Moving Towards a Finer Way of Light-Cured Resin-Based Restorative Dental Materials: Recent Advances in Photoinitiating Systems Based on Iodonium Salts

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Abstract: The photoinduced polymerization of monomers is currently an essential tool in various industries. The photopolymerization process plays an increasingly important role in biomedical applications. It is especially used in the production of dental composites. It also exhibits unique properties, such as a short time of polymerization of composites (up to a few seconds), low energy consumption, and spatial resolution (polymerization only in irradiated areas). This paper describes a short overview of the history and classification of different typical monomers and photoinitiating systems such as bimolecular photoinitiator system containing camphorquinone and aromatic amine, 1-phenyl-1,2-propanedione, phosphine derivatives, germanium derivatives, hexaarylbiimidazole derivatives, silane-based derivatives and thioxanthone derivatives used in the production of dental composites with their limitations and disadvantages. Moreover, this article represents the challenges faced when using the latest inventions in the field of dental materials, with a particular focus on photoinitiating systems based on iodonium salts. The beneficial properties of dental composites cured using initiation systems based on iodonium salts have been demonstrated.

Keywords: photopolymerization; light-cured composites; cationic photoinitiator; free radical photoinitiator; iodonium salt; polymerization shrinkage

1. Introduction

Nowadays, the most modern technologies for the production of polymeric materials are based on photochemically initiated processes. The synthesis of polymeric materials carried out by photopolymerization is one of the most efficient methods, thanks to which it is currently a very widespread and dynamically developing technique [1–5]. Compared to other methods, photopolymerization is considered environmentally friendly due to its low energy consumption, no use of solvents, and high speed at ambient temperature. In industrial practice, two types of photochemically initiated polymerization are most commonly used, namely radical and cationic polymerization [6–9]. Due to the presence of oxygen inhibition in the case of free radical photopolymerization, much attention is currently paid to the cationic, thiol-ene, and hybrid photopolymerization processes [10,11].

Polymerization using light, mainly ultraviolet (UV) light, was initially used in the coating industry, especially in varnishing for solvent-free paints and varnishes for the furniture and automotive industries [11]. Achieving high polymerization rates in fractions of seconds, resulting from the rapid formation of radicals or initiating ions, allows for high throughput of the production line [12]. Besides, the possibility of conducting photopolymerization processes at ambient temperature prepares polymeric
materials carried out by photoinduced polymerization process one of the most efficient photochemical technologies. Currently, this type of polymerization is also used in many other industries, namely in photolithography for the production of printed circuits, in micro-replication for the production of spherical lenses, for photo curing polymeric adhesives, and in microelectronics for encapsulating integrated circuits [13]. The dynamically developing printing industry is a different direction of the application of photopolymerization, which enables printing on plastic or metal materials. Moreover, in recent years, a particular emphasis has been put on the use of photopolymerization processes for 3D-printing technology [14–33], including stereolithography in the design and formation of three-dimensional models [34].

All this means that not only has recently been an astonishingly rapid growth in the applications of technologies based on photopolymerization processes, but also the development of new materials determining the pace of this development [35]. Dynamic progress in the field of chemistry and technology of photoinitiated processes leads to the emergence of more and more sophisticated solutions in this field, an example of which may be successively developed new generation monomers [36,37], new, more effective photoinitiation systems [38–40] or new light sources [1,29] and methods of monitoring the online polymerization processes [41–44].

Photopolymerization processes play an increasingly important role in biomedical applications, for instance, in obtaining hydrogel polymer materials [45–54] or in vivo photocurable dental composites [55–73]. Applying photochemically initiated polymerization for obtaining dental polymer composites enables the use of unique and innovative features. The most important are:

- Short time of monomer/filler compositions curing (up to a few seconds);
- Conducting the reaction at room temperature;
- Low energy consumption;
- Spatial resolution (polymerization only in irradiated areas).

Nevertheless, obtaining polymer composites of the demanded properties, that is, above all, of favorable mechanical properties and reduction polymerization shrinkage, is still a significant challenge for the researchers. This is because many different factors, such as the selection of appropriate monomers, initiators, inorganic fillers, photopolymerization process time range, or the source and power of a light source, influence the quality of the composite obtained (Figure 1) [74].

![Illustrative diagram showing the influence of factors on the quality of obtained dental composites.](image-url)

Recently, iodonium salts have become of particular interest and are used as a component of initiating systems for the preparation of dental composites. This is directly due to the relatively good
solubility of these salts in non-polar monomers. In addition, this group of compounds photodissociate with high initiation efficiency are thermally stable and show long-term stability under storage conditions [75,76].

In this paper, we aim to present commonly used monomers and photoinitiating systems for the photocurable dental composites and indicated their main disadvantages. Recent developments and progress in the future of photocurable resins have also been shown. A particular emphasis was placed on novel photoinitiating systems containing iodonium salts applied in dental adhesive resin.

2. Monomers Used for the Production of Dental Composites

The mechanism of photopolymerization depends on using monomers. There are two main types of photopolymerization: radical polymerization and cationic polymerization (Figure 2). The type of organic matrix has a considerable impact on the properties of dental composites. It primarily affects mechanical strength, sorption, solubility, polymerization shrinkage, abrasion resistance, color stability, and biocompatibility [74,77]. Generally, the organic components of a typical photocuring composition constitute about 10–30% wt. [78]. The remainder is inorganic filling in the form of microparticles (≥0.4 μm) or a mixture of micro and nanoparticles (50 nm > 400 nm) [78]. In addition to photoinitiators, adhesion promoters and possibly antibacterial compounds are also added to dental composites [79–81].

![Figure 2. Mechanism of free radical polymerization and cationic ring-opening polymerization with their corresponding photoinitiation systems.](image)

2.1. Monomers for Free Radical Photopolymerization Processes in Dental Adhesive Resin Application

The most popular materials for obtaining dental composites through photopolymerization are (meth)acrylate monomers (RCB—resin-based composites) characterized by high reactivity, which form an organic matrix [82–84]. They guarantee obtaining networks with a high degree of crosslinking [84,85]. By free radical polymerization of the matrix monomers, a three-dimensional network is formed. Among the currently available dental composites, the most common are 2,2-bis[4-2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) [86].

The use of BisGMA in dental materials, due to the presence of the aromatic structure of Bisphenol A in the core of the molecule, ensures low volatility of the composition and high modulus of the light-cured composite [87–89]. In turn, the use of the low-viscosity TEGDMA monomer, which is the so-called active diluent, allows the introduction of an appropriate amount of inorganic filler [90]. The weight proportions of both monomers are usually 7/3 or 8/2, where BisGMA is the main component. Another commonly used acrylate monomer is 1,6-bis-[2-methacryloyloxyethoxy)carbonylamino]-2,4,4-trimethylhexane (UDMA) [91]. The content of rigid urethane groups guarantees dental composites with favorable
strength properties [92–94]. In addition to the aforementioned BisGMA, TEGDMA, and UDMA, other common dental monomers polymerized via the free radical process are also ethoxylated bisGMA (BisEMA). This monomer is used for reducing water absorption by the organic matrix. In addition, the lack of -OH also causes this monomer to be less viscous than BisGMA. An array of monomer structures for the base dimethacrylate materials, as well as new monomers, are given in Figure 3 [95–101].

![Figure 3. Examples of methacrylate monomers used in commercial and conventional dental composites based on free radical photopolymerization mechanism.](image)

All dental composites based on crosslinking dimethacrylates exhibit an inherent problem of 2–14% volumetric shrinkage during the photopolymerization process [102]. These stresses may produce defects in the composite–tooth bond, leading to bond failure, microleakage, postoperative sensitivity, and recurrent caries. Such shrinkage stresses could also cause deformation of the surrounding tooth structure when the composite–tooth bond is strong, predisposing the tooth to fracture [103]. The polymerization shrinkage of low molecular monomers is more pronounced when compared to that of high molecular monomers; however, high molecular monomers are very viscous (Table 1). For these reasons, polymerization shrinkage is dictated by a complex interplay among resin viscosity, polymerization rate, degree of conversion, and network structural evolution, where each of these properties cannot be individually manipulated and studied without having a significant impact on other properties.

**Table 1.** Properties of the popular free radical monomers to obtained dental composites [84].

| Monomer | Molecular Weight [g/mol] | \(\rho_{\text{mon}}\) [g/cm\(^3\)] | \(\rho_{\text{pol}}\) [g/cm\(^3\)] | \(\Delta V\) [%] | Viscosity [mPa.s] |
|---------|-------------------------|-----------------|-----------------|-------------|-----------------|
| TEGDMA  | 286                     | 1.072           | 1.250           | −14.3       | 100             |
| UDMA    | 470                     | 1.110           | 1.190           | −6.7        | 5000–10,000     |
| Bis-GMA | 512                     | 1.151           | 1.226           | −6.1        | 500,000–800,000 |

\(\rho_{\text{mon}}\)—density of monomer, \(\rho_{\text{pol}}\)—density of polymer.

Moreover, due to the inhomogeneous network architecture, which is obtained during a free radical photopolymerization process, the final materials tend to show a somewhat brittle behavior, and the occurring shrinkage stress could lead to delamination, deformation or mechanical failure of the final composites materials. The observed shrinkage stress evolves during polymerization reaction upon transitioning of the applied formulation from the liquid to solid-state (i.e., gel point) and is built up upon vitrification until the final conversion is reached. Before free radical photopolymerization, the monomers are situated at van der Waal’s distance towards each other (approximately 3.4 Å) [104]. The occurring shrinkage stress upon gelation is partially due to the formation of covalent bonds between the respective monomers, where the revealing distance is only 1.5 Å [105]. Incomplete free radical
photopolymerization, volumetric shrinkage, and stress are some of the primary disadvantages of current methacrylates resin-based dental composites. Generally, attempts to increase the double-bond conversion and reduce polymerization shrinkage and stress have been conducted [105].

2.2. Monomers for Cationic Photopolymerization.

In recent years, the application of ring-opening cationic photopolymerizable epoxy–monomer-based compositions for dental fillings have found increasing attention in different articles and patent applications [84,106,107].

Thus, based on the cationic photopolymerization process, new-generation photocuring dental materials, including oxiranes [84], siloranes [108], oxetanes, and spiro-orthocarbonate [109], were developed (Figure 4). Dental materials based on these monomers have achieved clinical success because they have significantly reduced polymerization shrinkage to below 1% and minimized polymerization stress compared to traditional methacrylate materials [106]. The mechanism of compensation for systolic stress in this system was achieved by the phenomenon of opening the oxirane rings during the cationic photopolymerization process, which proceeds with a small change in the volume of the system [110].

![Table: CATIONIC MONOMERS USED IN DENTAL COMPOSITES](image)

**Figure 4.** Examples of monomers used in cationic photopolymerization (a) oxirane, (b) spiro-orthocarbonate, (c) silorane: a merger of siloxanes and oxiranes.

Crosslinking cycloaliphatic epoxy compounds were particularly of interest because they demonstrate significantly lower shrinkage than dental methacrylate resins (e.g., cycloaliphatic epoxide 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate and the diglycidyl ether of bisphenol A, which improved the mechanical properties of the cured composite). Moreover, these epoxy resins were reactive enough to be cured by cationic photopolymerization in an acceptable time frame and to an adequate depth using a dental Vis-LED light source. In addition to epoxy resins, oxetanes were evaluated for dental applications [111]. The reactivity of oxetanes is mainly controlled by the ring stress and the basicity of the ring oxygen. However, oxetanes demonstrate higher basicity. The ring-opening
cationic photopolymerization of oxetanes was also characterized by a significantly lower shrinkage in comparison to methacrylates. From the investigated oxetanes, the hydroxy group containing monomer possessed the highest polymerization rate [112].

In turn, spiroorthoesters (SOEs) and spiroorthocarbonates (SOCs) (Figure 4) are other monomers that are polymerized via the cationic mechanism and are increasingly used in dental applications. Spiroorthoesters (SOEs) and spiroorthocarbonates (SOCs) are the most widely studied expanding monomers. SOCs are double-cyclic acetals that polymerize under acidic catalysis but are stable under basic conditions. When these compounds polymerize by double ring-opening photopolymerization (ROP), poly(ether-carbonates) are produced. In general, bi-cyclic compounds cured by ROP shrink less as they harden because of an increase in the excluded free volume associated with the ring-opening process. Bailey [113] investigated bi-cyclic compounds, such as spiro-orthocarbonates (SOCs), that can be used as an expanding co-monomer in RBC formulations. Ring-opening reactions with SOCs produce expansion (3.5%), which could counteract normal shrinkage [114]. However, SOCs exhibit incomplete ring-opening, as well as limited solubility and minimal copolymerization in dimethacrylate resins, resulting in minimal shrinkage reduction.

