

Article

Photopolymerization Reactions: On the Way to a Green and Sustainable Chemistry

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Abstract: The present paper reviews some aspects concerned with the development of green technologies in the photopolymerization area: use of visible light sources (Xe and Hg-Xe lamps, diode lasers), soft irradiation conditions (household lamps: halogen lamp, fluorescence bulbs, LED bulbs), sunlight exposure, development of very efficient photoinitiating systems and use of renewable monomers. The drawbacks/breakthroughs encountered when going on the way of a greener approach are discussed. Examples of recent achievements are presented.

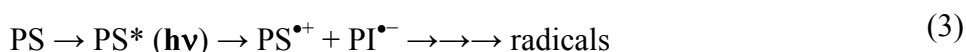
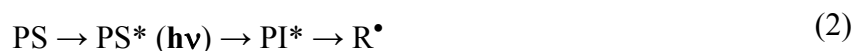
Keywords: cationic photopolymerization; radical photopolymerization; photoinitiators; visible light sources; soft irradiation conditions; sunlight exposure; LED; laser diodes; household lamps; halogen lamps; renewable monomers

1. Introduction

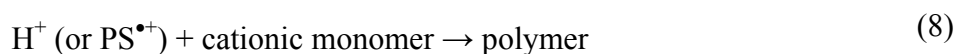
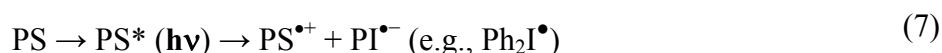
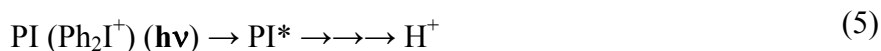
Photopolymerization reactions are commonly presented as belonging to a green technology characterized by low electrical power input and energy requirements, low temperature operation and no volatile organic compounds release (solvent-free systems) [1–18]. In industrial sectors, such as radiation curing, imaging, microelectronics, medicine or optics (with various and very different applications, e.g., in coatings, varnishes, paints, adhesives, graphic arts, printing plates, stereolithography, photoresists, laser direct imaging, computer-to-plate technology, holographic optical elements or tooth

repair), light-induced polymerization reactions have been very well-known for many years [19]. These reactions involve a polymerizable radical or cationic matrix and a more or less complex photoinitiating system (PIS) [19–26]. Mercury lamps are largely used as light sources together with doped Hg lamps or microwave powered lamps. The delivered lights in the 280–450 nm range often satisfactorily match the absorption of PIS. In the context of green chemistry, the avoidance of volatile organic compounds is also an important issue.

Free radical photopolymerization (FRP) is undoubtedly the most popular compared to cationic photopolymerization (CP). A PIS contains at least a photoinitiator (PI) and/or a photosensitizer (PS): PI (or PS) has to absorb the light [19]. Upon excitation, in FRP, PI becomes excited (PI*) and generates (1–4) a radical, R•, either directly through cleavage or in the presence of an electron/hydrogen donor. When PS is used and excited, the excitation has to move from PS* to PI by energy (2) or electron transfer (3): the same R• is formed or new ion radicals are created, respectively.



In CP (5–8), onium salts (e.g., the iodonium salt referred to here as Ph₂I⁺; several commercial derivatives that do not release benzene are known) are used as PI [19]. Their direct homolytic/heterolytic decomposition followed by hydrogen transfer reactions leads to a proton. Their photosensitized decomposition occurs according to energy (6) or electron transfer (7).



In free radical promoted cationic polymerization (FRPCP) (9–11), a radical, R•, is produced from a radical source (RS) (a PI or a PS can play such a role) and then oxidized by Ph₂I⁺ to form Ph₂I• and a cation, R⁺, suitable for the ring opening reaction (ROP) of epoxides or the cationic polymerization of vinyl ethers (the Ph₂I• species readily decomposes into PhI and Ph•) [19].



The PI, PS and RS have to be selected to absorb the irradiation wavelengths [19]. In FRP, the selection of near UV/visible photosensitive systems for industrial applications is quite easy (and almost feasible on laboratory scale experiments at any UV-visible wavelength). In CP, as the PIs mainly absorb in the UV, the search and the design of suitable PS compounds as energy or electron

donors for visible light-induced polymerizations are necessary, but this appears as a rather complex task for the photocuring of coatings in industrial lines. Due to its versatility, FRPCP is certainly one of the most interesting and promising ways for a cationic polymerization under exposure at $\lambda > 350$ nm (up to 700 nm), but the occurrence of efficient reactions (10 and 11) is not so trivial, and the oxygen quenching of the radicals is detrimental.

The development of photopolymerization reactions towards a green technology can be found in five directions:

(1) search for new PI or PS being able (i) to absorb the visible lights that are very often lost when employing conventional mercury lamps and PISs and/or (ii) to move the system towards a UV-free exposure (doped Hg lamps, Xe-Hg lamps, Xe lamps).

(2) use of newly developed high intensity LED or laser diodes operating at well-defined near UV/visible wavelengths avoiding the use of Hg-based lamps and the presence of more energetic UV wavelengths (254, 313 nm). Today, in industrial applications, LED technology allows highly packed arrays operating at 365 or 395 nm, together with a low heat generation, low energy consumption, low cost and low maintenance; the development of laser diode arrangements ensures high intensity monochromatic irradiations from the blue to the red part of the spectrum.

(3) development of PISs for soft irradiation conditions and use of low visible light intensity sources, e.g., household devices: halogen lamp, fluorescent bulbs and LED bulbs.

(4) use of sunlight, which is a cheap and inexhaustible energy source (but strongly affected by the weather and location) that might be of interest for (i) particular outdoor applications (e.g., for paint drying) and (ii) the possibility of curing large dimensioned pieces or surfaces without requiring any irradiation device.

(5) search of natural products or renewable monomers (the plant oil derivatives present attractive features, such as versatility, biodegradability and low cost).

In a general way, the questions that have to be solved for getting a high polymerization efficiency concern the PISs and the starting monomers, as well as their adaptation to the available light sources. In the present paper, we will (i) discuss the drawbacks/breakthroughs encountered when going on the particular way of a greener approach for photopolymerization reactions, (ii) define the key points for the design of a high performance PIS in such conditions and (iii) show, as examples, some of our new or recent achievements using soft illumination conditions (e.g., household lamps and sunlight exposure; typically $\sim 2\text{--}10$ mW/cm²), visible light irradiation (400 nm $< \lambda < 800$ nm), use of renewable monomers, *etc.*

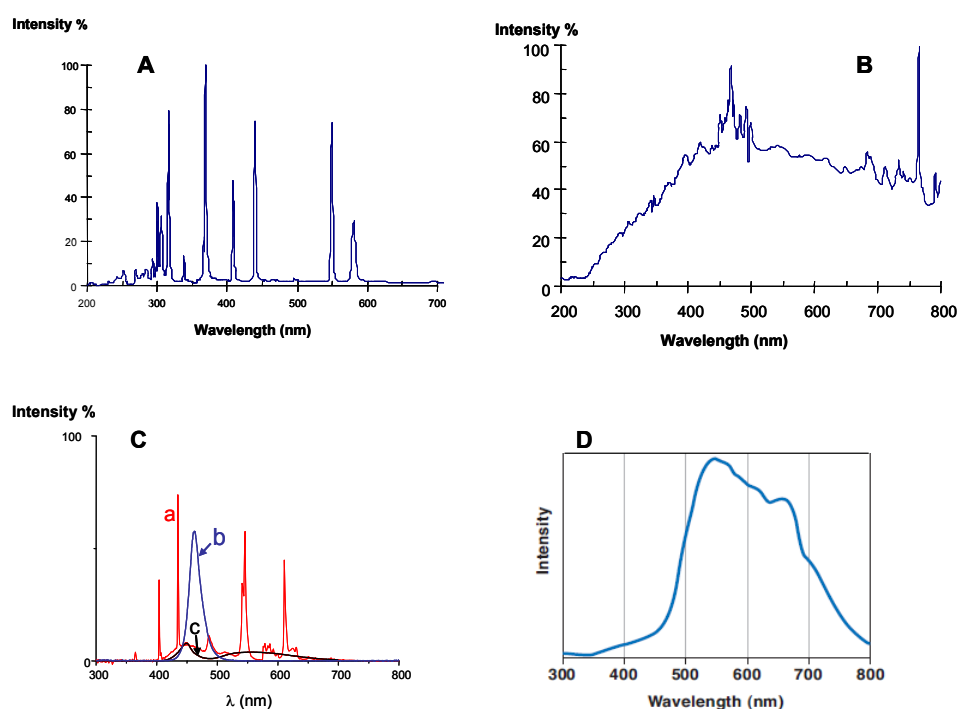
2. Drawbacks/Breakthroughs on the Way to Greener Photopolymerization Reactions

2.1. The Photopolymerization Reactions

In photopolymerization reactions [19], the matching of the PIS absorption spectrum with the emission spectrum of the light source, as well as the number of available incident photons, I_0 , is crucial. The absorption properties of PI, PS and PIS (ground state spectra and molar extinction coefficients, ϵ) play a decisive role, as the polymerization rate, R_p , is directly connected with the amount of light absorbed (I_{abs}): $I_{\text{abs}} = I_0 (1 - 10^{-\epsilon c l})$ where I_0 , ϵ , c and l stand for the incident light

intensity, the molar extinction coefficient, the photoinitiator concentration and the sample thickness, respectively. The delivered flux of photons can be very high with Hg lamps (Hg arc lamp, doped Hg lamps, electrodeless Hg lamps; typically $> 1\text{--}2\text{ W/cm}^2$), highly packed arrays of light emitting diodes (LED) at 365 or 395 nm (a few W/cm^2), Hg-Xe or Xe lamps and quite low with household devices (halogen lamps, fluorescent bulbs and white or blue LED bulbs; $<10\text{ mW/cm}^2$), diode lasers ($10\text{--}100\text{ mW/cm}^2$) or sun (2 mW/cm^2). Typical examples of emission spectra are given in Figure 1 for various sources.

Figure 1. Emission spectra of various light sources: Hg-Xe lamp (A), Xe lamp (B), household lamps (C) (fluorescent bulb (FB) (a) and blue (b) or white (c) LED bulb), Halogen lamp (D). Laser diodes can operate, e.g., at 405, 457, 473, 532, 635 and 808 nm.



