Chapter 18); and (xiii) the numerous applications in the biomedical area (Chapter 19).

The development of a green technology in the photopolymerization area occurs in three main directions where interesting progresses are noted:

- (i) Studies on the use of new light sources or novel applications of existing light sources for soft irradiation conditions have known a real development in the last years. Sunlight curing has been explored. Artificial light sources, more economic and emitting less UV, and less heat than the Hg lamps, such as LEDs, are now well accepted. The problems related to the photoinitiation step encountered in LED, household lamp (fluorescent bulbs and LED bulbs), and sunlight curing are discussed in Chapter 15.
- (ii) The search of natural compounds receives now a growing attention as (i) synthetic raw materials will become limited and (ii) the entire life cycle of the material has to be taken into account (production, durability, recycling, and waste). Apart from the design of new photopolymerizable compounds, there is now a greater emphasis on the search of efficient biosourced PIs (see Chapter 13).
- (iii) Decreasing the use of 100% organic formulations can be obtained through the design of water-based formulations such as water-reducible (homogeneous solution of the resin in water) and water-based dispersions (conventional resins dispersed in water with the aid of emulsifiers/surfactants). Oil and water-soluble PIs and PISs have to be adapted (Chapters 3, 4, 13, and 17).

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