Nevertheless, compared to traditional composite materials, spiroorthocarbonate-based composites show less polymerization shrinkage and twice as much adhesion to enamel [109].

However, the most recent modification on the polymer matrix is based on using ring-opening polymerization of the silorane molecules, instead of free radical polymerization of dimethacrylate monomers [115]. They are built of a siloxane backbone, which gives them hydrophobic and cycloaliphatic oxirane molecules responsible for low polymerization shrinkage. These monomers have provided particularly interesting and commercially viable results. Such monomers “open” their molecular structures with local volumetric expansion, and this may partly or totally compensate for volumetric shrinkage from C=C or similar polymerization [116,117]. Based on the literature reports, the use of siloranes has been shown to guarantee a reduction in the polymerization shrinkage to 0.94% [108].

Examples of monomers that polymerize thorough to the cationic mechanism and have reduced polymerization shrinkage are shown in Figure 4.

The development of new monomers polymerizing via the cationic mechanism contributed to a significant reduction in the polymerization shrinkage of dental composites and obtaining dental composites with better mechanical properties. Moreover, acrylate monomers, which often cause severe allergies, have been eliminated (Figure 5).

![Figure 5. Comparison of the properties of monomers polymerizable via free radical mechanism with monomers polymerizable via cationic mechanism.](image)

### 3. Commonly Used Photoinitiating Systems for Dental Application

Photoinitiating systems for obtaining dental composites are particularly important. They affect such parameters as the efficiency of the photopolymerization process and the choice of a light source (Figure 6).
The commonly used light-curing units are presented. In Figure 7, the absorption spectra of standard initiators in comparison with the emission characteristics of the commonly used light-curing units are presented.

To date, several initiation systems for radical photopolymerization processes have been developed. In Figure 7, the absorption spectra of standard initiators in comparison with the emission characteristics of the commonly used light-curing units are presented.

![Figure 6](image-url)  
**Figure 6.** The range of emission spectra of UV and visible light-curing units and the range of the absorption of standard co-initiators camphorquinone used in the dental application (UV—ultraviolet, LCU—light-curing units, LED—light-emitting diode, PAC—plasma arc).

![Figure 7](image-url)  
**Figure 7.** Comparison of the normalized molar extinction coefficient of standard type I initiators (top) and type II initiators together with amines (bottom) used in dental applications with the emission characteristics of standard light-curing units.
3.1. Bimolecular Photoinitiator System Containing Camphorquinone and Aromatic Amine

The commonly used photoinitiating system for the radical photopolymerization process for dental composites is the system based on camphorquinone/amine. Widely used camphorquinone (CQ) is a diketone that absorbs radiation in the range from 200 to 300 nm, which corresponds to the $\pi-\pi^*$ transition; however, this band is not useful for applications in vivo photocuring of dental materials. The second absorption range of camphorquinone is located in the visible light range from 400 to 500 nm (Figure 7), where the band is responsible for the transition of the $n-\pi^*$ carbonyl group. The presence of a long-term absorption band means that this compound has been used as a component of initiating systems, mainly free radical photopolymerization. Nevertheless, for camphorquinone, the value of the molar extinction coefficient in the range of 400–500 nm is only 40 [dm$^3$·mol$^{-1}$·cm$^{-1}$] [118,119]. Therefore, in the case of initiating systems based on CQ, a significant part of the energy emitted by Vis-LED light sources (emission range 420–515 nm) is lost. Therefore, the efficiency of polymerization of standard methacrylate dental materials in the presence of the only camphorquinone is insufficient.

Moreover, the addition of primary amines to the polymerization system does not significantly accelerate the radical photopolymerization process. However, the polymerization rate significantly increases when tertiary amines as co-initiators of radical photopolymerization are used. Amines such as ethyl-4-dimethylaminobenzoate (EDAB/EDMAB), 2-(dimethylamino)ethyl methacrylate (DMAEMA), N,N-dimethylptoluidine, N-phenylglycine (NPG), dimethylbenzoate are used as photosensitizers for CQ [120–127]. However, among these compounds, ethyl-4-dimethylaminobenzoate (EDB) is the most popular co-initiator in dental materials due to its high efficiency and low basicity.

In the step of generating radicals in the photolysis process, amine interacted with the excited camphorquinone molecule. This process involves the transfer of the electron from the amine to the ketone, followed by the proton’s abstraction [128]. The radicals initiating the polymerization process are mainly radicals formed from amines. Another mechanism that affects the amine’s efficiency as a co-initiator is the formation of free radicals during the oxygen scavenging reaction. Oxygen present in the monomer can react with amines to form a peroxide radical. This, in turn, can react with another amine to release a new free radical. In this way, the inhibitory effect of oxygen is weakened. The mechanism amine, with CQ and oxygen, is presented in Figure 8 [129,130].

![Figure 8. The initiation mechanism using bimolecular photoinitiator system containing camphorquinone and aromatic amine; mechanism of reaction amine with oxygen.](image)

Nerveless, the underlying problem of this system is the fact that a too high concentration of camphorquinone in dental composites may generate a yellow (Figure 9) or even brown color (Figure 10). Thomas Brömme et al. presented the initiating system in the form of iodonium salt bis(4-t-butylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (II), cyanines derivatives (I), camphorquinone (CQ) and dimethylamino ethylbenzoate (EMBO), which showed a brown color after light curing [131].
with the slope of the absorption band. For dental composites containing a PPD initiator, in order to with that containing CQ are obtained [138,139]. Moreover, the study shows that PPD is useful not only for photosensitizers but also for photocrosslinking agents for dental composite resins with similar 

camphorquinone (CQ) and dimethylamino ethylbenzoate (EMBO), which showed a brown color after photopolymerization.

Figure 10. Structure of the photoinitiating system, based on CQ (0.3 (wt.%)/EMBO (0.5 wt.%)

Such discoloration can influence the aesthetics and quality of the final product. A completely different problem of initiating systems based on camphorquinone and amine in composites (e.g., enamel–dentin adhesives or self-adhesive cement) containing monomers with carboxylic groups having acidic properties is because of the reaction of amines with these monomers. That, in turn, can contribute to amine consumption and decrease the efficiency of the initiating system. The limitations of amines, especially EDAB, include not only unstable in acidic conditions [132], unstable in acidic dental resin formulations [133,134], but also sensitivity to oxygen inhibition [135]. In addition, amines are a cytotoxic and genotoxic factor [101].

3.2. 1-Phenyl-1,2-propanedione as an Effective Alternative Photoinitiator

1-phenyl-1,2-propanedione (PPD) [136,137] as a Norrish type I photoinitiator, reacts by photolysis, where the cleavage of the C–C bond between the carbonyls functional groups of its molecule leads to the formation of free radicals starting the polymerization. However, PPD can also react via a co-initiator, since it bears the same diketone group as camphorquinone. Then, radicals derived from the amine-based co-initiator H-transfer are responsible for starting the polymerization. Therefore, PPD is an alternative to camphorquinone/amine systems initiating radical photopolymerization processes. The research proved that the higher mechanical properties of the model resin composite containing PPD compared with that containing CQ are obtained [138,139]. Moreover, the study shows that PPD is useful not only for photosensitzers but also for photocrosslinking agents for dental composite resins with similar efficiency to CQ [140].

Besides, PPD has reduced properties associated with the yellowing effect, which results directly from its absorption characteristics, which is mainly in the UV-A range and goes to the visible range with the slope of the absorption band. For dental composites containing a PPD initiator, in order to
achieve conversion rates compared to those of the camphorquinone/amine system, it is necessary to use LED light sources with two violet emission bands (380–420 nm and blue 420–520 nm) (Figure 7, Table 2). However, not all dental photocuring lamps guarantee such emission characteristics; therefore, the use of PPD initiator composites requires the use of dual-peak LEDs.

3.3. Phosphine Derivatives as Free radical Photoinitiators for in Visible Light Cure Polymerization

Mono-acylphosphine oxides (MAPO) and bis-acylphosphine oxide oxides (BAPO) are mainly photoinitiators used in a dental application that absorb in the 380–450 nm range. One of the first commercially available mono-acylphosphine initiators is diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO). This initiator is known on the market as Lucirin® TPO. The conduct of its photopolymerization follows an α-cleavage mechanism, in which TPO undergoes hemolytic α-cleavage of the carbon–phosphorus bond and generates two free radicals, (Table 2) both capable of initiating polymerization [141–144].

These initiators show the high efficiency of generating radicals; however, their disadvantage is the absorption characteristics, which is mainly located in the UV-A range, and the effective use of their absorption characteristics occurs when dual peaks LED lamps are used. This initiator absorbs in the range of only 350–380 nm. Nevertheless, Pedro Paulo A.C. Albuquerque et al. [145] showed that using a photoinitiator system containing TPO might improve the color stability of resin composites compared with the traditional CQ/amine system while attaining similar physicochemical properties for the composite. In particular, unlike the Q-based systems, TPO does not require the use of an amine co-initiator [141–143,146] so that the polymerization is not negatively affected by the acidic environment like itself-etch adhesives.

The other phosphine derivative is bis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). This photoinitiator is a promising alternative to initiating free radical photopolymerization upon halogen light to obtain dental resin.Remarkably, the efficiency of photoinitiating is similar to the conventionally used initiating system (CQ + EDAB). Additionally, the supplement of iodonium salt or amine can improve the effectiveness of these systems [147].

Moreover, the BAPO and TPO revealed concentration-dependent cytotoxic effects in human oral keratinocytes and V79 cells. However, in contrast to CQ, no generation of intracellular reactive oxygen/nitrogen species (ROS/RNS) was found. Only BAPO induced genotoxicity in V79 cells [148].

3.4. Germanium Derivatives—Extending the Scope of Visible Light Photoinitiators

Much progress was noted when Liska et al. developed visible light photoinitiators based on germanium compounds. For the first time, they showed that germanium compounds such as benzoyltrimethylgermane (Ge-1) or dibenzoyldiethylgermane (Ge-2) (Figure 11) represent efficient visible light photoinitiators for methacrylate monomers [149–151]. In contrast to Lucirin® TPO (λ_max = 385 nm), Ge-1 (λ_max = 411 nm) and Ge-2 (λ_max = 418 nm) show a pronounced redshift in their absorption. It means that they absorb light more strongly within the visible region.

Based on the results of these mechanistic investigations and the evaluation of different synthesis methods and structural variations of germanium compounds, bis-(4-methoxybenzoyl) diethyl-germane (Ge-3) was selected as the appropriate photoinitiator and protected by a patent under the name of Ivocerin®. Furthermore, this initiator showed no cytotoxicity. The synthesis of this compound is shown in Figure 12.

In addition, germanium derivatives exhibit quick curing and excellent bleaching behavior. The proposed reaction scheme of germanium derivatives as a photoinitiator in the presence of monomers is presented in Figure 13 [151]. They require a much lower concentration of photoinitiator to achieve comparable mechanical properties than commonly used photoinitiators. However, the main limitation of these systems is that they are active initiators for free radical polymerization [152], but they do not guarantee cationic polymerization initiation.
name of Ivocerin®. Furthermore, this initiator showed no cytotoxicity. The synthesis of this compound is presented in Figure 13 [151]. Figure 14 shows the structures of exemplary compounds, HABI derivatives [154].

3.5. Hexaarylbiimidazole Derivatives.

These initiators show the high efficiency of generating radicals; however, their disadvantage is that they do not guarantee cationic polymerization initiation.

The other phosphine derivative is bis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). This acidifying agent is used in the presence of the amine co-initiator [141–143,146] so that the polymerization is not negatively affected by the acidic environment like itself-etch adhesives.