2.2. Reactions under High Intensity Sources Emitting Visible Lights

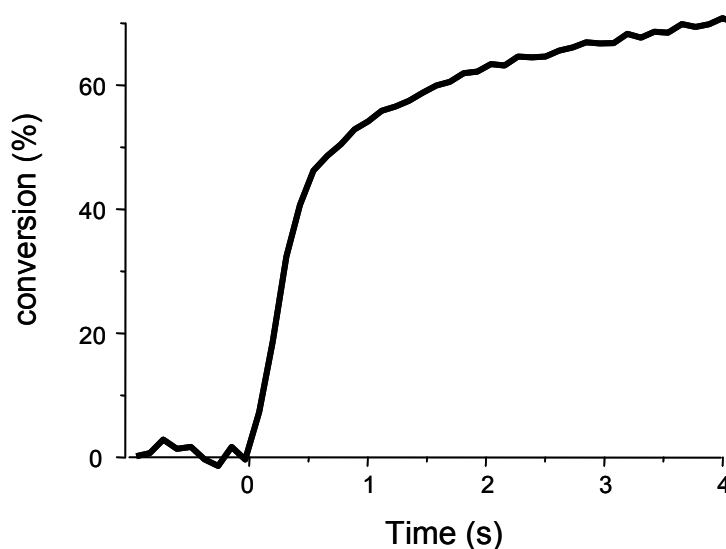
The FRP in the radiation curing area is largely and easily achieved upon irradiation with UV, near UV/visible light high intensity sources (various Hg lamps and, more recently, LED arrays) under air [1–18], as many efficient (commercially or laboratory available) PISs can operate in the 280–450 nm wavelength range [19]. This is exemplified in Figure 2 for the photopolymerization of an epoxy-acrylate matrix under air upon exposure to a laboratory Xe-Hg lamp. On industrial lines for coating applications, the exposure time is obviously much shorter and the attained cure speeds are really high.

The same holds true in CP as, in addition, oxygen inhibition does not occur. Fast curing speeds are reached under light exposure below 400 nm.

The situation is more complicated in FRPCP, as the usual photoinitiating systems are naturally less efficient and sensitive to the presence of oxygen, but new PISs have led to promising developments (see below).

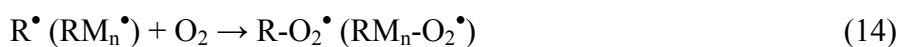
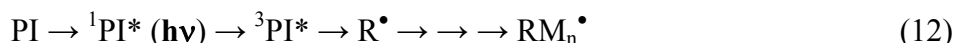
Going to longer wavelength exposures (450–700 nm) can also be achieved in FRP, CP and FRPCP using appropriate conventional PISs, provided that relatively high intensity light sources and viscous media are used. A real progress, however, has been realized in recent works and many PISs that meet this challenge (even with low intensity lights and low viscosity media) have been proposed in the last five years (see, e.g., [19,27–76] and references therein).

Figure 2. Polymerization kinetic of an epoxy-acrylate (Ebecryl 605 from Cytec) upon Hg-Xe lamp exposure (60 mW/cm²); photoinitiator: 2-2'-dimethoxy-2-phenylacetophenone. Under air; the polymerization only starts with the irradiation.



2.3. The Oxygen Inhibition

In FRP and FRPCP, a well-known drawback [19] concerns the oxygen inhibition (12–14), which is due to the excited triplet state quenching (³PI or ³PS) by O₂ and the scavenging of the initiating R[•] and propagating RM_n[•] radicals by O₂ (a nearly diffusion controlled reaction; highly stable peroxy radicals are formed). The polymerization starts in the film as soon as oxygen is consumed. The practical effects of this phenomenon strongly depend on the experimental conditions. In highly viscous or thick samples (e.g., epoxy acrylate matrices), the re-oxygenation process is slow, which leads to an efficient polymerization after an inhibition period. The top layer in contact with air is easily polymerized, provided that a high PI concentration and a high light intensity are used: this is easily feasible in thin samples; it might be more complicated in thick samples. On the opposite, in very low viscosity media (e.g., di- or tri-functional monomers, such as trimethylol-propane triacrylate (TMPTA) or 3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX), the re-oxygenation remains efficient, thereby reducing the monomer conversions. In addition, when the light intensity is attenuated, the oxygen inhibition has a dramatic effect on the polymerization profile, due to (i) the lowering of the initial O₂ consumption process and, as a consequence, (ii) the decrease of the initiating radical concentration (as a higher amount of these radicals are trapped by O₂). As is known, decreasing the oxygen inhibition effect can be achieved through various strategies (see a review in [19]). The recent introduction of a novel approach has led to successful results (see below).



2.4. The Soft Irradiation Conditions

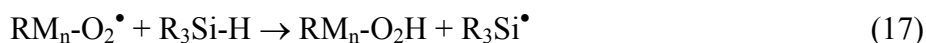
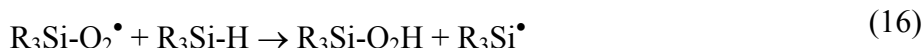
The above mentioned considerations explain why the FRP is difficult when using visible light and low intensity sources under air. For example, the development of sunlight photosensitive formulations (see, e.g., [77–85] and references therein; see also the patent literature aiming at industrial applications) for the drying of paints for crack-bridging applications, anti-soiling properties, the manufacture of interpenetrating polymer networks (IPN) usable as protective coatings and glues, the fabrication of glass fiber reinforced composites, hard and rigidified four layer glass cloth laminate, clearcoats and polymer–clay composites has been realized in the past, but these systems, except some of them (e.g., those described in [79,80,84]) suffer from oxygen inhibition and a relatively low photosensitivity.

As stated above, except some colored systems (e.g., the ferrocenium salts), the usually employed cationic PIs (onium salts) for CP absorb in the UV. Even in academic laboratories, efficient photosensitization reactions of cationic PISs upon visible light is rather limited, as the possible efficient electron donor/onium salt couples are in a very limited number, despite careful research [19].

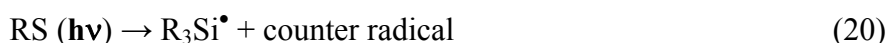
In FRPCP, the main problem concerns the choice of PIs, leading to an efficient R^\bullet initiating cation (3): few examples were known; most systems operated in the near UV; the efficiency/reactivity was not so high [86–95]. Interesting systems have been shown to work under sunlight, but in laminated conditions [96–98], they have, however, opened up promising perspectives. Through the very recent development of efficient visible light sensitive systems, FRPCP has known a substantial progress (see below).

2.5. The Development of New Photosensitive Systems

It clearly appeared that the development of PIS should proceed through new concepts, ensuring an increase of their photochemical/chemical reactivity. In this direction, a noticeable improvement was noted with the introduction of the silyl chemistry into PISs [99,100]. The silane (e.g., tris-(trimethylsilyl)silane (TTMSS)) becomes a magic additive, which renders more feasible the photopolymerization reactions in aerated conditions. In a silane containing PIS for FRP, initiating silyl radicals are generated: (i) they consume oxygen (15); (ii) scavenge the peroxy radicals (16 and 17) and (iii) regenerate new silyls. As a consequence, the oxygen inhibition is reduced, and the total amount of interesting $\text{R}_3\text{Si}^\bullet$ increases, so that oxygen becomes a mediator in the initiating radical production.

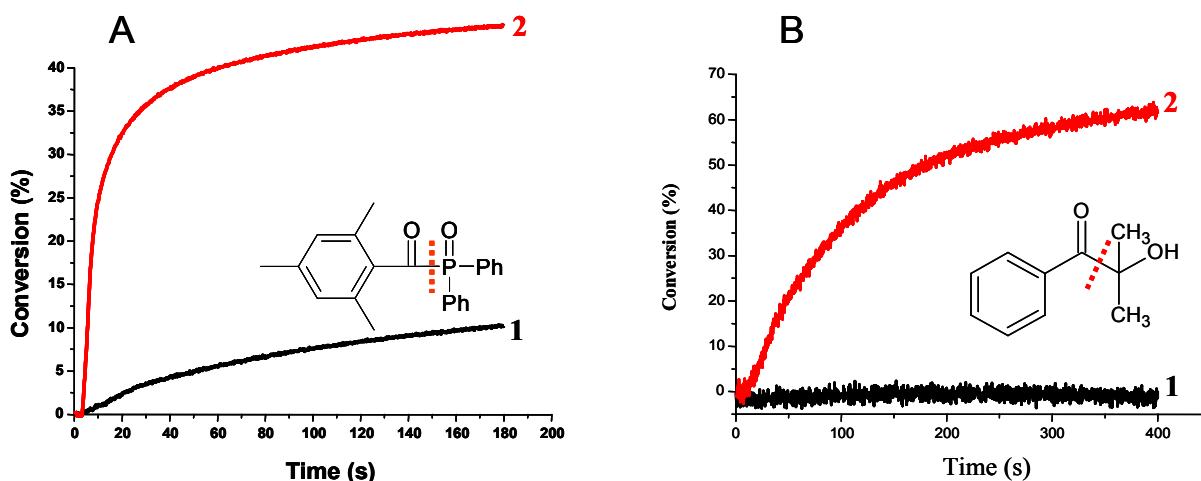


The same holds true in FRPCP, which is usually affected by the presence of oxygen. In a silane containing PIS, the oxygen inhibition is dramatically decreased as resulting from (15–17). Moreover, the addition of the iodonium salt allows an oxidation of the silyl radical (18): a R^+ cation is formed and can serve as a very efficient initiating species (19). In such PIS, an interesting feature relates to the possibility of forming the same cationic species, R^+ , whatever the starting absorbing radical source (RS) (contrary to reaction 10, where the nature of the cation is dependent on the starting PI). RS can be a usual PI or PS (but also any other compound) being able to form silyls by cleavage of, e.g., a C–Si or a Si–Si bond (20), and an electron/proton transfer with, e.g., ketones or dyes (21).



Therefore, the novel introduction of this silyl chemistry opens a new way to cure coatings under UV and visible lights. Interestingly, this also allows photocuring under soft conditions (visible light using exposure to Xe lamps, household halogen lamps, diode lasers (405, 457, 532, 635 nm), LED bulbs and sun; low intensity sources), under air, using relatively low viscosity matrices [101]. Figure 3 shows the role of the silane in the typical FRP and FRPCP of aerated curable formulations under near UV/visible lights. The germyl [102] and boryl [103] chemistries can play a similar role. In the same way, *N*-vinyl carbazole (NVK) was recently advantageously introduced into a formulation instead of the silane [104]; NVK is a cheap and efficient alternative to *tris*(trimethylsilyl)silane. Using other PISs and monomers (e.g., divinyl ethers), higher final conversions can be reached.

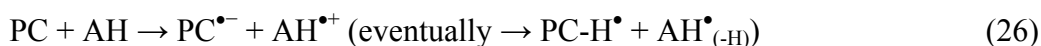
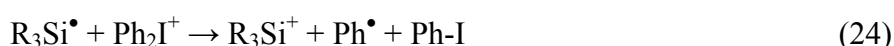
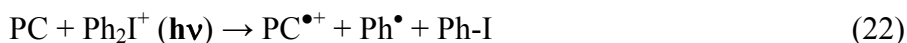
Figure 3. Photopolymerization kinetics of (A) an acrylate monomer (trimethylol-propane triacrylate (TMPTA) from Cytec) using a phosphine oxide as the photoinitiator in the absence (1) or in the presence (2) of *tris*-(trimethylsilyl)silane (TTMSS) (3% w/w); (B) an epoxy monomer ((3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX), Uvacure 1500 from Cytec) using an hydroxyl alkyl acetophenone/iodonium salt (1%/1% w/w) as the photoinitiating system in the absence (1) or in the presence (2) of TTMSS (3% w/w); under air; Xe lamp exposure.