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Germanium-based photoinitiators for methacrylate monomers [149–151]. In contrast to Lucirin® TPO (λ_{max} = 385 nm), Ge-1 (λ_{max} = 385 nm) and Ge-2 (λ_{max} = 411 nm) represent efficient initiators for free radical polymerization. For the first time, they showed that germanium compounds such as germanium compounds such as Ge-1 and Ge-2 (Figure 11) represent efficient initiators for free radical polymerization. The proposed reaction mechanism of germanium derivatives as a photoinitiator in the presence of monomers is shown in Figure 11. Figure 12 shows the synthetic pathway to obtain Ivocerin® product.

Additionally, the supplement of iodonium salt can improve the effectiveness of these systems [147].

Figure 11. Structure of novel germanium derivatives.

Figure 12. Synthetic pathway to obtain Ivocerin® product.

Figure 13. Proposed reaction mechanism of germanium derivatives as a photoinitiator in the presence of monomers.
3.5. Hexaarylbiimidazole Derivatives

Hexaarylbiimidazoles (HABIs) were synthesized for the first time in 1960 by Hayashi and Maeda [153]. Figure 14 shows the structures of exemplary compounds, HABI derivatives [154].

HABI derivatives are usually used for thiol-en systems. In turn, thiols are commonly used as co-initiators in combination with hexaarylbiimidazoles [155]. After irradiation, the binding between imidazole HABI undergoes homolytic cleavage, generating two relatively stable, long-lived lophyl radicals that are unreactive with oxygen and show slow recombination rates [156], attributable to steric hindrance as well as electron delocalization [157,158]. Then, HABI-derived lophyl radicals abstract hydrogen from the thiol to generate initiating thiyl radicals (Figure 15).

Other mechanisms of photoinduced cleavage of photoinitiator, derivatives HABI have also been proposed. Their schemes with an explanation are presented in Figures 16 and 17 [154,159].

Figure 14. Structures of different hexaarylbiimidazole (HABI) derivatives.

Figure 15. The radical-mediated thiol–ene polymerization mechanism.
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![Figure 16. Proposed mechanism of the photolysis of the carbon-nitrogen (C–N) bond between the imidazole rings of HABI.](image)

Figure 16. Proposed mechanism of the photolysis of the carbon-nitrogen (C–N) bond between the imidazole rings of HABI.

![Figure 17. Photoinitiation process of type-II photoinitiator systems based on 2-chlorohexaarylbiimidazole (o-Cl-HABI) and various N-phenylglycine (NPG) derivatives.](image)

Figure 17. Photoinitiation process of type-II photoinitiator systems based on 2-chlorohexaarylbiimidazole (o-Cl-HABI) and various N-phenylglycine (NPG) derivatives.

Unfortunately, commercially available HABI derivatives have several significant disadvantages: poor absorption in the visible spectrum, sometimes requiring a photosensitizer; low solubility in standard resins used in a dental application; and low solubility in organic solvents [160,161]. Nevertheless, despite the relatively low absorption of visible light, HABI photoinitiators are useful in initiating thiol-ene photopolymerization processes.

### 3.6. Silane-Based Derivatives

Formable, soluble, and high molecular weight polysilanes are widely used as photoconductors, photoresist materials, and photoinitiators for free radical polymerization. These compounds have strong absorption in the 300–350 nm range [162]. Upon irradiation at this band, polysilane undergoes fast photodegradation yielding silylenes and silyl radicals. Research on polysilanes has been carried out in the last century. For example, West et al. [163] proved that these compounds are highly effective in free radical photopolymerization. West et al. also assumed that the phoinitiating process consists of a reaction of silyl radicals with vinyl monomers. It has also been proven that polysilanes of which
iodonium salts [164] or pyridinium can be used for cationic photopolymerization of cyclic ethers (e.g., cyclohexene oxide) and vinyl ethers, (e.g., n-butyl vinyl ether).

Currently, a particular studied compound based on a silane derivative is tris (trimethylsilyl) silane (TTMSS). TTMMS was synthesized by Gilmanand et al. in 1965 [165]. Nearly 20 years later, Chatgilialoglu et al. proved that TMMS could be used as a radical reducing agent [166,167]. The TTMS radical is commonly used as a component in photoinitiating system [168–174] by Lalavé et al. They also reported that tris (trimethylsilyl) silane had the following attributes: a high inherent reactivity for the addition to double bonds, and also a low ionization potential (which is associated with an oxidation process and/or the formation of silylium cations). Currently, the photoinitiating system consisting of TTMS is reactive in free radical polymerization (FRP) [175] as well as in free radical-promoted cationic polymerization (FRPCP) [176]. Systems based on TTMSS have the ability for effective oxygen consumption. Therefore, it can overcome the classic and well-known inhibition of FRP or FRPCR by oxygen [169]. Moreover, TTMSS indicated no toxic reaction when tested in biological research [177]. Photoinitiating system based on TTMSS and other co-initiator such as benzophenone (BP), isopropylthioxanthone (ITX), camphorquinone (CQ) is highly reactive and even better than EDB using in dental composites [169]. Moreover, Song et al. in 2016 proved that TTMSS could be used as a substitute for amine-type co-initiator for free radical photopolymerization of methacrylate monomers used to obtain a dental composite.
Table 2. Summary of the photoinitiators used in dental application, their basic properties, and photoinduced cleavage of photoinitiators.

| Acronym of Photoinitiator | Structure, Together with a Scheme of Photoinduced Cleavage of Photoinitiator | Maximum Absorbance/Characteristic of Absorbance | Advantages | Disadvantages | Ref. |
|---------------------------|--------------------------------------------------------------------------------|-----------------------------------------------|------------|--------------|------|
| CQ                        | ![Structure of CQ](image)                                                      | $\lambda_{\text{max}} = 468\text{nm}$        | wide absorption range based on the visible range | molar extinction coefficient in the range of 400–500 nm is only 40 [dm$^3$ · mol$^{-1}$ · cm$^{-1}$], strongly yellow color | [118,119] |
| PPD                       | ![Structure of PPD](image)                                                    | $\lambda_{\text{max}} = 400\text{nm}$        | improve the color stability                        | necessary to use LED light sources with two violet emission bands (380–420 nm and blue 420–520 nm), dual peak LEDs | [136,138,139] |
| TPO                       | ![Structure of TPO](image)                                                    | $\lambda_{\text{max}} = 382\text{nm}$        | high efficiency of generating radicals, improve the color stability | low initiation efficiency, the need for UV light sources | [141–143] |
| IVO                       | ![Structure of IVO](image)                                                    | $\lambda_{\text{max}} = 445\text{nm}$        | no cytotoxicity, high initiation rate and excellent bleaching | initiators only for free radical polymerization | [149–151] |
| HABI                      | ![Structure of HABI](image)                                                   | display extended absorption tails well into the visible spectral region | effective in initiating thiol-ene photopolymerization | poor absorption in the visible spectrum, sometimes requiring a photosensitizer, low solubility in standard resins used in a dental application and low solubility in organic solvents | [154,160,161] |
| Acronym of Photoinitiator | Structure, Together with a Scheme of Photoinduced Cleavage of Photoinitiator | Maximum Absorbance/Characteristic of Absorbance | Advantages | Disadvantages | Ref. |
|--------------------------|--------------------------------------------------------------------------------|-----------------------------------------------|------------|--------------|-----|
| Silane derivatives       | ![Structure](structure.png)                                                                 | $\lambda_{\text{max}} = 425 \text{ nm}$       | ultraviolet strong absorption in the 300–350 nm region | need for UV light sources | [162–164] |
|                         | ![Structure](structure.png)                                                                 | $\lambda_{\text{max}} = 486 \text{ nm}$       | suitable for free radical photopolymerization | low value of molar extinction coefficient $\epsilon$: 120 dm$^3$ · mol$^{-1}$ · cm$^{-1}$ in toluene and 100 dm$^3$ · mol$^{-1}$ · cm$^{-1}$ in acetonitrile | [178,179] |
|                         | ![Structure](structure.png)                                                                 | $\lambda_{\text{max}} = 486 \text{ nm}$       | excellent bleaching properties, a high water solubility, and a very good stability in acidic | not suitable for methacrylate photopolymerization | [181] |
|                         | ![Structure](structure.png)                                                                 | $\lambda_{\text{max}} = 378 \text{ nm}$       | water-soluble co-initiators, instant bond strength to dentin | generally, less reactive than CQ/amine system | [151,182,183] |
In 2016, Mariem Bouzrati-Zerelli et al. developed an entirely new class of initiators, silyl glyoxylicates (DKSi, Et-DKSi, Bn-DKSi), to free radical photopolymerization for obtained dental composites. Silyl glyoxylicates are high-performance type I photoinitiators in the visible range. In combination with an appropriate amine, iodonium salt, or a phosphine, photopolymerization efficiency is improved. DKSi-based PIs outperformed the performance of the CQ to induce FRP under blue LED at 477 nm for thin (20 µm) and thick (1.4 and 6 mm) films. Excellent bleaching properties for this initiator were also observed [178].

Other articles have proven that the same silyl glyoxylate, combined with an iodonium salt, can be useful for initiating cationic photopolymerization and, thus, hybrid polymerization [179]. The proposed mechanism of formation cations from a two-component photoinitiation system based on DKSi and iodonium salt (Ar₂I⁺) under irradiation is presented in Figure 18.

![Figure 18. Proposed mechanism of formation cations from the photoinitiating system DKSi/iodonium salt.](image-url)

Kirscher et al. continued research on new silane derivatives, where the alkoxy group of the ester function of the previously developed silane derivatives was replaced, alkyl(trialkylsilyl)glyoxylate, by an aryl group to form 1-aryl-2-(triisopropylsilyl)ethane-1,2-diones (SEDs). Compared to CQ and DKSi, these compounds present shifted absorption spectra to longer wavelengths (λ\text{max} = 486 nm for SED1 and 468 nm for SED2 in toluene). Therefore, they are suitable for free radical photopolymerization under air upon exposure to blue (@ 455 nm) and even green (@ 520 nm) LEDs. Additionally, just like DKSi, show photobleaching properties [180]. The same team modified the structure of DKSi, replacing the ester function of the DKSi with a carboxylic acid function to form 2-oxo-2-(tert-butyldimethylsilyl)acetic acid (DKSi-COOH). This way, DKSi-COOH, with its excellent bleaching properties, high water solubility, and excellent stability in acidic conditions, were obtained. Moreover, it is a photoinitiator that is useful for the free radical photopolymerization processes of BisGMA/TEGDMA monomers composition and leads to remarkably high polymerization performances in monomer under exposure to the LED at 477 nm [181]. The structures of the silane derivatives are presented in Figure 19.
**3.7. Thioxanthone Derivatives (TX)**

Some ionic derivatives of thioxanthone dyes are miscible with water and may constitute an attractive alternative to the photopolymerization of dental adhesive [182]. Derivatives of thioxanthone are type II bimolecular photoinitiators used for free radical and cationic photopolymerization [183]. Photoinitiation by thioxanthone derivatives is based on the reaction of their triplet excited states with the hydrogen donor, resulting in the formation of the initiating radical (Table 2). In turn, they suffer from a diffusion-controlled reduction of reactivity and deactivation by back electron transfer.

Several articles on the use of thioxanthone as components of initiation systems for a dental application have been reported [184]. They are usually in two or three-component systems with co-initiators, e.g., an amine or an iodonium salt. The use of such a system leads to comparable conversion rates to the use of the CQ/aromatic amine system; however, the thioxanthone system is generally less reactive [184]. Ely et al. proved that the combination of an elastomeric methacrylic monomer used in a dental application and a water-soluble photoinitiator (2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)N,N,N-trimethyl-1-propanium chloride (QXT) (Figure 20) in a self-etching adhesive showed promising instant bond strength to dentin. Moreover, this composition can minimize the effects of concentration stress and phase separation in aquatic environments [151].

![Chemical structures of the silane derivatives: TTMMS—tris (trimethylsilyl) silane; DKSi—tert-butyl (tert-butyldimethylsilyl) glyoxylate; Et-DKSi—ethyl (tert-butyldimethyl)silyl glyoxylate; Bn-DKSi—benzyl (tert-butyldimethyl)silyl glyoxylate; SED1—1-phenyl-2-(triisopropylsilyl)ethane-1,2-dione; SED2—1-(3,4,5-trimethoxyphenyl)-2-(triisopropylsilyl)ethane-1,2-dione; DKSi-COOH—2-oxo-2(tert-butyldimethyl)silyl acetic acid.](Figure 19)

Figure 20. Structure of QTX.

**4. Onium Salts as an Innovative Component of Photoinitiating Systems for Photopolymerization Processes in Dental Applications**

In recent times, onium salts, i.e., sulfonium and iodonium salts, particularly in the form of diaryliodonium salts, have been playing an increasingly important role in initiating photopolymerization processes [185–192].
All the properties of ionic compounds supporting their commercial use as photoinitiators depend only on their structure. It has been shown that the cation of iodonium salt, absorbing electromagnetic radiation, is responsible for the photochemical properties of these compounds as photoinitiators. Thus, the structure of the cation determines the initiator’s properties, such as the location of the maximum absorption ($\lambda_{\text{max}}$), molar absorption coefficient ($\varepsilon$), the quantum efficiency of the initiator, and even thermal stability. On the other hand, the nature of anion has a decisive influence on the suitability of the initiating system as a photoinitiator. The type of anion determines the power of protic acid generated during photolysis, directly affecting the efficiency of initiation and the kinetics of the polymerization process. However, the essential properties of iodonium salts, from their applications in cationic polymerization processes (in addition to solubility in monomers) are their optical properties, i.e., the location of the maximum absorption ($\lambda_{\text{max}}$) and molar extinction coefficient ($\varepsilon$) [75,76].

Diaryliodonium salts, with a weakly nucleophilic counter ion, are efficient photoinitiators for cationic photopolymerization. Due to the low C-I binding energy, which is 26–27 kcal/mol, after irradiation, diaryliodonium salts are broken down to a radical-cation, and reactive aryl radical and an anion [193–195] (Figure 21).

However, commercial iodonium salts currently used in the industry have light absorption characteristics in the UV-C range, i.e., $\lambda_{\text{max}} = 220–280$ nm, and that have very low or zero light absorption in the long-term UV-A range ($\lambda > 300$ nm). Table 3 shows the names and formulas of the commercially available iodonium salts along with their positions of the maximum absorbance.

**Figure 21.** Photodissociation of iodonium salts by the mechanism: A—heterolytic and B—homolytic.

However, commercial iodonium salts currently used in the industry have light absorption characteristics in the UV-C range, i.e., $\lambda_{\text{max}} = 220–280$ nm, and that have very low or zero light absorption in the long-term UV-A range ($\lambda > 300$ nm). Table 3 shows the names and formulas of the commercially available iodonium salts along with their positions of the maximum absorbance.
This makes them unsuitable for initiating photopolymerization processes in the UV-A range and in the visible area, which is a significant technological problem due to the low efficiency of the obtained polymer materials. Therefore, the light sensitivity of commercial cationic photoinitiators is in the short wavelength range of UV light, which is a significant technological problem in their different applications, as well as dental materials applications.

This is because the light sources used in dentistry usually have emission in the range from 420 to 515 nm (Single peak LCUs) (in modern lamps 380–440 nm) or possibly from 380 to 520 nm (Dual peak LCUs). The result is that commercially available cationic photoinitiators have mismatching of the absorption characteristics with the emission characteristics of these light sources (Figure 22). This makes them unsuitable for initiating photopolymerization processes in the UV-A range and in the visible area, which is a significant technological problem due to the low efficiency of the obtained polymer materials. Although this activation strategy is satisfactory in some applications, such as commercial iodonium photoinitiators used in industrial practice [196].

| Photoinitiator                | Structure | Wavelength of Maximum Absorbance ($\lambda_{\text{max}}$) [nm] |
|------------------------------|-----------|---------------------------------------------------------------|
| Hycure-810 (ChemFine)        | ![Structure](image1) | 230–260 nm                                                   |
| Uvacute 1600 (Surface Specialties [UCB]) | ![Structure](image2) | 240 nm                                                        |
| Sarcat CD-1012 (Sartomer)    | ![Structure](image3) | 240 nm                                                        |
| OMNICAT 440 (IGM) or Hycure-820 (ChemFine) | ![Structure](image4) | 267 nm                                                        |
| Irgacure 250 (Ciba)          | ![Structure](image5) | 240–245 nm                                                   |
| UV 9310 (GE)                 | ![Structure](image6) | 240 nm                                                        |
| Rhodorsil 2076 (Rhodia)      | ![Structure](image7) | 240 nm                                                        |
| Rhodorsil 2074 (Rhodia)      | ![Structure](image8) | 240–250 nm                                                   |
| Sylanto-7MP                  | ![Structure](image9) | 350 nm                                                        |
| Sylanto-7MS                  | ![Structure](image10) | 349 nm                                                        |

Therefore, the light sensitivity of commercial cationic photoinitiators is in the short wavelength range of UV light, which is a significant technological problem in their different applications, as well as dental materials applications.
coating materials, the use of UV light is not recommended in the biological field. However, the use of absorbing dyes in the visible light area as sensitizers may allow the reaction with onium salts [197–199].

Figure 22. Comparison of the absorption characteristics of commercial iodonium photoinitiators with the emission characteristics of a commercially available dental lamp D-LIGHT® PR and photograph of the lamp.

Two- or Three-Component Photoinitiating Systems Containing Iodonium Salt for Initiating Free Radical Photopolymerization Processes for an Obtained Dental Composites

The hydrophobicity of commonly used photoinitiating systems based on camphorquinone (CQ) and ethyl 4-(dimethylamino)benzoate (EDMAB) has limited their performance in the wet, oral environment. Therefore, to eliminate this limitation, a water-soluble iodonium salt is added mainly diphenyliodonium hexafluorophosphate (DPIHP) [129]. Iodonium salt as an accelerator in dental applications is usually found in a ternary initiating system containing CQ and a tertiary aromatic amine. However, it is also possible to use a two-component initiating system based on CQ and an iodonium salt (without a tertiary aromatic amine), except that, compared to the three-component system, slightly lower conversion rates are usually obtained.

In a two-component initiating system based on CQ/onium salt, after being irradiated with blue light, the exciplex state is formed; next, the onium salt is reduced by electron transfer. The resulting diphenyliodine free radical is unstable and quickly degrades to phenyliodine and phenyl free radical, which causes the reaction to be irreversible. These reactive phenyl forms are useful in initiating the photopolymerization. Radicals generated during polymerization propagation effectively cleave the C–I bond, releasing another radical and allowing the photopolymerization [200].

The three-component initiating system is usually based on CQ/aromatic amine/iodonium salt, and this system is characterized that the additional amine radicals are produced. In addition, CQ is regenerated through substitution of inactive and also termination radicals to active radicals in the form of phenyl radicals and the generation of positive active phenyl radicals [193].

This makes the photopolymerization process initiated by the ternary initiation system extremely efficient and fast. A similar degree of conversion and rate of polymerization compared to acylphosphine oxide (MAPO) or bis-acylphosphine oxide (BAPO) photoinitiators is even obtained [201–203].

The photoinitiating system based on CQ/iodonium salt or CQ/iodonium salt/amine have mainly found application in initiating traditional methacrylate monomers used in the production of dental composites [201,202,204–207]. The addition of iodonium salt to the photoinitiating systems used to prepare dental composites brings many benefits. The most important are the
• Increase conversion in short photo-activation time;
• Reduced inhibitory polymerization effect from an organic solvent;
• Improved dentin bonding performance;
• Improved reactivity and mechanical properties;
• Decreased sorption and water solubility;
• Reduced initial color and improved color stability.

Many publications have been reported about the beneficial effect of onium salts on the properties of the final dental product obtained by free radical photopolymerization [79,130,138,147,184,205,206,208–216]. Researchers from Brazil in 2007 showed that the addition of onium salt improves the polymerization kinetics in dental adhesive resin. The three-component photoinitiating system based on camphorquinone (CQ), ethyl 4-dimethylaminobenzoate (EDAB) and diphenyliodonium hexafluorophosphate (DPIHFP) showed an improvement on the polymerization rate of standard methacrylate monomers (bisphenol A glycidyl dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA)), leading to high conversion of monomers in short photo-activation time [130]. In another study, the same science team demonstrated that onium salt reduces the inhibitors polymerization effect from ethanol in a model dental adhesive resin [214]. Four years later (in 2012), they proved that the same three-component photoinitiating system using iodonium salt showed similar microtensile bond strength to dentin when compared to the commercial light-cured binding system—Clearfil SE Bond (CSEB). Moreover, after one year of storage, dentin’s bond strength was higher for three-component initiating systems [205]. That the addition of iodonium salt in a photoinitiating ternary system combined with with CQ and EDB increases the conversion of standard methacrylate monomers used in the production of dental composites and do not affect the dentin bond strength has also been confirmed in the work of Borges et al. [215]. They proved that iodonium salt increased conversion for the CQ-based system but had no significant influence on 1-phenyl-1,2-propanedione (PPD) or phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO) systems. The fact that the addition of iodonium salt significantly improves the conversion rates for the CQ/EDAB/idoonium salt system and does not significantly increase the conversion rate for the PPD/EDAB/idoonium salt or BAPO/EDAB/idoonium salt systems results directly from the molar extinction coefficient values of photoinitiators. High extinction coefficients indicate a high probability of light absorption at a specific wavelength, leading to high quantum yields and overall conversion improvement [217]. As CQ has the lowest $\varepsilon_{\lambda_{\text{max}}} (-28 \text{ dm}^3/\text{mol cm})$ compared to PPD ($\sim 150 \text{ dm}^3/\text{mol cm}$) and BAPO ($\sim 300 \text{ dm}^3/\text{mol cm}$) [119] additional improvement the degree of the conversion provided by iodonium salt is more effective for CQ-system. The ternary system (BAPO + EDAB + iodonium salt) showed a slight increase degree of conversion in short photo-activation time compared to the binary BAPO/EDAB system. Nevertheless, it is extremely interesting that this ternary system showed significantly higher conversion rates ($\sim 7\%$) than the ternary photoinitiating system based on camphorquinone [147].

Iodonium salt can also be used as a component of photoinitiating systems containing thioxanthone. For example, the initiating systems in the form of 2-hydroxy-3-(3,4 dimethyl-9-oxo-9H-thioxanthen-2-yl-oxy)-N,N,N-trimethyl-1-propanaminium chloride (QTX), ethyl 4-dimethylaminobenzoate (EDAB), diphenyliodonium hexafluorophosphate (DPIHFP) and 2-hydroxy-3-(3,4 dimethyl-9-oxo-9H-thioxanthen-2-yl-oxy)-N,N,N-trimethyl-1-propanaminium chloride (QTX), diphenyliodonium hexafluorophosphate (DPIHFP) and p-toluenesulfonic acid sodium salt hydrate (SULF) are effective in initiating the process of radical photopolymerization of acrylate monomers used in dentistry. The use of these initiation systems leads to similar conversion rates as in the case of the standard two-component system (CQ + EDAB). Nevertheless, these systems showed lower reactivity [184].

The addition of iodonium salt to conventional initiating systems also improves the physical and mechanical properties of dental composites. Gonçalves et al. have reported that, with diligent use,
a ternary photoinitiator system including camphorquinone (CQ), 2-dimethylamino)ethyl methacrylate (DMAEMA) and diphenyliodonium hexafluorophosphate (DPI) in BisGMA/TEGDMA in 1:1 mass ratio may improve not only reactivity but also the mechanical properties of dental resin without significantly increasing the polymerization stress [216]. This work demonstrates that the use of 0.5 mol% DPI showed the best balance between increasing photopolymerization kinetics and producing a polymer with appropriate physical properties. Moreover, C.R. Augusto et al. demonstrated that the addition of 0.5 mol% iodonium salt for commercially available dual-polymerizing self-adhesive resin types of cement-based on RelyX U100 (3M ESPE) and BisCem improved the physical properties of these materials, increasing the degree of conversion, microhardness and push-out bond strength [206]. In turn, Dressano et al. proved that methacrylate resin containing PPD + CQ with iodonium salt improved not only the conversion of the materials but also influenced their physicochemical properties positively. These systems had higher flexural strength and modulus of elasticity, cohesive strength, and lower sorption and water solubility [138]. Sauro et al. noticed that the inclusion of the hydrophilic ionic salt such as DPIHP increased the affinity between amphiphilic monomers (ethoxylated-Bisphenol-A-dimethacrylates and 2-hydroxyethyl methacrylate) and two-component photoinitiating system, enhanced the degree of conversion, glass transition temperature (Tg) and also resin permeability (rP) [208]. The research confirms that the introduction of an iodonium salt to the three-component initiator system based on CQ and aromatic amine or the two-component initiator system containing only CQ improves the aesthetic properties of the dental composite. Shin et al. proved that the introduction of iodonium salt affects to reduce initial color and improve color stability [79].