The current efforts result in an amazing series of proposals of new PISs [27–76]. For example, we have recently introduced PISs ([51–76,99–107]) exhibiting really novel absorption properties (red-shift absorptions, multicolor absorptions, enhanced molar extinction coefficients, ϵ): e.g., colored substituted or functionalized ketones [60], modified organometallic derivatives [70–72,108–117] (ruthenium-, iridium-, platinum-, zirconium- and zinc-based complexes, titanocene derivatives...), various series of dye-based skeletons [61–63,65–68,74–76] (e.g., phenylenediamine, polystilbene, polyazine, violanthrone, acridinedione, 2,7-di-tert-butylidimethyldihydropyrene, bodipy, boranyl, thiophene, perylene bis-dicarboximide, hydrocarbons, pyrromethene, pyridinium salt...), di- and *tri*-functional architectures of photo initiators [64], light harvesting compounds [57,58] (where a strong molecular orbital coupling occurs, leading to ϵ huge values) and push-pull and multicolor photoinitiators (novel chromophores; donor- π -acceptor arrangements; unusual broad absorptions from the blue to the red wavelengths...).

2.6. The Photoredox Catalysis

The further introduction of the silyl chemistry into photoredox cycles (as those known in organic synthesis purposes using photocatalysts (PC) [108–117]) has recently led to interesting possibilities of FRP and FRPCP reactions under soft conditions in aerated media [75,76,105–107]. Novel PIs working as PCs through an oxidation cycle (metal complexes or organic metal-free compounds) in combination with a silane and an iodonium salt have been designed (22–25); they allow successful excitations of cationic or radical matrices up to 635 nm under air. Other systems involving a PC, an amine AH and an alkyl halide R-Br operate through a reduction cycle (26 and 27). When PC stands for a PI that is regenerated in these PISs, the photoinitiator becomes a photoinitiator catalyst (PIC).

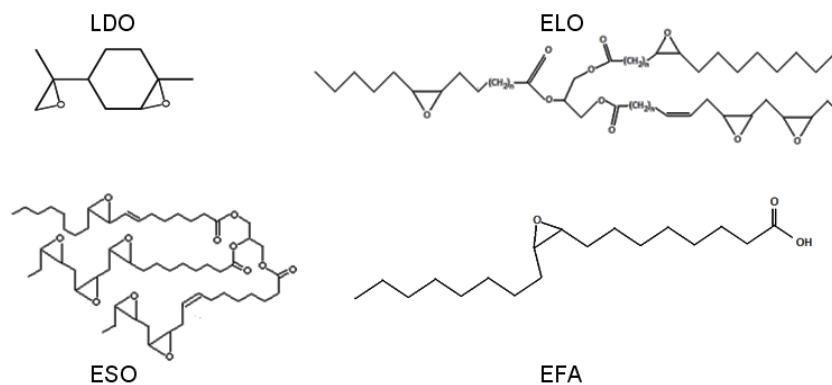


2.7. Renewable Monomers and Oligomers

Renewable monomers/oligomers have been proposed and studied; e.g., (i) acrylates: acrylated vegetable oils [118], natural or naturally derived products (photocrosslinkable polylactides [119], ϵ -caprolactone [120,121], poly (lactide-co-ethylene oxide-co-fumarate) [122], poly(caprolactone-co-lactic acid) [123], methacrylate based gelatine derivatives [124], acrylate modified starch [125] and itaconic acid based photocurable polyesters [126]; (ii) epoxides: epoxidized sunflower [127,128], epoxidized soybean oil (ESO), linseed oil, vernonia oil or castor oil (see in [129]), limonene dioxide (LDO) [130] (limonene is a liquid terpene found in various volatile oils, such as cardamom, nutmeg and turpentine; LDO can be formed through oxidation of limonene by peracids), epoxidized natural rubbers [131], vegetable oils [132] and epoxidized fatty acid (EFA); or (iii) resins based on vegetable

oil [133,134], soybean [135], rosin ester [136], tung [137] and palm stearin [138,139] and castor oil. The photopolymerization of such monomers is more or less efficient as a function of the chemical structure, the multifunctional character or the irradiation conditions. Some typical renewable monomer compounds are shown in Scheme 1.

Scheme 1. Investigated Renewable Monomers.



3. Greener Photopolymerization Reactions: Attained Performance in Recent Laboratory Scale Experiments

3.1. 3a/ Soft or Eco-Friendly Photopolymerization of Synthetic Monomers

In this part, we will show some examples (extracted from our own work [51–76]), which illustrate today's green character of the photopolymerization reactions of synthetic monomers (other experiments using renewable monomers will be presented below with more details). TMPTA (trimethylol propane acrylate) and EPOX ((3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate) will be used as representative low viscosity monomers. Divinyl ethers (e.g., triethylene glycol divinyl ether (DVE-3)) can also be photopolymerized. All the formed coatings are tack-free.

3.1.1. Design of New PIS Allowing a UV-Free Exposure and Ensuring the Use of Visible Light

Figure 4 shows some polymerization profiles of EPOX using typical visible light absorbing PISs. A Xe lamp ensures fast CP and FRPCP processes. The FRP of acrylates is also feasible under such irradiation conditions. Therefore, visible photons can be successfully used and Hg lamps avoided. The recent development of di- and *tri*-functional architectures of PIs, light harvesting PIs and push-pull and multicolor PIs opens a route towards highly absorbing PIs in the 400–800 nm range [57,58,64,73].

3.1.2. Use of Newly Developed LEDs and Laser Diodes Avoiding Hg-Based Lamps

Excellent conversion *vs.* time curves can be recorded upon excitation with a laboratory LED device at 365 nm (Figure 5) [64]. Commercial highly packed LED systems lead to the cure speeds attained with Hg lamps. According to the usual absorption spectra of PIs in the UV, many PIs work in these conditions [19]. A smaller number of systems can operate at 395 nm. Recently developed PISs operating in the near-UV/visible range (e.g., [57,58]) noticeably extend the scope of the existing structures and should be efficient upon a 395 nm LED irradiation.

Figure 4. Photopolymerization profiles of 3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) under air upon Xenon lamp exposure ($\sim 60 \text{ mW/cm}^2$) in the presence of (1) bis(acyl)phosphine oxide (BAPO)/iodonium salt (1%/1% w/w); (2) BAPO/iodonium salt/TTMSS (1%/1%/3% w/w); (3) BAPO/iodonium salt/tetraphenyldisilane (1%/1%/3% w/w). Instead of BAPO, more colored structures, such as titanocenes and other dyes, can be used.

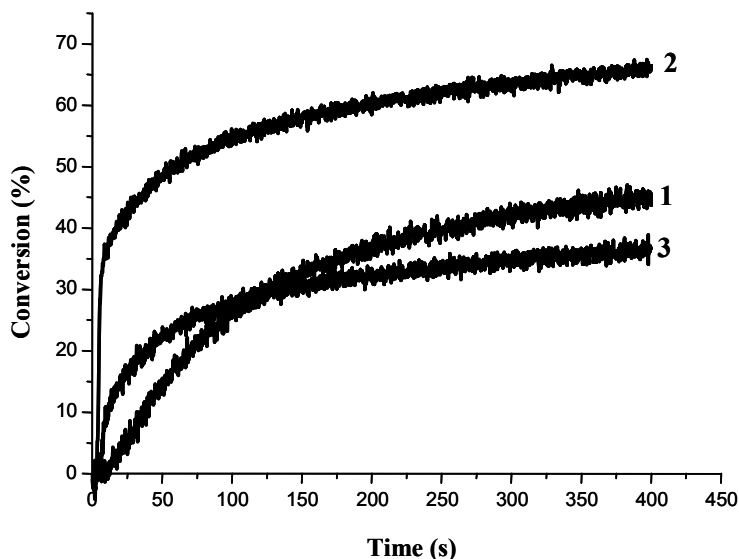
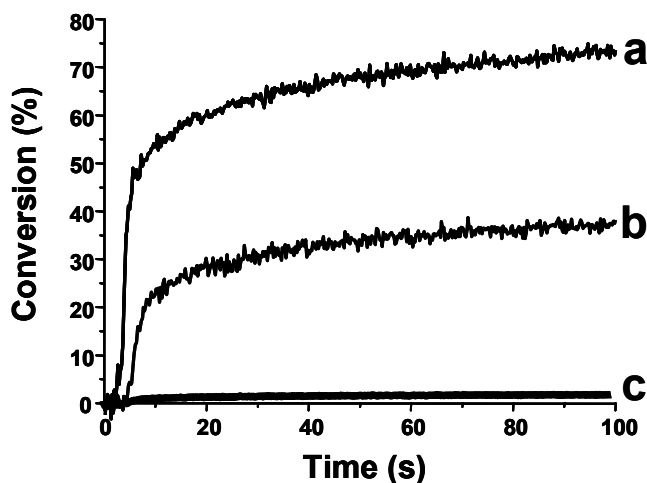
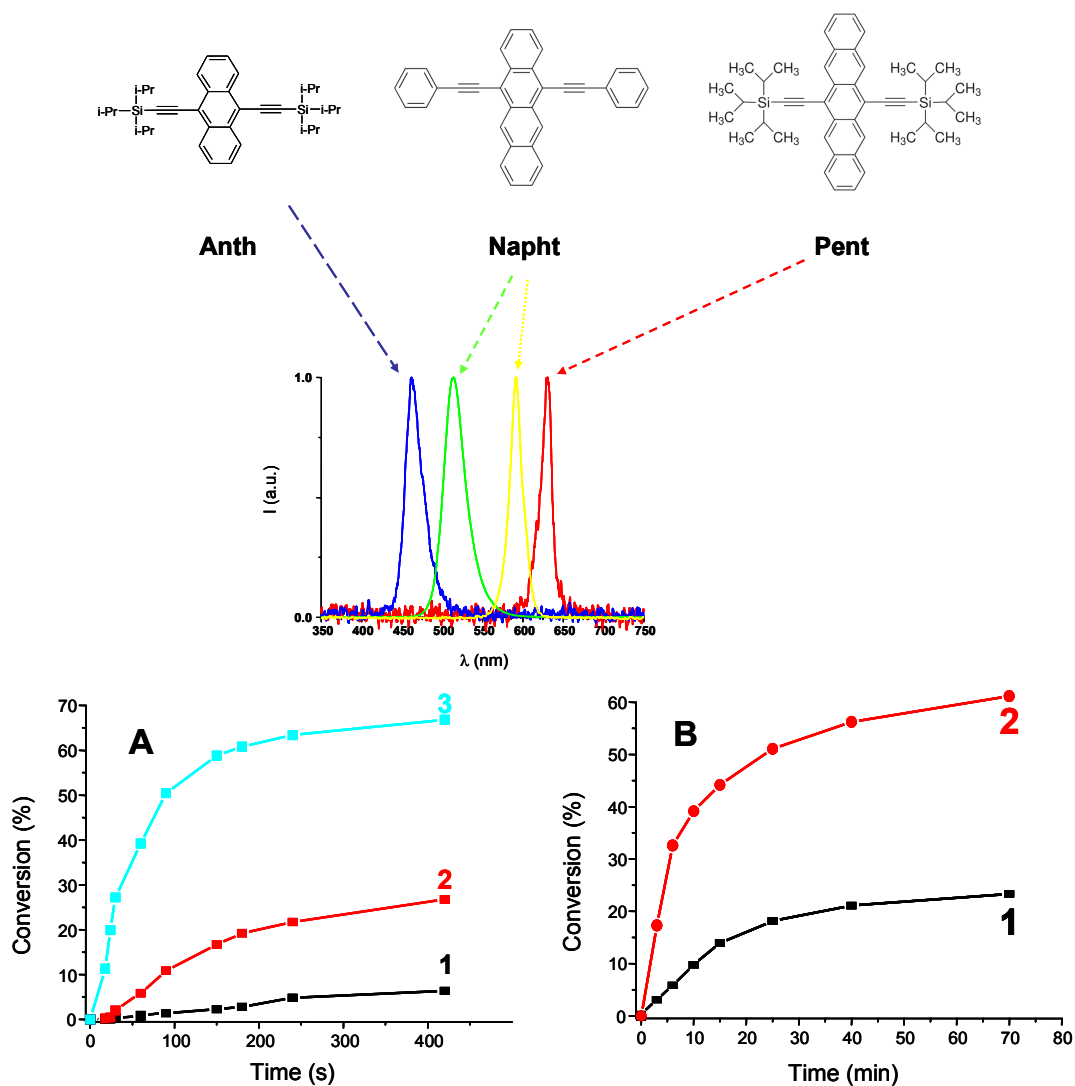