In 2016, Bouzrati-Zerelli et al. developed the new ternary system based on camphorquinone/triphenylgermanium hydride/iodonium salt as a powerful system for initiating photopolymerization of methacrylate monomers used in the production of dental composites in thin films or thick composites upon exposure to a dental blue LED centered at 477 nm. Higher conversion rates were recorded for this system than for the standard CQ/amine system. Excellent bleaching properties were also observed under irradiation in the presence of these photoinitiating system [209].

In turn, Kirschner et al. proposed completely new iodonium salts, iodonium sulfonates, as an amine replacement. PISs based on CQ/iodonium sulfonate presents an excellent performance in methacrylate monomers upon blue light irradiation, similar to the CQ/amine system. Moreover, particularly useful bleaching properties were obtained [210]. The same team in 2019 proposed another compound, aryliodonium ylides (AY), as high-performance iodonium salts and efficient additives to CQ/amine-based systems methacrylate polymerization under blue light. Aryliodonium ylides (Table 4) present a broadband of absorption spectra in the 300–400 nm region. This work demonstrates that enhanced polymerization performances were achieved for the CQ/amine/AY system compared to the reference CQ/amine system. Besides, these PISs showed good bleaching properties after polymerization, and interestingly, excellent initiating ability in strongly oxygen-inhibited conditions [211].
Table 4. Summary of the photoinitiating systems consisting iodonium salt for free radical photopolymerization used in dental application.

| MONOMERS       | IODONIUM SALT                  |
|----------------|-------------------------------|
| BisGMA         | DPHF/DPI/SC938                |
| BisEMA/E-BisADM| OPPI                          |
| HEMA           | DPIpTS                        |
| MA             | Iod DPPBS                     |
| TEGDMA         | S5                             |
| UDMA           | S6                             |
| GDMA           | IS1                            |
|                 | IS2                            |
|                 | IS3                            |
|                 | IS4                            |
|                 | IS5                            |

**MONOMERS**
- BisGMA
- BisEMA/E-BisADM
- HEMA
- MA
- TEGDMA
- UDMA
- GDMA

**IODONIUM SALT**
- DPHF/DPI/SC938
- OPPI
- DPIpTS
- Iod DPPBS
- S5
- S6

R= H or CH₃ (~1:1)
### photoinitiating systems based on Iodonium Salts

| Photoinitiating Systems Based on Iodonium Salts | Reference of Photoinitiating System | Monomers/Solution | Influence of Addition Iodonium Salt/Properties of the Dental Composition with Iodonium Salt | Ref. |
|-----------------------------------------------|-------------------------------------|-------------------|-------------------------------------------------------------------------------------------------|------|
| 1 mol% CQ + 0.25 mol% DPIHFP                  | 1 mol% CQ                           | 50 wt.% Bis-GMA   | increase conversion in short photo-activation time                                              | [130]|
| 1 mol% CQ + 0.5 mol% DPIHFP                  | 1 mol% CQ + 0.25 mol% EDAB          | 25 wt.% TEGDMA    |                                                                                                 |      |
| 1 mol% CQ + 1 mol% DPIHFP                    | 1 mol% CQ + 1 mol% EDAB             | 25 wt.% HEMA      |                                                                                                 |      |
| 1 mol% CQ + 2 mol% DPIHFP                    | 1 mol% CQ + 2 mol% EDAB             |                   |                                                                                                 |      |
| 1 mol% CQ + 4 mol% DPIHFP                    | 1 mol% CQ + 4 mol% EDAB             |                   |                                                                                                 |      |

### ADDITIVES

- **CQ**
- **EDAB/ETDA**
- **PPD**
- **BAPO**
- **PhGeH**
- **BARB**
- **QTX**
- **SULF**
- **DMAEMA**
- **DMABN**
- **NapTS**
- **NaMeSP**
- **ZnBnS**
- **NaAcABS**
- **ZniPrS**
- **NaBuNS**
- **NapTSo**
- **DPPBS**
| Photoinitiating Systems Based on Iodonium Salts | Reference of Photoinitiating System | Monomers/Solution | Influence of Addition Iodonium Salt/Properties of the Dental Composition with Iodonium Salt | Ref. |
|-----------------------------------------------|------------------------------------|------------------|------------------------------------------------------------------------------------------|-----|
| 1 mol% CQ + 1 mol% EDAB + 1 mol% DPIHFP      | 1 mol% CQ + 1 mol% EDAB            | 50 wt.% Bis-GMA  | reduce the inhibitory polymerization effect from an organic solvent                     | [214] |
| 1 mol% CQ + 1 mol% DPIHFP                    | 1 mol% CQ                          | 50 wt.% Bis-GMA  | improve dentin bonding performance                                                     | [205] |
| 1 mol% CQ + 1 mol% EDAB + 1 mol% DPIHFP      | 1 mol% CQ + 1 mol% EDAB            | BisGMA:HEMA (60:40 wt.%) | increase conversion, does not affect the dentin bond strength                      | [215] |
| 1 mol% BAPO + 1 mol% DPIHFP                  | 1 mol% BAPO                        | 50 wt.% Bis-GMA  | highest polymerization and conversion rate for 1 mol% BAPO/1 mol% EDAB/1 mol% DPIHFP in short photo-activation time | [147] |
| QTX + DPIHFP                                 | QTX + EDAB                         | 50 wt.% Bis-GMA  | similar conversion rates as in the case of the standard two-component system (CQ + EDAB); lower reactivity | [184] |
| QTX + EDAB + DPIHFP                          | CQ + EDAB                          | 50 wt.% Bis-GMA  |                                                                        | [184] |
| QTX + BAQB                                   | QTX + EDAB                         | 50 wt.% Bis-GMA  |                                                                        | [184] |
| QTX + DPIHFP + SULF                          | QTX + EDAB                         | 50 wt.% Bis-GMA  |                                                                        | [184] |
| QTX + DPIHFP + SULF                          | QTX + EDAB                         | 50 wt.% Bis-GMA  |                                                                        | [184] |
| 1 mol% CQ + 2 mol% DMAEMA/0.25, 0.5, 1, 2 or 4 mol% DPI| 1 mol% CQ/2 mol% DMAEMA            | 20 wt.% Bis-GMA  | improve the reactivity and mechanical properties                                      | [216] |

Table 4. Cont.
### Table 4. Cont.

| Photoinitiating Systems Based on Iodonium Salts | Reference of Photoinitiating System | Monomers/Solution | Influence of Addition Iodonium Salt/Properties of the Dental Composition with Iodonium Salt | Ref. |
|-----------------------------------------------|-------------------------------------|-------------------|------------------------------------------------------------------------------------------|-----|
| 0.5 mol% CQ + 0.5 mol% DPI                    | commercially available dual-polymerizing self-adhesive resin cements: RelyX U100 (3M ESPE) and BisCem (Bisco Inc.) | 0.5 mol% CQ       | increase the degree of conversion, microhardness and push-out bond strength              | [206]|
| 0.5 mol% CQ + 0.5 mol% PPD + 0.5 mol% DPI   |                                                    | 0.5 mol% PPD      |                                                                                          |     |
| 1.0 mol% CQ + 1.0 mol% PPD + 0.5 mol% DPI   |                                                    | 1.0 mol% PPD      |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD | improve flexural strength and modulus of elasticity, cohesive strength, as well as lower sorption and water solubility | [138]|
| 1.0 mol% CQ + 1.0 mol% PPD + 0.5 mol% DPI   |                                                    | 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 0.5 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 0.5 mol% PPD |                                                                                          |     |
| 1.0 mol% CQ + 0.5 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 0.5 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 0.5 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 0.5 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 0.5 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.5 mol% CQ + 1.0 mol% PPD + 1.0 mol% DPI   |                                                    | 1.0 mol% CQ + 1.0 mol% PPD |                                                                                          |     |
| 0.25 wt.% CQ + 1 wt.% ETDA + 1 wt.% DPIHP    | 0.25 wt.% CQ + 1 wt.% ETDA                       | 0.25 wt.% CQ + 1 wt.% ETDA | enhance the degree of conversion, glass transition temperature (Tg) as well as resin permeability (rP). | [208]|
| 1 part of CQ and 2 parts of OPPI             | CQ only                                           | CQ only           | reduce initial color and improve color stability                                           | [79] |
| Equally proportioned CQ, OPPI, and DMAEMA   | 1 part of CQ and 2 parts of DMAEMA               | 37.5 wt.% BisGMA, 37.5 wt.% BisEMA, 25 wt.% TEGDMA | excellent bleaching properties,                                                            |     |
| Total concentrations of 1 wt.% and 3 wt.%   | Total concentrations of 1 wt.% and 3 wt.%        | 37.5 wt.% BisGMA, 37.5 wt.% BisEMA, 25 wt.% TEGDMA |                                                                                          |     |
| CQ + Ph₃GeH + DPI                           | CQ + EDB                                          | 70 wt.% Bis-GMA, 30 wt.% TEGDMA |                                                                                          | [209]|
| in different mass ratio                     | CQ + EDB                                          | 70 wt.% Bis-GMA, 30 wt.% TEGDMA |                                                                                          |     |
|                                               | CQ + EDB                                          | 70 wt.% Bis-GMA, 30 wt.% TEGDMA |                                                                                          |     |
### Table 4. Cont.

| Photoinitiating Systems Based on Iodonium Salts | Reference of Photoinitiating System | Monomers/Solution | Influence of Addition Iodonium Salt/Properties of the Dental Composition with Iodonium Salt | Ref. |
|-----------------------------------------------|------------------------------------|-------------------|--------------------------------------------------------------------------------------|------|
| 0.5 wt.% CQ + 1 wt.% IS1                     | 0.5 wt.% CQ + 1 wt.% EDB           | 30 wt.% BisGMA    | excellent bleaching properties, very good performance,                                 | [210]|
| 0.5 wt.% CQ + 1 wt.% IS2                     | 0.2 wt.% CQ + 0.2 wt.% EDB         | 70 wt.% TEGDMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% IS3                     | 0.2 wt.% CQ + 0.2 wt.% EDB + 1 wt.% SC938 | 63 wt.% BisGMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% IS4                     | 0.2 wt.% CQ + 0.2 wt.% EDB         | 27 wt.% TEGDMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% IS5                     | 0.2 wt.% CQ + 0.2 wt.% EDB + 1 wt.% SC938 | 10 wt.% MA        |                                                                                       |      |
| 0.2 wt.% CQ + 0.2 wt.% EDB + 1 wt.% IS3      | 0.2 wt.% CQ + 0.5 wt.% EDB         | 63 wt.% BisGMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% NaMeSP + 1 wt.% SC938   | 0.5 wt.% CQ + 1 wt.% NaMeSP        | 30 wt.% BisGMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% ZnBuS + 1 wt.% SC938    | 0.5 wt.% CQ + 1 wt.% ZnBuS         | 70 wt.% TEGDMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% NaAcABS + 1 wt.% SC938  | 0.5 wt.% CQ + 1 wt.% NaAcABS       | 10 wt.% MA        |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% ZniPrS + 1 wt.% SC938   | 0.5 wt.% CQ + 1 wt.% ZniPrS        | 63 wt.% BisGMA    |                                                                                       |      |
| 0.5 wt.% CQ + 1 wt.% NapTSo + 1 wt.% SC938   | 0.5 wt.% CQ + 1 wt.% NapTSo        | 27 wt.% TEGDMA    | strongly oxygen-inhibited conditions, excellent bleaching properties                  | [211]|
| 0.2 wt.% CQ + 0.5 wt.% EDB + 1 wt.% NaMeSP+ 1 wt.% SC938 | 0.2 wt.% CQ + 0.5 wt.% EDB       | 30 wt.% BisGMA    |                                                                                       |      |
| 0.2 wt.% CQ + 0.5 wt.% EDB + 1 wt.% NapTSo+ 1 wt.% SC938 | 0.2 wt.% CQ + 0.5 wt.% EDB       | 70 wt.% TEGDMA    |                                                                                       |      |
| 0.2 wt.% CQ + 0.5 wt.% EDB + 1 wt.% SC938    | 0.2 wt.% CQ + 0.5 wt.% EDB         | 10 wt.% MA        |                                                                                       |      |
| 0.2 wt.% CQ + 0.5 wt.% EDB + 1 wt.% SC938    | 0.2 wt.% CQ + 0.5 wt.% EDB         | 63 wt.% BisGMA    |                                                                                       |      |
| 0.2 wt.% CQ + 0.5 wt.% EDB + 1 wt.% SC938    | 0.2 wt.% CQ + 0.5 wt.% EDB         | 27 wt.% TEGDMA    | excellent bleaching properties, color stability, excellent mechanical properties       | [212]|

Spectrum® TPH®/3 resin received from Dentsply Sirona consisting of a mixture of modified BisGMA, TEGDMA and other methacrylate monomers.
| Photoinitiating Systems Based on Iodonium Salts | Reference of Photoinitiating System | Monomers/Solution | Influence of Addition Iodonium Salt/Properties of the Dental Composition with Iodonium Salt | Ref. |
|-----------------------------------------------|-----------------------------------|-------------------|---------------------------------------------------------------------------------|------|
| 0.5 wt.% CQ + 1 wt.% DPPBS + 1 wt.% Iod      |                                   |                   |                                                                                 |      |
| 0.5 wt.% CQ + 1 wt.% Iod-DPPBS               |                                   |                   |                                                                                 |      |
| 0.4 wt.% CQ + 0.1 wt.% Iod-DPPBS             |                                   |                   |                                                                                 |      |
| 0.4 wt.% CQ + 0.4 wt.% Iod-DPPBS             |                                   |                   |                                                                                 |      |
| 0.4 wt.% CQ + 0.6 wt.% Iod-DPPBS             |                                   |                   |                                                                                 |      |
| 0.5 wt.% CQ + 0.2 wt.% EDB + 1 wt.% DPPBS    | 0.5 wt.% CQ + 0.2 wt.% EDB        | 30 wt.% BisGMA    | oxygen inhibition                                                              | [213]|
| 0.4 wt.% CQ + 0.6 wt.% DPPBS + 1 wt.% Iod    | 0.4 wt.% CQ + 0.2 wt.% EDB        | 70 wt.% TEGDMA    |                                                                                 |      |
| 0.4 wt.% CQ + 1 wt.% Iod-DPPBS               | 0.5 wt.% CQ + 0.2 wt.% EDB        |                   |                                                                                 |      |
| 0.4 wt.% CQ + 0.4 wt.% Iod-DPPBS             | 0.5 wt.% CQ + 0.4 wt.% EDB        |                   |                                                                                 |      |
| 0.4 wt.% CQ + 0.6 wt.% Iod-DPPBS             | 0.5 wt.% CQ + 0.6 wt.% Iod-DPPBS  |                   |                                                                                 |      |
| 0.5 wt.% CQ + 0.2 wt.% EDB + 1 wt.% DPPBS    | 0.5 wt.% CQ + 0.2 wt.% EDB + 1 wt.% DPPBS + 1 wt.% Iod | 0.5 wt.% CQ + 0.1 wt.% Iod |                                                                                 |      |
| 0.5 wt.% CQ + 1 wt.% EDB + 1 wt.% DPPBS + 1 wt.% Iod | 0.4 wt.% CQ + 0.2 wt.% EDB + 1 wt.% DPPBS + 1 wt.% Iod | 0.5 wt.% CQ + 0.2 wt.% EDB + 1 wt.% DPPBS + 1 wt.% Iod |                                                                                 |      |

BisGMA—bisphenol glycidyl methacrylate; BisEMA/E-BisADM—ethoxylated Bisphenol A dimethacrylate; HEMA—2-hydroxyethyl methacrylate; TEGDMA—triethylene glycol dimethacrylate; UDMA—urethane dimethacrylate; GDMA—1,3-glycerol dimethacrylate; DPHFP/DPI/SC938—diphenyliodonium hexafluorophosphate; OPPI—p-octyloxy-phenyl-phenyl iodonium hexafluoroantimonate; DPlpTS—diphenyliodonium p-toluenesulfonate; S5—aryliodonium ylides; S6—aryliodonium ylides; IS1—phenyl(2,4,6-trimethoxyphenyl)iodonium p-toluene sulfonate; IS2—(4-methylphenyl)(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate; IS3—bis(4-tert-butylphenyl) iodonium p-toluene sulfonate; IS4—3,5-dichlorophenyl(2,4,6-trimethoxyphenyl)iodonium p-toluene sulfonate; IS5—bis(4-fluorophenyl)iodonium trifluoromethanesulfonate; (IS5); CQ—camphorochinone; EDAB/ETDA—dimethylaminoethyl amine benzoate; PPD—1-phenyl-1,2-propanedione; BAPO—phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide; Pb₃GeH—triphenylermanium hydride; BARB—1,3-diethyl-2-thio-barbituric acid; QTX—2-hydroxy-3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yl)-N,N,N-trimethyl-1-propanaminium chloride; SULF—p-toluenesulfonic acid sodium salt hydrate; DMAEMA—2-dimethylamoethy methyl methacrylate; NaAcABS—sodium 4-(acetylamo)benzenesulfinat; ZniPrS—zinc isopropylsulfinate; NaBuNS—sodium butynaphtalenesulfinate; NapTSo—sodium p-toluene sulfonate; DPPBS—sodium 3-(diphenylphophino)benzenesulfonate.
PISs based on camphorquinone (CQ)/sulfinate and CQ/sulfonate, with iodonium salt, are also proposed by Kirchner et al. [212]. These photoinitiating systems were compared to the traditionally CQ/amine system. They proved that sulfinates and sulfonates combination with CQ is a perfect alternative to the replacement of standard amines used in methacrylate dental resin. With the participation of these initiating systems, dental composites with excellent bleaching properties, color stability, and excellent mechanical properties were obtained. An interesting derivative of iodonium salt developed is also diphenylidonium p-toluenesulfonate (DPipTS) (Table 4). It is used in combination with camphorquinone as an amine replacement [212]. In turn new iodonium salt based on phosphine derivative proposed by Kirchner et al. exhibits two essential functions: phosphine moiety to overcome oxygen inhibition and an iodonium salt moiety as counter cation to initiate the polymerization process [213].

The structures of the tested compounds, composition, and the influence of iodonium salt on the properties of dental composites are presented in Table 4.

5. Iodonium Salts as Photoinitiators for Cationic and IPN Photopolymerization to Obtain a Dental Composites

In recent years, researchers from around the world have designed new initiating systems based on onium salts for cationic and thiol-ene photopolymerization processes for obtained dental composites.

In 2014, it was first described using composites based on cationic systems for dental applications [106]. It has been shown that the two-component system of the CQ/[4(1-methylethyl)phenyl][4-methylphenyl] iodonium tetrakis (pentafluorophenyl)borate, Rhodorsil 2074 is useful for initiating the cationic photopolymerization process of bis[2-(3,4-epoxycyclohexyl)ethyl]tetramethylsiloxane, UV30. CQ promotes the photopolymerization process even in the absence of amines as a hydrogen donor. It can separate labile hydrogen from an epoxy monomer; carbon-concentrated radicals are formed, which are oxidized by onium salt. The complete conversion of the epoxy group was achieved after 50 s with blue irradiation.

Fu et al. proposed the use a three-component photoinitiation system comprising 1 wt.% CQ (camphorquinone), 2 wt.% DMAEMA (2-(dimethylamino) ethyl meth acrylate) and 2 wt.% diphenylidonium hexafluorophosphate to initiate the copolymerization of the matrix resins which combine bisphenol-S-bis(3-methacrylate-2-hydroxy propyl) ether (BisS-GMA) with the expanding monomer unsaturated spiro orthoesters 2-methylene-1,4,6-trispiro[4,4] nonane (MTOSN), for minimizing the volumetric shrinkage that generally occurs during polymerization. The results supported that the dental composites based on the expanding monomer and three-component photoinitiator system engendered a more significant decrease of volumetric shrinkage and better mechanical properties [68].

Danso, R. et al. proposed new resins (Oxirane-Acrylate IPN System—OASys) based on p-Cycloaliphatic diepoxide EPALLOY 5000™ (EP5000) and dipenta erythritol hexaacrylate (DPHA). A three-component initiating system in the form of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate (OPPI), CQ, and a co-reactant oligomeric diol 250 Mn poly(tetrahydrofuran) was used. These results demonstrate that OASys resins cure well, are more hydrophobic, and have lower shrinkage stress than BisGMA-based resins. However, they are mechanically weaker [218].

This new class of photoinitiators based on silyl glyoxylates to initiate cationic polymerization combined with an iodonium salt was presented in an article by Kirschner [179]. This system can be used to initiate free radical/cationic hybrid polymerization and for the synthesis of interpenetrating polymer networks. The system silyl glyoxylate/iodonium exhibits excellent polymerization performances and exceptional bleaching properties compared to other well-established photoinitiators (e.g., camphorquinone) [179]. This system is also suitable for initiating a hybrid monomer (2-vinylxethoxyethyl methacrylate [VEEM]). This monomer leads to a considerable improvement of the mechanical properties of the final polymer through hybrid polymerization [179].
Zang et al. proposed the use 1,2-diketone/iodonium salt (and optional NVK) systems to initiate cationic photopolymerization of epoxides or free radical photopolymerization of methacrylates. Most of the photoinitiating systems have exhibited higher initiation ability than the well-known CQ-based systems. Nevertheless, the study of the biocompatibility indicates that these materials exhibit cytotoxicity [219].

Summary of the photoinitiating systems consisting of iodonium salt for cationic and IPN photopolymerization used in a dental application is presented in Table 5.
Table 5. Summary of the photoinitiating systems consisting of iodonium salt for cationic and IPN photopolymerization used in a dental application.

| Iodonium Salt | Other Co-initiators | Monomers | Properties | Ref. |
|---------------|---------------------|----------|------------|------|
| Rhodosil 2074 | CQ, EMBO            | UV 30    | lowering of shrinkage | [106] |
| DPIHFP        | CQ                  | DMAEMA, BisGMA | greater decrease of volumetric shrinkage and better mechanical properties | [68] |
| OPPi          | CQ, Diol            | DPHA, EPS5000 | lower shrinkage stress more hydrophobic mechanically weaker | [218] |
Table 5. Summary of the photoinitiating systems consisting of iodonium salt for cationic and IPN photopolymerization used in a dental application.

| Iodonium Salt | Other Co-initiators | Monomers | Properties | Ref. |
|---------------|---------------------|----------|------------|------|
| DPI (TMS) 3SiH DVE-3 DEGVE | (TMS)$_3$SiH | DVE-3 DEGVE | exceptional bleaching properties | [179] |
| SC938 Ph$_3$GeH CHDVE DODECYL VINYL ETHER | Ph$_3$GeH | CHDVE DODECYL VINYL ETHER | better mechanical properties | [68] |
| PI 2074 EDB DEGDVE VEEM | EDB | DEGDVE VEEM | higher initiation ability than the well-known CQ-based systems, but cytotoxicity | [219] |
| IOD | | | | |
| ANPQ | | | | |
| AATQ | | | | |
| PANQ | | | | |
6. Challenges of Photoinitiator Systems for Dental Applications, Future Trends and Practical Aspects

In recent years, several new initiating systems for dental composites have been developed. However, these are mainly photoinitiating systems used to obtain dental composites by radical photopolymerization [220]. Most of them have several of the significant disadvantages mentioned earlier in this article. Despite such significant progress, new initiating systems with improved properties are still being sought, mainly to produce dental composites obtained by cationic photopolymerization, which

- Are entirely safe for humans, eliminating the cytotoxic amines and acrylate monomers that often cause severe allergies;
- Do not generate yellow color-eliminating camphorquinone, greater aesthetics, and quality of the final product;
- Have better and/or comparable mechanical properties and, due to the use of polymerizable monomers via the cationic mechanism, have reduced polymerization shrinkage;
- Is possible to be used with dental lamps emitting radiation in the visible light range for the curing process, eliminating harmful UV radiation.