Figure 5. Photopolymerization profiles of EPOX under air upon 365 nm LED exposure ($\sim 50 \text{ mW/cm}^2$) in the presence of (a) triazine-pyrene/TTMSS/iodonium salt (1%/3%/2% w/w); (b) pyrene/(TTMSS/iodonium salt (1%/3%/2% w/w); (c) iodonium salt (2% w/w).



Laser diodes also lead to efficient FRP, CP and FRPCP [51–76]. New PIS exhibit an absorption that satisfactorily matches the emission of the sources from the blue to the red: this is exemplified in Figure 6, where three kinds of PI can be used with four examples of LED bulbs; TMPTA, as well as EPOX can be polymerized. Laser diode arrays obviously allow faster curing speeds.

Figure 6. (A) Polymerization profiles of TMPTA upon Xe-Hg lamp irradiation ($\lambda > 390$ nm) in laminated conditions in the presence of (1) Napht (0.5% w/w); (2) Napht/Ethyl-dimethylaminobenzoate (EDB) (0.5%/4.5% w/w); (3) Napht/EDB/phenacyl bromide (0.5%/4.5%/3% w/w). (B) Compared polymerization profiles of EPOX under air upon a red LED bulb irradiation in the presence of: (1) Pent/ Ph_2I^+ (0.5%/ 2% w/w) and (2) Pent/TTMSS/ Ph_2I^+ (0.5%/3%/ 2% w/w). Insert: emission spectra of the used LED bulbs (2–12 mW/cm²); different photoinitiators recently proposed [75,76].



3.1.3. Development of PISs for Soft Irradiation Conditions

Household devices, such as halogen lamps, fluorescent bulbs and LED bulbs, deliver low intensity visible light and are used in organic synthesis. They have been recently introduced for the photopolymerization of low viscosity monomers under air [51–76] (see, again, the polymerization profiles under a red LED bulb exposure in Figure 6). Today, many PIS allow FRP, CP and FRPCP in these irradiations conditions: e.g., Figure 7 shows an efficient polymerization of EPOX under halogen lamp exposure. It is obvious that all the work on the design of PISs carried out in this area should be very helpful for potential and promising applications with more energetic light sources in both laboratory scale devices and industrial lines.

Metal-based, as well as metal-free photoinitiator catalysts operating on the basis on a photoredox catalysis can efficiently initiate a radical or a cationic photopolymerization or a radical/cationic hybrid curing [75,76,105]. Figure 8 shows the achieved performance when using a Ru complex as a photocatalyst for the FRPCP of EPOX under a household fluorescent bulb exposure. Ir-, Pt- or Zn-based complexes also lead to interesting results under soft visible irradiation; interpenetrated radical/cationic networks can be formed (see, e.g., [51–76,105]).

Figure 7. Compared polymerization profiles of EPOX under air upon halogen lamp irradiation ($\sim 12 \text{ mW/cm}^2$) in the presence of: (1) BAPO/ Ph_2I^+ (1%/2% w/w); (2) NVK/ Ph_2I^+ (1%/2% w/w); and (3) BAPO/N-vinylcarbazole (NVK)/ Ph_2I^+ (1%/3%/2% w/w). Other PIs, such as bodipy, boranyl, violanthrone, pyrromethene dyes, *etc.*, can operate [61–63,65–68,74,75].

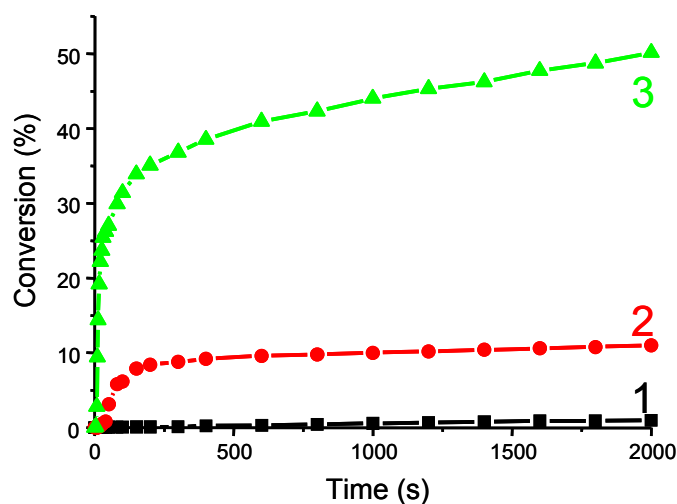
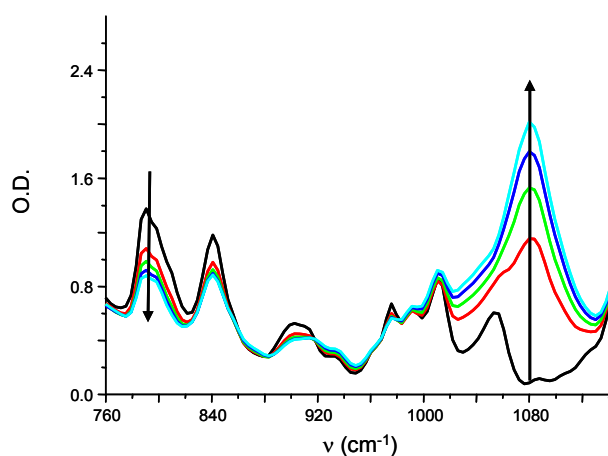


Figure 8. IR spectra recorded in the course of a photopolymerization of EPOX; initiating system: $\text{Ru}(\text{bpy})^{2+}/\text{Ph}_2\text{I}^+(\text{TTMSS})$ (0.2%/2%/3% w/w) upon fluorescence bulb irradiation ($\sim 5\text{--}12 \text{ mW/cm}^2$). A final conversion of 60% is obtained after 4 min.



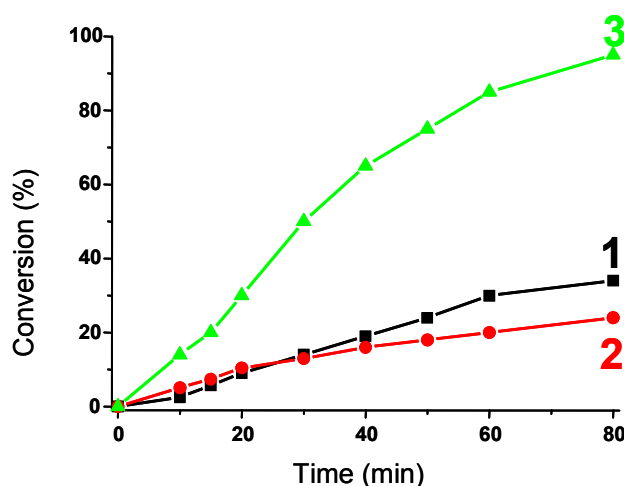
3.1.4. Use of Sunlight Irradiation

Sun is the lowest intensity source used in this paper (2 mW/cm^2). Efficient photopolymerization reactions still appear as relatively extremely hard. The FRP was mainly restricted to complex paint

formulations (see the patent literature) or acrylates dispersed in a solid matrix [80,92]. On the opposite side, CP and FRPCP were reported as possible [96–98].

Recently, the FRP of a viscous matrix under air (e.g., an epoxy-acrylate having a viscosity of ~14,000 cP) has been carried out using efficient PISs based on silyl radical chemistry (50% conversion within 20 s and a final conversion of 75% at $t = 8$ mn using a bis(acyl)phosphine oxide (BAPO) and a silane) [77]. CP and FRPCP now appear as relatively easily feasible (see e.g., Figure 9); once again, the use of a three-component photoinitiating system based on a photoinitiator, an iodonium salt and a silane (or *N*-vinylcarbazole) allows an efficient curing of a usual difunctional epoxide matrix under air (see, e.g., in [51–76]).

Figure 9. Compared polymerization profiles of EPOX under air upon sunlight (Mulhouse-France, 2 mW/cm²); in the presence of: (1) BAPO/Ph₂I⁺ (1%/2% w/w); (2) NVK/Ph₂I⁺ (1%/2% w/w); and (3) BAPO/NVK/Ph₂I⁺ (1%/3%/2% w/w).



3.2. 3b-Photopolymerization of Renewable Monomers

Some typical examples of photopolymerization profiles of renewable epoxy resins upon visible light exposure (Xe lamp) are displayed in Figure 10 (see also Table 1). Among the different compounds depicted in Scheme 1, LDO is the most reactive monomer. This is in agreement with the cyclohexyl epoxy structure, where the ring opening process is highly favorable [19]. The polymerization is slower with ESO, ELO (epoxidized linseed oil) and EFA, but quite good final monomer conversions can be reached (40%–60%; Figure 10B) using a combination of the photoinitiator with an iodonium salt and a silane; moreover, tack-free coatings are formed. In any case, a decrease of the band at ~790 cm⁻¹ (due to the epoxy ring) is monitored, whereas an increase of the IR absorption band of the polyether network is observed in the 1050–1150 cm⁻¹ range. The photoinitiating system is important for getting a high reactivity, as exemplified by Figures 10A and 11, where different photoinitiating systems lead to very different polymerization profiles. Photoinitiating systems based on bis-acylphosphine-oxides (BAPO) are very efficient (Table 2).

Extremely soft irradiation conditions can also be used. Figure 12 shows the epoxide consumption and the formation of the polyether network under a household fluorescent bulb or sunlight exposure under air. In outdoor conditions, tack-free coatings are obtained with LDO, ELO and ESO (Table 2).

As before, the polymerization profiles of these monomers are also clearly improved by the presence of a silane, *i.e.*, for ELO, a tack-free coating is obtained within only 9 min in the presence of a silane (TTMSS) vs. 50 min in the absence of the silane.

Figure 10. Photopolymerization kinetics of (A) an epoxy monomer, limonene dioxide (LDO) using different photoinitiating systems: (a) benzophenone-sulfonyl ketone (BPSK)/Ph₂I⁺/TTMSS (1%/2%/3% w/w); (b) BAPO/Ph₂I⁺/TTMSS (1%/2%/3% w/w); (c) 3,3-carbonylbis-(7-methoxycoumarin)/Ph₂I⁺/TTMSS (1%/2%/3% w/w); (B) different epoxy monomers: (a) LDO; (b) epoxidized soybean oil (ESO); (c) epoxidized fatty acid (EFA); (d) ELO using an initiating systems: BPSK/Ph₂I⁺/TTMSS (1%/2%/3% w/w). Xenon lamp exposure ($\lambda > 400$ nm; (~60 mW/cm²)); under air; BPSK is a benzophenone-sulfonyl ketone difunctional photoinitiator [19].

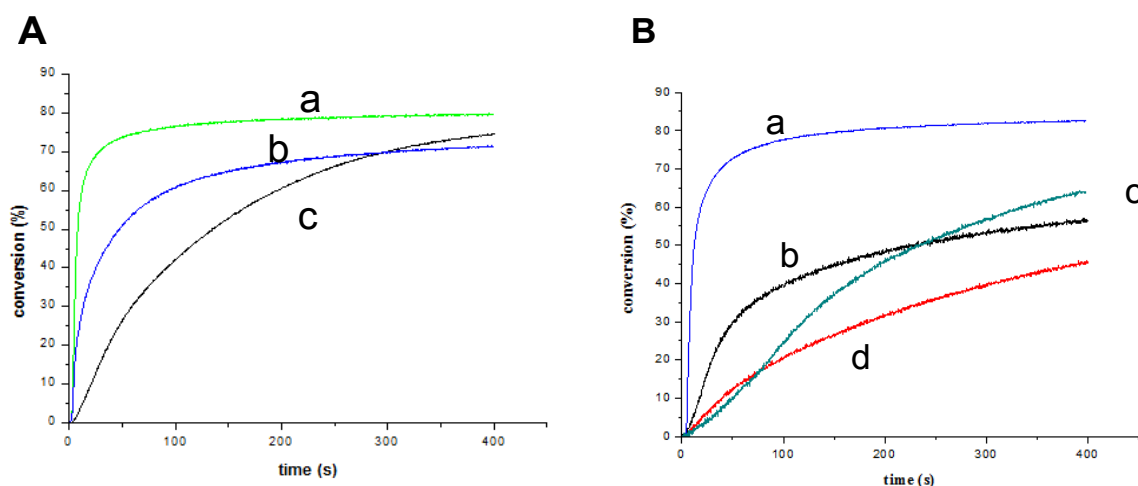
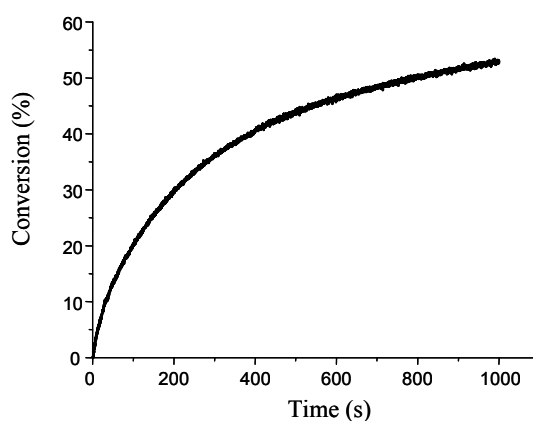


Figure 11. Photopolymerization profile of ELO using an initiating system: BAPO/Ph₂I⁺/TTMSS (1%/2%/3% w/w) upon Xenon lamp exposure; under air.



As the polymerization efficiency in the presence of EPOX, LDO or ESO in the same experimental conditions are relatively close, it is obvious that renewable monomers can be successfully used in photocurable formulations operating in a large range of excitation wavelengths delivered by polychromatic (Xe lamps, household lamps) and (quasi) monochromatic (LED and laser diodes) light sources and sun. Some high performance PISs developed in the last year (see, e.g., the 2012 and 2013

references in [57–76]) should ensure a faster formation of tack-free coatings upon sunlight exposure under air: work is under progress.

Table 1. Polymerization rates and final conversions of different renewable epoxides using BAPO/Ph₂I⁺ (1%/2% w/w) as the photoinitiating system in the absence (a) or in the presence (b) of *tris*(trimethylsilyl)silane (TTMSS) (3% w/w); under air; Xenon lamp irradiation ($\lambda > 400$ nm).

Monomers	R _p /[M ₀] ^c (s ⁻¹)	Conversion
LDO ^a	0.016	71.4%
ESO ^a	0.002	21.5%
ELO ^a	0.0002	7.0%
EFA ^a	0.001	9.0%
LDO ^b	0.05	81.4%
ESO ^b	0.006	43.1%
ELO ^b	0.0006	29.7%
EFA ^b	0.001	29.0%

^a in absence of silane; ^b in presence of silane; ^c [M₀] is the initial monomer concentration.

Figure 12. IR spectra recorded in the course of a photopolymerization of ELO; initiating system: BPSK/Ph₂I⁺/TTMSS (1%/2%/3% w/w): (A) fluorescent bulb irradiation (from $t = 0$ to 30 min) and (B) sunlight exposure (from $t = 0$ to 30 min); under air.

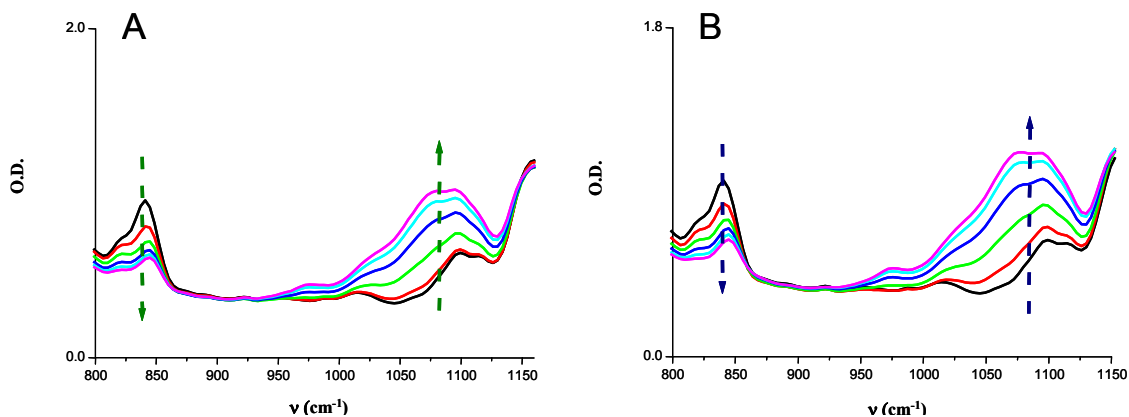


Table 2. Irradiation times to get tack-free coatings using BAPO/Ph₂I⁺ (1%/2% w/w) in the absence (a) or in the presence (b) of *tris*(trimethylsilyl)silane (TTMSS) (3% w/w) upon sunlight exposure; under air.

Monomer	Tackfree
LDO ^a	48 min
ESO ^a	*
ELO ^a	50 min
EFA ^a	*
LDO ^b	12 min
ESO ^b	45 min
ELO ^b	9 min
EFA ^b	*

^a in absence of silane; ^b in presence of silane; *: no tack-free coating after 1 h.

4. Conclusions

This paper has reviewed some aspects concerned with the development of green technologies in the photopolymerization area. Interesting visible light irradiation sources (Xe lamps, diode lasers, LEDs, household lamps and, obviously, sun) today allow large possibilities of excitation from the near-UV to the near-infra-red. The development of very efficient PISs sensitive in the blue-to-red wavelength range for radical and cationic polymerization reactions undoubtedly opens new opportunities of polymerization reactions. Working in the absence of UV lights under air is on the right path today. Harmful Hg lamps can be avoided. Applications where (i) low light intensities are available (e.g., with sunlight) or required or (ii) quite low viscosity monomers (particular acrylates or cationic monomers) or thin films have to be employed become possible. Using sunlight, which has been a dream for a long time, might be within reach. The photopolymerization of renewable monomers is quite feasible. However, such monomers have to be designed as a function of the applications and the desired final material properties.

Many new additional works have to likely be proposed, for example, in the radiation curing area. It seems difficult today to find renewable acrylates exhibiting a performance close to that of the usual synthetic di- and *tri*-functional monomer/oligomers. The situation is different with the renewable epoxides, *i.e.*, the compared performance of LDO and artificial epoxides are close in terms of polymerization rates and conversions, and the fabrication of glass fiber-reinforced composites with epoxidized vegetable oils has already been reported. Important questions may appear, e.g., about the physical/mechanical/surface, *etc.*, properties of the cured material when starting from a conventional synthetic monomer or a modified natural raw compound. All the work described here was conducted in organic media: the use of water-borne formulations is noticeably less developed and the investigation of the photopolymerization of water-reducible, as well as water-based dispersions upon visible light exposure under air might also deserve to be carried out.

In the different topics discussed throughout this paper, much has been done, but much still remains to be done. The efforts deployed during the last thirty years to develop green aspects of the photopolymerization area begin to change, however, what was a challenge into a reality.

References

1. *Radiation Curing of Polymeric Materials*; Hoyle, C.E., Kinstle, J.F., Eds.; American Chemical Society: Washington, DC, USA, 1990.
2. *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.P., Rabek, J.F., Eds.; CRC Press: Boca Raton, FL, USA, 1990.
3. Pappas, S.P. *UV-Curing: Science and Technology*; Plenum Press: New York, NY, USA, 1992.
4. *Radiation Curing in Polymer Science and Technology*; Fouassier, J.P., Rabek, J.F., Eds.; Chapman & Hall: London, UK, 1993.
5. *Photoresponsive Polymers*; Krongauz, V., Trifunac, A., Eds.; Chapman and Hall: New York, NY, USA, 1994.
6. Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; Wiley: New York, NY, USA, 1989.