7. Conclusions

In conclusion, it can be stated that in the scope of initiating systems for photocuring dental composites according to the radical mechanism [152], a significant milestone towards solutions guaranteeing the active initiation of this type of process has now been realized. In addition, in recent years, new initiating systems containing iodonium salt to initiate cationic and/or IPN photopolymerization processes have been developed. In this way, dental composites with better mechanical properties and reduced polymerization shrinkage were obtained. Nevertheless, in most cases, these are camphorquinone-containing systems that generate yellow color or toxic co-initiators. In addition, the complete elimination of acrylate monomers that often cause severe allergies is still a significant challenge for researchers.

The literature review has presented previous achievements in the field of radical photoinitiators dedicated to the preparation of dental composites; their advantages and disadvantages are discussed. The advantages of iodonium salts and their potential to initiate cationic photopolymerization processes of silorane monomers to obtain new-generation dental composites were also indicated.

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References
1. Dietlin, C.; Schweizer, S.; Xiao, P.; Zhang, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P.; Lalevée, J. Photopolymerization upon LEDs: New photoinitiating systems and strategies. Polym. Chem. 2015, 6, 3895–3912. [CrossRef]
2. Funke, W. UV Curing: Science and Technology. Prog. Org. Coat. 1980, 8, 110. [CrossRef]
3. Ligon, S.C.; Husár, B.; Wutzel, H.; Holman, R.; Liska, R. Strategies to reduce oxygen inhibition in photoinduced polymerization. Chem. Rev. 2014, 114, 577–589. [CrossRef] [PubMed]
4. Yagci, Y.; Jockusch, S.; Turro, N.J. Photoinitiated polymerization: Advances, challenges, and opportunities. Macromolecules 2010, 43, 6245–6260. [CrossRef]
5. Sangermano, M.; Razza, N.; Crivello, J.V. Cationic UV-curing: Technology and applications. Macromol. Mater. Eng. 2014, 299, 775–793. [CrossRef]
6. Ortyl, J.; Popielarz, R. The performance of 7-hydroxycoumarin-3-carbonitrile and 7-hydroxycoumarin-3-carboxylic acid as fluorescent probes for monitoring of cationic photopolymerization processes by FPT. J. Appl. Polym. Sci. 2013, 128, 1974–1978. [CrossRef]

7. Ortyl, J.; Galek, M.; Milart, P.; Popielarz, R. Aminophthalimide probes for monitoring of cationic photopolymerization by fluorescence probe technology and their effect on the polymerization kinetics. Polym. Test. 2012, 31, 466–473. [CrossRef]

8. Noé, C.; Malburet, S.; Bouvet-Marchand, A.; Graillot, A.; Loubat, C.; Sangermano, M. Cationic photopolymerization of bio-renewable epidoxized monomers. Prog. Org. Coat. 2019, 133, 131–138. [CrossRef]

9. Ortyl, J.; Galica, M.; Popielarz, R.; Bogdał, D. Application of a carbazole derivative as a spectroscopic fluorescent probe for real time monitoring of cationic photopolymerization. Polish J. Chem. Technol. 2014, 16, 75–80. [CrossRef]

10. Ortyl, J.; Topa, M.; Kamińska-Borek, I.; Popielarz, R. Mechanism of interaction of aminocoumarins with reaction medium during cationic photopolymerization of triethylene glycol divinyl ether. Eur. Polym. J. 2019, 116, 45–55. [CrossRef]

11. Schwalm, R. UV Coatings: Basics, Recent Developments and New Applications, 1st ed.; Elsevier Science: Amsterdam, The Netherlands, 2006.

12. Schnabel, W. Polymers and Light: Fundamentals and Technical Applications; Wiley VCH: Hoboken, NJ, USA, 2007.

13. Andrzejewska, E. Photopolymerization kinetics of multifunctional monomers. Prog. Polym. Sci. 2001, 26, 605–665. [CrossRef]

14. Hola, E.; Topa, M.; Chachaj-Brekiesz, A.; Pilch, M.; Fiedor, P.; Galek, M.; Ortyl, J. New, highly versatile bimolecular photoinitiating systems for free-radical, cationic and thiol-ene photopolymerization processes under low light intensity UV and visible LEDs for 3D printing application. RSC Adv. 2020, 10, 7509–7522. [CrossRef]

15. Weems, A.C.; Delle Chiaie, K.R.; Yee, R.; Dove, A.P. Selective Reactivity of Myrcene for Vat Photopolymerization 3D Printing and Postfabrication Surface Modification. Biomacromolecules 2020, 21, 163–170. [CrossRef] [PubMed]

16. Xu, Y.; Noirbent, G.; Brunel, D.; Liu, F.; Gigmes, D.; Sun, K.; Zhang, Y.; Liu, S.; Morlet-Savary, F.; Xiao, P.; et al. Ketone derivatives as photoinitiators for both radical and cationic photopolymerizations under visible LED and application in 3D printing. Eur. Polym. J. 2020, 132, 109737. [CrossRef]

17. Tang, L.; Nie, J.; Zhu, X. A high performance phenyl-free LED photoinitiator for cationic or hybrid photopolymerization and its application in LED cationic 3D printing. Polym. Chem. 2020, 11, 2855–2863. [CrossRef]

18. Sivasankar, V.S.; Sachar, H.S.; Sinha, S.; Hines, D.R.; Das, S. 3D Printed Microdroplet Curing: Unravelling the Physics of On-Spot Photopolymerization. ACS Appl. Polym. Mater. 2020, 2, 966–976. [CrossRef]

19. You, S.; Wang, P.; Schimelman, J.; Hwang, H.H.; Chen, S. High-fidelity 3D printing using flashing photopolymerization. Addit. Manuf. 2019, 30, 100834. [CrossRef]

20. Lin, J.T.; Cheng, D.C.; Chen, K.T.; Liu, H.W. Dual-wavelength (UV and blue) controlled photopolymerization confinement for 3D-printing: Modeling and analysis of measurements. Polymers 2019, 11, 1819. [CrossRef]

21. Malas, A.; Isakov, D.; Couling, K.; Gibbons, G.J. Fabrication of high permittivity resin composite for vat photopolymerization 3D printing: Morphology, thermal, dynamic mechanical and dielectric properties. Materials 2019, 12, 3818. [CrossRef]

22. Sun, K.; Pigot, C.; Chen, H.; Nechab, M.; Gigmes, D.; Morlet-Savary, F.; Graff, B.; Liu, S.; Xiao, P.; Dumur, F.; et al. Free radical photopolymerization and 3D printing using newly developed dyes: Indane-1,3-dione and 1H-cyclopentanaphthalene-1,3-dione derivatives as photoinitiators in three-component systems. Catalysts 2020, 10, 463. [CrossRef]

23. Sirrine, J.M.; Zlatanic, A.; Meenakshisundaram, V.; Messman, J.M.; Williams, C.B.; Dvornic, P.R.; Long, T.E. 3D printing amorphous polysiloxane terpolymers via vat photopolymerization. Macromol. Chem. Phys. 2019, 220, 1800425. [CrossRef]

24. Zhao, T.; Yu, R.; Li, X.; Zhang, Y.; Yang, X.; Zhao, X.; Huang, W. A comparative study on 3D printed silicone-epoxy/acrylate hybrid polymers via pure photopolymerization and dual-curing mechanisms. J. Mater. Sci. 2019, 54, 5101–5111. [CrossRef]
25. Wilts, E.M.; Pekkanen, A.M.; White, B.T.; Meenakshisundaram, V.; Aduba, D.C.; Williams, C.B.; Long, T.E. Vat photopolymerization of charged monomers: 3D printing with supramolecular interactions. Polym. Chem. 2019, 10, 1442–1451. [CrossRef]

26. Bağheri, A.; Jin, J. Photopolymerization in 3D Printing. ACS Appl. Polym. Mater. 2019, 1, 593–611. [CrossRef]

27. Aduba, D.C.; Margarreta, E.D.; Marnot, A.E.C.; Heifferon, K.V.; Surbey, W.R.; Chartrain, N.A.; Whittington, A.R.; Long, T.E.; Williams, C.B. Vat photopolymerization 3D printing of acid-cleavable PEG-methacrylate networks for biomaterial applications. Mater. Today Commun. 2019, 19, 204–211. [CrossRef]

28. Chen, Z.; Li, J.; Liu, C.; Liu, Y.; Zhu, J.; Lao, C. Preparation of high solid loading and low viscosity ceramic slurries for photopolymerization-based 3D printing. Ceram. Int. 2019, 45, 11549–11557. [CrossRef]

29. Mokbel, H.; Anderson, D.; Plenderleith, R.; Dietlin, C.; Morlet-Savary, F.; Dumur, F.; Gigmes, D.; Fouassier, J.P.; Lalevée, J. Simultaneous initiation of radical and cationic polymerization reactions using the “GI” copper complex as photoredox catalyst: Applications of free radical/cationic hybrid photopolymerization in the composites and 3D printing fields. Prog. Org. Coat. 2019, 132, 50–61. [CrossRef]

30. Vaut, L.; Zeng, G.; Tosello, G.; Boisen, A. Sacrificial polymer substrates in photopolymerization-based micro 3D printing for fabrication and release of complex micro components. Adv. Mater. Technol. 2019, 4, 1900378. [CrossRef]

31. Metral, B.; Bischoff, A.; Ley, C.; Ibrahim, A.; Allonas, X. Photochemical study of a three-component photocyclic initiating system for free radical photoinitiating polymer: Implementing a model for digital light processing 3D printing. ChemPhotoChem 2019, 3, 1109–1118. [CrossRef]

32. Tomal, W.; Pilch, M.; Chachaj-Brekiesz, A.; Ortyl, J. Development of new high-performance biphenyl and terphenyl derivatives as versatile photoredox photoinitiating systems and their applications in 3D printing photopolymerization processes. Catalysts 2019, 9, 827. [CrossRef]

33. Fiedor, P.; Pilch, M.; Szymaszek, P.; Chachaj-Brekiesz, A.; Galek, M.; Ortyl, J. Photochemical study of a new bimolecular photoinitiating system for vat photopolymerization 3D printing techniques under visible light. Catalysts 2020, 10, 284. [CrossRef]

34. Corcione, C.E.; Greco, A.; Maffezzoli, A. Photopolymerization kinetics of an epoxy-based resin for stereolithography. J. Appl. Polym. Sci. 2004, 92, 3484–3491. [CrossRef]

35. Lalevée, J.; Morlet-Savary, F.; Dietlin, C.; Graff, B.; Fouassier, J.P. Photochemistry and radical chemistry under low intensity visible light sources: Application to photopolymerization reactions. Molecules 2014, 19, 15026–15041. [CrossRef]

36. Nowak, D.; Ortyl, J.; Kamińska-Borek, I.; Kukula, K.; Topa, M.; Popielarz, R. Photopolymerization of hybrid monomers: Part I: Comparison of the performance of selected photoinitiators in cationic and free-radical polymerization of hybrid monomers. Polym. Test. 2017, 64, 313–320. [CrossRef]

37. Nowak, D.; Ortyl, J.; Kamińska-Borek, I.; Kukula, K.; Topa, M.; Popielarz, R. Photopolymerization of hybrid monomers, Part II: Determination of relative quantum efficiency of selected photoinitiators in cationic and free-radical polymerization of hybrid monomers. Polym. Test. 2018, 67, 144–150. [CrossRef]

38. Topa, M.; Petko, F.; Galek, M.; Machowski, K.; Pilch, M.; Szymaszek, P.; Ortyl, J. Applicability of 1,6-Diphenylquinolin-2-one derivatives as fluorescent sensors for monitoring the progress of photopolymerisation processes and as photosensitisers for bimolecular photoinitiating systems. Polymers 2019, 11, 1756. [CrossRef] [PubMed]

39. Ortyl, J.; Milart, P.; Popielarz, R. Applicability of aminophthalimide probes for monitoring and acceleration of cationic photopolymerization of epoxides. Polym. Test. 2013, 32, 708–715. [CrossRef]

40. Hola, E.; Ortyl, J.; Jankowska, M.; Pilch, M.; Galek, M.; Morlet-Savary, F.; Graff, B.; Dietlin, C.; Lalevée, J. New bimolecular photoinitiating systems based on terphenyl derivatives as highly efficient photosensitzers for 3D printing application. Polym. Chem. 2020, 11, 922–935. [CrossRef]