7. Fouassier, J.P. *Photoinitiation, Photopolymerization, Photocuring: Fundamentals and Applications*; Carl Hanser GmbH: Munich, Germany, 1995.
8. Davidson, S. *Exploring the Science, Technology and Application of UV and EB Curing*; SITA Technology Ltd.: London, UK, 1999.
9. Neckers, D.C. *UV and EB at the Millenium*; SITA Technology Ltd.: London, UK, 1999.
10. Crivello, J.V.; Dietliker, K. *Photoinitiators for Free Radical, Cationic and Anionic Photopolymerization*; Bradley, G., Ed.; Surface Coatings Technology Series; Wiley: New York, NY, USA, 1999; Volume III.
11. Dietliker, K. *A Compilation of Photoinitiators Commercially Available for UV Today*; SITA Technology Ltd.: London, UK, 2002.
12. Belfied, K.D.; Crivello, J.V. *Photoinitiated Polymerization*; ACS Symp. Ser. 847; American Chemical Society: Washington, DC, USA, 2003.
13. *Photochemistry and UV Curing*; Fouassier, J.P., Ed.; Research Signpost: Trivandrum, India, 2006.
14. *Photochemistry and Photophysics of Polymer Materials*; Allen, N.S., Ed.; Wiley: Hoboken, NJ, USA, 2010.
15. *Basics of Photopolymerization Reactions*; Fouassier, J.P., Allonas, X., Eds.; Research Signpost: Trivandrum, India, 2010.
16. Green, W.A. *Industrial Photoinitiators*; CRC Press: Boca Raton, FL, USA, 2010.
17. Peiffer, R.W. *Photopolymerization: Fundamentals and Applications*; Scranton, A.B., Bowman, A., Eds.; ACS Symp. Ser. 673; American Chemical Society: Washington, DC, USA, 1997.
18. *Handbook of Vinyl Polymers*; Mishra, M.K., Yagci, Y., Eds.; CRC Press: Boca Raton, FL, USA, 2009.
19. Fouassier, J.P.; Lalevée, J. *Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency*; Wiley VCH: Weinheim, Germany, 2012.
20. Esposito Corcione, C.; Previderio, A.; Frigione, M. Kinetics characterization of a novel photopolymerizable siloxane-modified acrylic resin. *Thermochim. Acta* **2010**, *509*, 56–61.
21. Esposito Corcione, C.; Greco, A.; Maffezzoli, A. Photopolymerization kinetics of an epoxy-based resin for stereolithography. *J. Appl. Polym. Sci.* **2004**, *92*, 3484–3491.
22. Esposito Corcione, C.; Greco, A.; Maffezzoli, A. Time–temperature and time-irradiation intensity superposition for photopolymerization of an epoxy based resin. *Polymer* **2005**, *46*, 8018–8027.
23. Esposito Corcione, C.; Greco, A.; Maffezzoli, A. Temperature evolution during stereolithography building with a commercial epoxy resin. *Polym. Eng. Sci.* **2006**, *46*, 493–502.
24. Greco, A.; Esposito Corcione, C.; Cavallo, A.; Maffezzoli, A. Influence of stone particles on the rheological behavior of a novel photopolymerizable siloxane-modified acrylic resin. *J. Appl. Polym. Sci.* **2011**, *122*, 942–947.
25. Frigione, M.; Esposito Corcione, C. Rheological and kinetic characterization of UV photopolymerizable formulations as a function of the boehmite nanoparticle content. *Open Mater. Sci. J.* **2012**, *6*, 68–76.

26. Esposito Corcione, C.; Frigione, M. Factors influencing photo curing kinetics of novel UV-cured siloxane-modified acrylic coatings: Oxygen inhibition and composition. *Thermochim. Acta* **2012**, *534*, 21–27.
27. Yilmaz, G.; Iskin, B.; Yilmaz, F.; Yagci, Y. Mesoporous graphitic carbon nitride as a heterogeneous visible light photoinitiator for radical polymerization. *ACS Macro Lett.* **2012**, *1*, 1212–1215.
28. Karaka-Balta, D.; Temel, G.; Okal, N.; Arsu, N. Thioxanthone–diphenyl anthracene: Visible light photoinitiator. *Macromolecules* **2012**, *45*, 119–125.
29. Yilmaz, G.; Acik, G.; Yagci, Y. Counteranion sensitization approach to photoinitiated free radical polymerization. *Macromolecules* **2012**, *45*, 2219–2224.
30. Kumbaraci, V.; Aydogan, B.; Talinli, N.; Yagci, Y. Naphthodioxinone-1,3-benzodioxole as photochemically masked one-component Type II photoinitiator for free radical polymerization. *J. Polym. Sci. Part A* **2012**, *50*, 2612–2618.
31. Temel, G.; Enginol, B.; Aydin, M.; Karaca Balta, D.; Arsu, N. Photopolymerization and photophysical properties of amine linked benzophenone photoinitiator for free radical polymerization. *J. Photochem. Photobiol. A* **2011**, *219*, 26–31.
32. Keskin Dogruyol, S.; Dogruyol, Z.; Arsu, N. A thioxanthone-based visible photoinitiator. *J. Polym. Sci. Part A* **2011**, *49*, 4037–4040.
33. Sevinc Esen, D.; Karasu, F.; Arsu, N. The investigation of photoinitiated polymerization of multifunctional acrylates with TX-BT by Photo-DSC and RT-FTIR. *Progr. Org. Coat.* **2011**, *70*, 102–107.
34. Korkut, S.E.; Temel, G.; Karaca Balta, D.; Arsu, N.; Kasım Şener, M. Type II photoinitiator substituted zinc phthalocyanine: Synthesis, photophysical and photopolymerization studies. *J. Luminescence* **2013**, *136*, 389–394.
35. Asvos, X.; Siskos, M.G.; Zarkadis, A.K.; Hermann, R.; Brede, O. The 2-benzoyl xanthone/triethylamine system as a type II photoinitiator: A laser flash photolysis and computational study. *J. Photochem. Photobiol. A* **2011**, *219*, 255–264.
36. Santos, W.G.; Schmitt, C.C.; Neumann, M.G. Polymerization of HEMA photoinitiated by the Safranin/diphenylborinate system. *J. Photochem. Photobiol. A* **2013**, *252*, 124–130.
37. Kitano, H.; Ramachandran, K.; Bowden, N.B.; Scranton, A.B. Unexpected visible-light-induced free radical photopolymerization at low light intensity and high viscosity using a titanocene photoinitiator. *J. Appl. Polym. Sci.* **2013**, *128*, 611–618.
38. Han, J.; Wang, J.; Shen, K.; Wang, G.; Li, Y.; Zhao, D. Synthesis of novel photochromic spiropyran dyes containing quaternary ammonium salt or cinnamoyl moiety and their properties as photoinitiators. *J. Appl. Polym. Sci.* **2012**, *126*, 30–37.
39. Ivan, M.G.; Scaiano, J.C. Photoimaging and Photolithographic Process in Polymers. In *Handbook on Photochemistry and Photophysics of Polymer Materials*; Allen, N.S., Ed.; Wiley: Hoboken, NJ, USA, 2010; pp. 479–508.
40. Muftuoglu, A.E.; Tasdelen, M.A.; Yagci, Y. Photografting of Polymeric Materials. In *Handbook on Photochemistry and Photophysics of Polymer Materials*; Allen, N.S., Ed.; Wiley: Hoboken, NJ, USA, 2010; pp. 509–540.

41. Yang, J.; Shi, S.; Xu, F.; Nie, J. Synthesis and photopolymerization kinetics of benzophenone sesamol one-component photoinitiator. *Photochem. Photobiol. Sci.* **2013**, *12*, 323–329.
42. Rosspeintner, A.; Griesser, M.; Pucher, N.; Iskra, K.; Liska, R.; Gescheidt, G. Toward the photoinduced reactivity of 1,5-diphenylpenta-1,4-diyne-3-one (DPD): Real-time investigations by magnetic resonance. *Macromolecules* **2009**, *42*, 8034–8038.
43. Moszner, N.; Lamparth, I.; Angermann, J.; Fischer, U.K.; Zeuner, F.; Bock, T.; Liska, R.; Rheinberger, V. Synthesis of bis(3-([2-(allyloxy)ethoxy]methyl)-2,4,6-trimethylbenzoyl)(phenyl)phosphine oxide—A tailor-made photoinitiator for dental adhesives. *Beilstein J. Org. Chem.* **2010**, *6*, 1–9.
44. Dworak, C.; Kopeinig, S.; Hoffmann, H.; Liska, R. Photoinitiating monomers based on di- and triacryloylated hydroxylamine derivatives. *J. Polym. Sci. Part A* **2009**, *47*, 392–403.
45. Li, Z.; Siklos, M.; Pucher, N.; Cicha, K.; Ajami, A.; Husinsky, W.; Rosspeintner, A.; Vauthey, E.; Gescheidt, G.; Stampfl, J.; *et al.* Synthesis and structure-activity relationship of several aromatic ketone-based two-photon initiators. *J. Polym. Sci. Part A* **2011**, *49*, 3688–3699.
46. Yagci, Y.; Jockusch, S.; Turro, N.J. Photoinitiated polymerization: advances, challenges, and opportunities. *Macromolecules* **2010**, *43*, 6245–6260.
47. Kabatc, J.; Jurek, K. Free radical formation in three-component photoinitiating systems. *Polymer* **2012**, *53*, 1973–1980.
48. Czech, Z.; Butwin, A.; Kabatc, J. Photoreactive s-triazine as crosslinking agents for UV-crosslinkable acrylic pressure-sensitive adhesives. *J. Appl. Polym. Sci.* **2011**, *120*, 3621–3627.
49. Jedrzejewska, B.; Urbanski, S. Studies on an argon laser-induced photopolymerization employing both mono- and bischromophoric hemicyanine dye-borate complex as a photoinitiator. Part III. *J. Appl. Polym. Sci.* **2010**, *118*, 1395–1405.
50. Kabatc, J.; Krzyzanowska, E.; Jedrzejewska, B.; Pietrzak, M.; Paczkowski, J. Novel *N*-ethyl-2-styrylquinolinium iodides as sensitizers in photoinitiated free radical polymerization of trimethylolpropane triacrylate (TMPTA). *J. Appl. Polym. Sci.* **2010**, *118*, 165–172.
51. Lalevée, J.; Tehfe, M.A.; Allonas, X.; Foussier, J.P. Photoinitiating systems based on unusual radicals. In *Polymer Initiators*; Ackrine, W.J., Ed.; Nova Science Publishers, Inc.: Hauppauge, NY, USA, 2010; chapter 8.
52. Lalevée, J.; Tehfe, M.A.; Blanchard, N.; Morlet-Savary, F.; Fouassier, J.P. Redox or photoinduced ring opening polymerization: Initiating systems based on organosilanes bearing a Si–Si bond. In *Radical Polymerization: New Developments*; Pauloskas, I.O., Urbonas, L.A., Eds.; Nova Science Publishers, Inc.: Hauppauge, NY, USA, 2011; chapter 7.
53. Fouassier, J.P.; Lalevée, J. Three-component photoinitiating systems: Towards innovative tailor made high performance combinations. *Adv. Chem.* **2012**, *2*, 2621–2629.
54. Lalevée, J.; Fouassier, J.P. Overview of Radical Initiation. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Studer, A., Chatgililoglou, C., Eds.; Wiley: New York, NY, USA, 2012; Volume 1, chapter 2.
55. Lalevee, J.; EL Roz, M.; Allonas, X.; Fouassier, J.P. On the silyl radical chemistry in photopolymerization reactions. In *Organosilanes: Properties, Performance and Applications*; Wyman, E., Skief, M.C., Eds.; Nova Science Publishers: Hauppauge, NY, USA, 2009; chapter 6.

56. Fouassier, J.P.; Lalevée, J. Design of Chromophores for Photoinitiators of Polymerization: Brief Survey and Recent Achievements. In *New Developments in Chromophore Research*; Nova Science Publishers: Hauppauge, NY, USA; in press.
57. Lalevée, J.; Tehfe, M.A.; Dumur, F.; Gigmes, D.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P. Green light induced cationic ring opening polymerization reactions: Perylene bis-dicarboximides as efficient photosensitizers. *Macromol Chem. Phys.* **2013**, doi:10.1002/macp.201200728.
58. Tehfe, M.A.; Dumur, F.; Graff, B.; Clément, J.L.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J.P.; Lalevée, J. A new cleavable photoinitiator architecture with huge molar extinction coefficients for polymerization in the 340–420 nm range. *Macromolecules* **2013**, *46*, 736–746.
59. Lalevée, J.; El Roz, M.; Tehfe, M.A.; Allonas, X.; Fouassier, J.P. Long wavelength cationic photopolymerization in aerated media: A remarkable titanocene/tris(trimethylsilyl)silane/onium salt photoinitiating system. *Macromolecules* **2009**, *42*, 8669–8674.
60. Lalevée, J.; Blanchard, N.; Fries, C.; Tehfe, M.A.; Morlet-Savary, F.; Fouassier, J.P. New thioxanthone and xanthone derivative based on silyl radical chemistry. *Polym. Chem.* **2011**, *2*, 1077–1084.
61. Tarzi, O.I.; Allonas, X.; Ley, C.; Fouassier, J.P. Pyrromethene derivatives in three-component photoinitiating systems for free radical photopolymerization. *J. Polym. Sci. Part A* **2010**, *48*, 2594–2603.
62. Tehfe, M.A.; Dumur, F.; Contal, E.; Graff, B.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J.P.; Lalevée, J. New insights in radical and cationic polymerization upon visible light exposure: Role of novel photoinitiator systems based on the pyrene chromophore. *Polym. Chem.* **2013**, *4*, 1625–1634.
63. Telitel, S.; Blanchard, N.; Schweitzer, S.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P.; Lalevée, J. Bodipy derivatives and boranil as new photoinitiating systems of cationic polymerization exhibiting a tunable absorption in the 400–600 nm spectral range. *Polymer* **2013**, doi:10.1016/j.polymer.2013.02.013.
64. Tehfe, M.A.; Dumur, F.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P.; Gigmes, D.; Lalevée, J. Trifunctional photoinitiators based on a triazine skeleton for visible light sources and UV LED induced polymerizations. *Macromolecules* **2012**, *45*, 8639–8647.
65. Telitel, S.; Lalevée, J.; Blanchard, N.; Kavalli, T.; Tehfe, M.A.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P. Photopolymerization of cationic monomers and acrylate/divinylether blends under visible lights using pyrromethene dyes. *Macromolecules* **2012**, *45*, 6864–6868.
66. Tehfe, M.A.; Zein-Fakih, A.; Lalevée, J.; Dumur, F.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J.P. Pyridinium salts: New systems for photopolymerization reactions upon visible light exposure. *Eur. Polym. J.* **2013**, *49*, 567–574.
67. Tehfe, M.A.; Lalevée, J.; Dumur, F.; Zein-Fakih, A.; Gigmes, D.; Morlet-Savary, F.; Fouassier, J.P. Dye photosensitized cationic ring-opening polymerization: search for new dye skeletons. *Polymer* **2012**, *53*, 4947–4954.
68. Tehfe, M.A.; Lalevée, J.; Fouassier, J.P. A breakthrough for long wavelength absorbing photoinitiating systems under soft irradiation conditions based on violanthrone derivatives. *Macromolecules* **2011**, *44*, 8374–8379.

69. Lalevée, J.; Tehfe, M.A.; Morlet-Savary, F.; Fouassier, J.P. Cationic photosensitive formulations based on the silyl radical chemistry for green and red diode laser exposure. *Polym. Chem.* **2012**, *3*, 1899–1902.
70. Lalevée, J.; Blanchard, N.; Tehfe, M.A.; Peter, M.; Morlet-Savary, F.; Fouassier, J.P. Household LED irradiation under air: Cationic polymerization using iridium or ruthenium complex photocatalysts. *Polym. Bull.* **2012**, *68*, 341–347.
71. Lalevée, J.; Dumur, F.; Mayer, C.R.; Gigmes, D.; Nasr, G.; Tehfe, M.A.; Morlet-Savary, F.; Telitel, S.; Graff, B.; Fouassier, J.P. Photopolymerization of *N*-vinylcarbazole using visible-light harvesting iridium complexes as photoinitiators. *Macromolecules* **2012**, doi:10.1021/ma3005229.
72. Tehfe, M.A.; Lalevée, J.; Telitel, S.; Sun, J.; Zhao, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P. Iridium complexes incorporating coumarin moiety as photocatalysts for ring opening photopolymerizations. *Polymer* **2012**, *53*, 2803–2808.
73. Tehfe, M.A.; Dumur, F.; Graff, B.; Morlet-Savary, F.; Gigmes, D.; Fouassier, J.P.; Lalevée, J. Design of new Type I & Type II photoinitiators possessing highly coupled pyrene-ketone moieties. *Polym. Chem.* **2013**, *4*, 2313–2324.
74. Tehfe, M.A.; Dumur, F.; Graff, B.; Morlet-Savary, F.; Gigmes, D.; Fouassier, J.P.; Lalevée, J. Light harvesting organic photoinitiators of polymerization. *Macromol. Rapid Comm.* **2013**, *34*, 239–245.
75. Tehfe, M.A.; Lalevée, J.; Morlet-Savary, F.; Graff, B.; Blanchard, N.; Fouassier, J.P. Organic photocatalyst for polymerization reactions: 9,10-bis[(triisopropylsilyl)ethynyl] anthracene. *ACS Macro Lett.* **2012**, *1*, 198–203.
76. Tehfe, M.A.; Lalevée, J.; Telitel, S.; Contal, E.; Dumur, F.; Gigmes, D.; Bertin, D.; Nechab, M.; Bertrand, M.; Morlet-Savary, F.; *et al.* Polyaromatic structures as organophotocatalysts for efficient dual radical/cationic photopolymerizations under visible lights and interpenetrated polymer networks synthesis. *Macromolecules* **2012**, *45*, 4454–4460.
77. Lalevée, J.; Fouassier, J.P. Recent advances in sunlight induced polymerization: Role of new photoinitiating systems based on the silyl chemistry. *Polym. Chem.* **2011**, *2*, 1107–1113.
78. Eiselé, G.; Fouassier, J.-P.; Reeb, R. Kinetics of photocrosslinking reactions of a DCPA/EA matrix in the presence of thiols and acrylates. *J. Polym. Sci. Part A* **1997**, *35*, 2333–2345.
79. Bibaut-Renaud, C.; Burget, D.; Fouassier, J.-P.; Varelas, C.-G.; Thomatos, J.; Tsagaropoulos, G.; Ryrfors, L.O.; Karlsson, O.J. Use of α -diketones as visible photoinitiators for the photocrosslinking of waterborne latex paints. *J. Polym. Sci. Part A* **2002**, *40*, 3171–3181.
80. Decker, C.; Bendaikha, T. Interpenetrating polymer networks. II. Sunlight-induced polymerization of multifunctional acrylates. *J. Appl. Polym. Sci.* **1998**, *70*, 2269–2282.
81. Chiang, W.; Lin, W.T. Syntheses and cured films properties of UV-autocurable BTDA-based multiacrylate resins. *J. Appl. Polym. Sci.* **1994**, *51*, 1901–1909.
82. Chiang, W.; Ding, F.C. Synthesis and properties of ultraviolet-curable resins via a thio-ene (thiol and allyl) addition reaction. *J. Appl. Polym. Sci.* **2002**, *86*, 1878–1885.
83. Zang, H.L.; Massingilland, J.L.; Woo, J.T. Zero VOC sunlight curable coatings. *J. Coat. Technol.* **2000**, *72*, 79–81.
84. Decker, C.; Zahouily, K.; Decker, D.; Nguyen Thi Viet, T. Performance analysis of acylphosphine oxides in photoinitiated polymerization. *Polymer* **2001**, *42*, 7551–7560.

85. Paczkowska, B.; Strzelec, S.; Linden, L.A.; Packowski, D. Photochemical preparation of polymer-clay composites. *J. Appl. Clay Sci.* **2004**, *25*, 221–227.
86. Ledwith, A. Possibilities for promoting cationic polymerization by common sources of free radicals. *Polymer* **1978**, *19*, 1217–1219.
87. Baumann, H.; Timpe, H.J. Lichtinitiierte polymer- und polymerisationsreaktionen. photoinduzierte zersetzung von diaryliodonium- und triarylsulfoniumsalzen durch benzoinderivate und benzilketale. *Z. Chem.* **1984**, *24*, 18–19.
88. Yagci, Y.; Schnabel, W. Acylphosphine oxides as free radical promoters in cationic polymerizations. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 209–213.
89. Yagci, Y.; Kminek, I.; Schnabel, W. Long wavelength photoinitiated cationic polymerization using diphenyliodonium salt and catena-poly (phenyl-4-phenylphenylsilicon). *Polymer* **1993**, *34*, 426–428.
90. Yagci, Y.; Ledwith, A. Mechanistic and kinetic studies on the photoinitiated polymerization of tetrahydrofuran. *J. Polym. Sci. Part A* **1988**, *26*, 1911–1918.
91. Crivello, J.V.; Sangermano, M. Visible and long-wavelength photoinitiated cationic polymerization. *J. Polym. Sci. Part A* **2001**, *39*, 343–356.
92. Dursun, C.; Degirmenci, M.; Yagci, Y.; Jockusch, S.; Turro, N.J. Free radical promoted cationic polymerization by using bisacylphosphine oxide photoinitiators: Substituent effect on the reactivity of phosphinoyl radicals. *Polymer* **2003**, *44*, 7389–7396.
93. Crivello, J.V. Radical-promoted visible light photoinitiated cationic polymerization of epoxides. *J. Macromol. Sci. Part A* **2009**, *46*, 474–483.
94. Yagci, Y.; Denizligil, S. Photoinitiated cationic polymerization using *O*-phthaldehyde and pyridinium salt. *J. Polym. Sci. Part A* **1995**, *33*, 1461–1464.
95. Yagci, Y.; Reetz, I. Externally stimulated initiator systems for cationic polymerization. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.
96. Bulut, U.; Gunbas, G.E.; Topare, L. A quinoxaline derivative as a long wavelength photosensitizer for diaryliodonium salts. *J. Polym. Sci. Part A* **2010**, *48*, 209–213.
97. Crivello, J.V. A new visible light sensitive photoinitiator system for the cationic polymerization of epoxides. *J. Polym. Sci. Part A* **2009**, *47*, 866–875.
98. Crivello, J.V.; Bulut, U. Curcumin: A naturally occurring long-wavelength photosensitizer for diaryliodonium salts. *J. Polym. Sci. Part A* **2005**, *43*, 5217–5321.
99. Lalevée, J.; Blanchard, N.; Tehfe, M.A.; Chany, A.C.; Morlet-Savary, F.; Fouassier, J.P. Green bulb lamp induced cationic photopolymerization reactions under air. *Macromolecules* **2010**, *43*, 10191–10195.
100. Lalevée, J.; Tehfe, M.A.; Morlet-Savary, F.; Graff, B.; Allonas, X.; Fouassier, J.P. Oxygen mediated and wavelength tunable cationic photopolymerization reactions under air and low Intensity: A new concept. *Progr. Organ. Coat.* **2011**, *70*, 23–31.
101. Tehfe, M.A.; Lalevée, J.; Gimes, D.; Fouassier, J.P. Green Chemistry: sunlight induced cationic polymerization of renewable epoxy monomer under air. *Macromolecules* **2010**, *43*, 1364–1370.
102. Tehfe, M.A.; Blanchard, N.; Fries, C.; Lalevée, J.; Allonas, X.; Fouassier, J.P. Bis(germyl)ketones: Toward a new class of type I photoinitiating systems under visible light irradiation. *Macromol. Rapid Comm.* **2010**, *31*, 473–478.

103. Telitel, S.; Schweitzer, S.; Morlet-Savary, F.; Graff, B.; Tschamber, T.; Blanchard, N.; Fouassier, J.P.; Lelli, M.; Lacôte, E.; Lalevée, J. Soft photopolymerizations initiated by dye-sensitized formation of NHC-boryl radicals under visible lights. *Macromolecules* **2013**, *46*, 43–48.
104. Lalevée, J.; Tehfe, M.A.; Zein-Fakih, A.; Ball, B.; Telitel, S.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P. *N*-vinylcarbazole: an additive for free radical promoted cationic polymerization upon visible-light. *ACS Macro Lett.* **2012**, *1*, 802–806.
105. Tehfe, M.-A.; Lalevée, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J.-P. On the use of bis(cyclopentadienyl)titanium(IV) dichloride in visible light induced ring opening photopolymerization. *Macromolecules* **2011**, *44*, 8374–8379.
106. Lalevée, J.; Tehfe, M.-A.; Dumur, F.; Gignes, D.; Blanchard, N.; Morlet-Savary, F.; Fouassier, J.-P. Iridium photocatalysts in free radical polymerization under visible lights. *ACS Macro Lett.* **2012**, *1*, 286–290.
107. Tehfe, M.-A.; Lalevée, J.; Morlet-Savary, F.; Graff, B.; Blanchard, N.; Fouassier, J.-P. Tunable Organophotocatalysts for polymerization reactions under visible lights, macromolecules. *Macromolecules* **2012**, *45*, 1746–1752.
108. Nicewicz, D.A.; MacMillan, D.W.C. Merging photoredox catalysis with organocatalysis: The direct asymmetric alkylation of aldehydes. *Science* **2008**, *322*, 77–80.
109. Shih, H.-W.; Vander Wal, M.N.; Grange, R.L.; MacMillan, D.W.C. Enantioselective α -benzylation of aldehydes via photoredox organocatalysis. *J. Am. Chem. Soc.* **2010**, *132*, 13600–13603.
110. Zeitler, K. Photoredox catalysis with visible light. *Angew. Chem. Int. Ed.* **2009**, *48*, 9785–9789.
111. Narayanam, J.M.R.; Stephenson, C.R.J. Visible light photoredox catalysis: Applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102–113.
112. Dai, C.; Narayanam, J.M.R.; Stephenson, C.R.J. Visible-light-mediated conversion of alcohols to halides. *Nat. Chem.* **2011**, *3*, 140–145.
113. Ischay, M.A.; Lu, Z.; Yoon, T.P. [2+2] cycloadditions by oxidative visible light photocatalysis. *J. Am. Chem. Soc.* **2010**, *132*, 8572–8574.
114. Yoon, T.P.; Ischay, M.A.; Du, J. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527–532.
115. Larraufie, M.H.; Pellet, R.; Fensterbank, L.; Goddard, J.P.; Lacôte, E.; Malacria, M.; Ollivier, C. Visible-light-induced photoreductive generation of radicals from epoxides and aziridines. *Angew. Chem. Int. Ed.* **2011**, *50*, 4463–4466.
116. Courant, T.; Masson, G. Photoredox-initiated α -alkylation of imines through a three-component radical/cationic reaction. *Chem. Eur. J.* **2012**, *18*, 423–427.
117. Zhang, G.; Song, I.Y.; Ahn, K.H.; Park, T.; Choi, W. Free radical polymerization initiated and controlled by visible light photocatalysis at ambient temperature. *Macromolecules* **2011**, *44*, 7594–7599.
118. Pelletier, H.; Belgacem, N.; Gandini, A. Acrylated vegetable oils as photocrosslinkable materials. *J. Appl. Polym. Sci.* **2006**, *99*, 3218–3221.
119. Durmaz, Y.Y.; Karagoz, B.; Bicak, N.; Yagci, Y. Synthesis of block copolymers by combination of ATRP and photoiniferter processes. *Polym. Intern.* **2008**, *57*, 1182–1187.

120. Dworak, C.; Koch, T.; Varga, F.; Liska, R. Photopolymerization of biocompatible phosphorus-containing vinyl esters and vinyl carbamates. *J. Polym. Sci. Part A* **2010**, *48*, 2916–2924.
121. Nagata, M.; Inaki, K. Biodegradable and photocurable multiblock copolymers with shape-memory properties from poly(ϵ -caprolactone) diol, poly(ethylene glycol), and 5-cinnamoyloxyisophthalic acid. *J. Appl. Polym. Sci.* **2011**, *120*, 3556–3564.
122. Jabbari, E.; He, X. Synthesis and characterization of bioresorbable *in situ* crosslinkable ultra low molecular weight poly(lactide) macromer. *J. Mater. Sci. Mater. Med.* **2008**, *19*, 311–318.
123. Bayramoğlu, G.; Kayaman-Apohan, N.; Vezir Kahraman, M.; Karadenizli, S.; Erdem Kuruca, S.; Güngör, A. Preparation of bow tie-type methacrylated poly(caprolactone-co-lactic acid) scaffolds: Effect of collagen modification on cell growth. *Polym. Adv. Techn.* **2012**, *23*, 1403–1413.
124. Schuster, M.; Turecek, C.; Weigel, G.; Saf, R.; Stampfl, J.; Varga, F.; Liska, R. Vinyl esters: Low cytotoxicity monomers for the fabrication of biocompatible 3D scaffolds by lithography based additive manufacturing. *J. Polym. Sci. Part A* **2009**, *47*, 7078–7089.
125. Hedin, J.; Oestlund, A.; Nyden, M. UV induced cross-linking of starch modified with glycidyl methacrylate. *Carbohydr. Polym.* **2010**, *79*, 606–613.
126. Barrett, D.G.; Merkel, T.J.; Luft, J.C.; Yousaf, M.N. One-step syntheses of photocurable polyesters based on a renewable resource. *Macromolecules* **2010**, *43*, 9660–9667.
127. Jiratumnukul, N.; Itarat, R. Ultraviolet curable epoxidized sunflower oil/organo clay nanocomposite coatings. *J. Appl. Polym. Sci.* **2008**, *110*, 2164–2167.
128. Shibata, M.; Teramoto, N.; Someya, Y.; Suzuki, S. Bio-based nanocomposites composed of photo-cured epoxidized soybean oil and supramolecular hydroxystearic acid nanofibers. *J. Polym. Sci. Part B* **2009**, *47*, 669–673.
129. Gupta, M.K.; Singh, R.P. Cationic Initiators in Photocuring Applications. In *Basics of Photopolymerization Reactions*; Fouassier, J.P., Allonas, X., Eds.; Research Signpost: Trivandrum, India, 2010; Volume 1, pp. 23–35.
130. Acosta Ortiz, R.; Prieto López, D.; Guillén Cisneros, M.L.; Rico Valverde, J.C.; Crivello, J.V. A kinetic study of the acceleration effect of substituted benzyl alcohol on the cationic photopolymerization rate of epoxidized natural oils. *Polymer* **2005**, *46*, 1535–1541.
131. Decker, C.; Nguyen Thi Viet, T.; Le Xuan, H. Photoreticulation de caoutchoucs fonctionnalisés: Polymérisation cationique de caoutchoucs époxydés. *Eur. Polym. J.* **1996**, *32*, 1319–1326.
132. Crivello, J.V.; Narajan, R.; Sternstein, S.S. Fabrication and mechanical characterization of glass fiber reinforced UV-cured composites from epoxidized vegetable oils. *J. Appl Polym Sci.* **1997**, *64*, 2073–2087.
133. Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R.; Boutevin, B. Synthesis of biobased polyols by thiol-ene coupling from vegetable oils. *Macromolecules* **2011**, *44*, 2489–2500.
134. Raj Mahendran, A.; Wuzella, G.; Aust, N.; Kandelbauer, A. Photocrosslinkable modified vegetable oil based resin for wood surface coating application. *Progr. Org. Coatings* **2012**, *74*, 697–704.
135. Kollbe Ahn, B.; Sung, J.; Kim, N.; Kraft, S.; Susan Sun, X. UV-curable pressure-sensitive adhesives derived from functionalized soybean oils and rosin ester. *Polym. Int.* **2012**, doi:10.1002/pi.4420.

136. Thanamongkollit, N.; Miller, K.R.; Soucek, M.D. Route to co-acrylic modified alkyd resins via a controlled polymerization technique. *Progr. Org. Coat.* **2012**, *73*, 425–434.
137. Teck Chye Ang, D.; Neon Gan, S. Novel approach to enhance film properties of environmentally friendly UV-curable alkyd coating using epoxidised natural rubber. *Progr. Org. Coat.* **2012**, *73*, 409–414.
138. Teck Chye Ang, D.; Neon Gan, S. Environment friendly UV-curable resins from palm stearin alkyds. *J. Appl. Polym. Sci.* **2012**, *125*, 306–313.
139. Bao, Y.; He, J.; Li, Y. Facile and efficient synthesis of hyperbranched polyesters based on renewable castor oil. *Polym. Int.* **2012**, doi:10.1002/pi.4440.

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