41. Ortyl, J.; Wilamowski, J.; Milart, P.; Galek, M.; Popielarz, R. Relative sensitization efficiency of fluorescent probes/sensitizers for monitoring and acceleration of cationic photopolymerization of monomers. Polym. Test. 2015, 48, 151–159. [CrossRef]

42. Kamińska, I.; Ortyl, J.; Popielarz, R. Applicability of quinolizino-coumarins for monitoring free radical photopolymerization by fluorescence spectroscopy. Polym. Test. 2015, 42, 99–107. [CrossRef]

43. Kamińska, I.; Ortyl, J.; Popielarz, R. Mechanism of interaction of coumarin-based fluorescent molecular probes with polymerizing medium during free radical polymerization of a monomer. Polym. Test. 2016, 55, 310–317. [CrossRef]
44. Topa, M.; Ortyl, J.; Chachaj-Brekiesz, A.; Kamińska-Borek, I.; Pilch, M.; Popielarz, R. Applicability of samarium(III) complexes for the role of luminescent molecular sensors for monitoring progress of photopolymerization processes and control of the thickness of polymer coatings. Spectrochim. Acta-Part A Mol. Biomol. Spectrosc. 2018, 199, 430–440. [CrossRef]

45. Zuo, X.; Morlet-Savary, F.; Schmitt, M.; Le Nouën, D.; Blanchard, N.; Goddard, J.P.; Lalevée, J. Novel applications of fluorescent brighteners in aqueous visible-light photopolymerization: High performance water-based coating and LED-assisted hydrogel synthesis. Polym. Chem. 2018, 9, 3952–3958. [CrossRef]

46. Staneva, D.; Grabchev, I.; Bosch, P. Fluorescent hydrogel-textile composite material synthesized by photopolymerization. Int. J. Polym. Mater. Polym. Biomater. 2015, 64, 838–847. [CrossRef]

47. Xia, B.; Jiang, Z.; Debrey, D.; Li, D.; Oakley, J. Cytocompatible cell encapsulation via hydrogel photopolymerization in microfluidic emulsion droplets. Biomicrofluidics 2017, 11, 044102. [CrossRef]

48. Larsen, E.K.U.; Larsen, N.B.; Almdal, K.; Larsen, E.K.U.; Larsen, N.B.; Almdal, K. Multimaterial hydrogel with widely tunable elasticity by selective photopolymerization of PEG diacrylate and epoxy monomers. J. Polym. Sci. Part B Polym. Phys. 2016, 54, 1195–1201. [CrossRef]

49. Tseng, S.J.; Chien, C.C.; Liao, Z.X.; Chen, H.H.; Kang, Y.D.; Wang, C.L.; Hwu, Y.; Margaritondo, G. Controlled hydrogel photopolymerization inside live systems by X-ray irradiation. Soft Matter 2012, 8, 1420–1427. [CrossRef]

50. Young, C.J.; Poole-Warren, L.A.; Martens, P.J. Combining submerged electrospray and UV photopolymerization for production of synthetic hydrogel microspheres for cell encapsulation. Biotechnol. Bioeng. 2012, 109, 1561–1570. [CrossRef]

51. Patton, J.N.; Palmer, A.F. Photopolymerization of bovine hemoglobin entrapped nanoscale hydrogel particles within liposomal reactors for use as an artificial blood substitute. Biomacromolecules 2005, 6, 414–424. [CrossRef]

52. Schmocker, A.; Khoushabi, A.; Farahi, S.; Pioletti, D.; Bourban, P.-E.; Manson, J.A.; Moser, C. Multi-scale modeling of photopolymerization for medical hydrogel-implant design. In Biomedical Applications of Light Scattering VII; SPIE: Bellingham, WA, USA, 2013; Volume 8592, p. 85921D.

53. Zhou, Y.; Yang, D.; Ma, G.; Tan, H.; Jin, Y.; Nie, J. A pH-sensitive water-soluble N-carboxyethyl chitosan/poly(hydroxyethyl methacrylate) hydrogel as a potential drug sustained release matrix prepared by photopolymerization technique. Polym. Adv. Technol. 2008, 19, 1133–1141. [CrossRef]

54. Lorusso, E.; Ali, W.; Hildebrandt, M.; Mayer-Gall, T.; Gutmann, J.S. Hydrogel functionalized polyester fabrics by UV-induced photopolymerization. Polymers 2019, 11, 1329. [CrossRef]

55. Ingrasso, C.; Esposito Corcione, C.; Striani, R.; Comparelli, R.; Striccoli, M.; Agostiano, A.; Curri, M.L.; Frigione, M. UV-Curable Nanocomposite Based on Methacrylic-Siloxane Resin and Surface-Modified TiO₂ Nanocrystals. ACS Appl. Mater. Interfaces 2015, 7, 15494–15505. [CrossRef] [PubMed]

56. Liu, D.; Liu, F.; He, J.; Lassila, L.V.J.; Vallittu, P.K. Synthesis of a novel tertiary amine containing urethane dimethacrylate monomer (UDMTA) and its application in dental resin. J. Mater. Sci. Mater. Med. 2013, 24, 1595–1603. [CrossRef] [PubMed]

57. Fu, J.; Jia, F.; Xu, H.; Ji, B.; Liu, X. Properties of a new dental photocurable matrix resin with low shrinkage. J. Wuhan Univ. Technol. Mater. Sci. Ed. 2011, 26, 236–241. [CrossRef]

58. Ahn, K.D.; Han, D.K.; Lee, S.H.; Lee, C.W. New aromatic tert-amines for application as photoinitiator components in photocurable dental materials. Macromol. Chem. Phys. 2003, 204, 1628–1635. [CrossRef]

59. Park, J.; Ye, Q.; Singh, V.; Kieweg, S.L.; Misra, A.; Spencer, P. Synthesis and evaluation of novel dental monomer with branched aromatic carboxylic acid group. J. Biomed. Mater. Res.-Part B Appl. Biomater. 2012, 100B, 569–576. [CrossRef] [PubMed]

60. Bouzrati-Zerelli, M.; Maier, M.; Fik, C.P.; Dietlin, C.; Morlet-Savary, F.; Fouassier, J.P.; Klee, J.E.; Lalevée, J. A low migration phosphine to overcome the oxygen inhibition in new high performance photoinitiating systems for photocurable dental type resins. Polym. Int. 2017, 66, 504–511. [CrossRef]

61. Gatti, A.; Rastelli, A.N.S.; Ribeiro, S.J.L.; Messaddeq, Y.; Bagnato, V.S. Polymerization of photocurable commercial dental methacrylate-based composites: Photocalorimetry study. J. Therm. Anal. Calorim. 2007, 87, 631–634. [CrossRef]

62. Andreani, L.; Silva, L.L.; Witt, M.A.; Meier, M.M.; Joussef, A.C.; Soldi, V. Development of dental resinous systems composed of bisphenol a ethoxylated dimethacrylate and three novel methacrylate monomers: Synthesis and characterization. J. Appl. Polym. Sci. 2013, 128, 725–734. [CrossRef]
63. Podgórski, M. Synthesis and characterization of acetyloxypropylene dimethacrylate as a new dental monomer. *Dent. Mater.* **2011**, *27*, 748–754. [CrossRef]

64. Makvandi, P.; Ghaemy, M.; Ghadiri, A.A.; Mohseni, M. Photocurable, antimicrobial quaternary ammonium-modified nanosilica. *J. Dent. Res.* **2015**, *94*, 1401–1407. [CrossRef] [PubMed]

65. Makvandi, P.; Ghaemy, M.; Mohseni, M. Synthesis and characterization of photo-curable bis-quaternary ammonium dimethacrylate with antimicrobial activity for dental restoration materials. *Eur. Polym. J.* **2016**, *74*, 81–90. [CrossRef]

66. Cao, W.; Zhang, Y.; Wang, X.; Li, Q.; Xiao, Y.; Li, P.; Wang, L.; Ye, Z.; Xing, X. Novel resin-based dental material with anti-biofilm activity and improved mechanical property by incorporating hydrophilic cationic copolymer functionalized nanodiamond. *J. Mater. Sci. Mater. Med.* **2016**, *27*, 748–754. [CrossRef] [PubMed]

67. Cao, W.; Zhang, Y.; Wang, X.; Chen, Y.; Li, Q.; Xing, X.; Xiao, Y.; Peng, X.; Ye, Z. Development of a novel resin-based dental material with dual biocidal modes and sustained release of Ag<sup>+</sup> ions based on photocurable core-shell AgBr/cationic polymer nanocomposites. *J. Mater. Sci. Mater. Med.* **2017**, *28*, 103. [CrossRef]

68. Fu, J.; Liu, W.; Liu, X.; Tuladhar, S.L.; Wan, Q.; Wang, H. Properties of a new dental photocurable resin based on the expanding monomer and three-component photoinitiator system. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2014**, *24*, 384–390. [CrossRef]

69. He, J.; Garoushi, S.; Säilynoja, E.; Vallittu, P.K.; Lassila, L. The effect of adding a new monomer “Phene” on the polymerization shrinkage reduction of a dental resin composite. *Dent. Mater.* **2019**, *35*, 627–635. [CrossRef]

70. Zhou, D.; Ito, Y. Visible light-curable polymers for biomedical applications. *Sci. China Chem.* **2014**, *57*, 510–521. [CrossRef]

71. Hsu, S.H.; Chen, R.S.; Chang, Y.L.; Chen, M.H.; Cheng, K.C.; Su, W.F. Biphenyl liquid crystalline epoxy resin as a low-shrinkage resin-based dental restorative nanocomposite. *Acta Biomater.* **2012**, *8*, 4151–4161. [CrossRef]

72. Pan, Y.; Wang, J.; Yang, Y.; Nie, R.; Meng, X. Study on Preparation of Antibacterial Dental Resin Materials. *J. Biomater. Tissue Eng.* **2019**, *8*, 1580–1587. [CrossRef]

73. Rodrigues, M.C.; Xavier, T.A.; Arana-Chavez, V.E.; Braga, R.R. Polymer-based material containing calcium phosphate particles functionalized with a dimethacrylate monomer for use in restorative dentistry. *J. Biomater. Appl.* **2017**, *31*, 871–877. [CrossRef] [PubMed]

74. Rüttermann, S.; Dluzhevskaya, I.; Großsteinbeck, C.; Raab, W.H.M.; Janda, R. Impact of replacing Bis-GMA and TEGDMA by other commercially available monomers on the properties of resin-based composites. *Dent. Mater.* **2010**, *26*, 353–359. [CrossRef] [PubMed]

75. Ortyl, J. Chapter 3: Cationic Photoinitiators. In *Photopolymerisation Initiating Systems*; Lalevée, J., Fouassier, J.-P., Eds.; Royal Society of Chemistry: Cambridge, UK, 2018; pp. 74–130.

76. Jandt, K.D.; Sigusch, B.W. Future perspectives of resin-based dental materials. *Dent. Mater.* **2009**, *25*, 1001–1006. [CrossRef] [PubMed]

77. Ferracane, J.L. Resin composite—State of the art. *Dent. Mater.* **2011**, *27*, 29–38. [CrossRef] [PubMed]

78. Shin, D.H.; Rawls, H.R. Degree of conversion and color stability of the light curing resin with new photoinitiator systems. *Dent. Mater.* **2009**, *25*, 1030–1038. [CrossRef] [PubMed]

79. Oxman, J.D.; Jacobs, D.W. Ternary Photoinitiator System for Curing of Epoxy Resins. U.S. Patent 6,043,295, 28 July 1999.

80. Moszner, N.; Salz, U. New developments of polymeric dental composites. *Prog. Polym. Sci.* **2001**, *26*, 535–576. [CrossRef]
85. Fouassier, J.P.; Rabek, J.F. *Radiation Curing in Polymer Science and Technology: Practical Aspects and Applications*; Springer Science & Business Media: Berlin/Heidelberg, Germany, 1993.

86. Xu, X.; He, L.; Zhu, B.; Li, J.; Li, J. Advances in polymeric materials for dental applications. *Polym. Chem.* 2017, 8, 807–823. [CrossRef]

87. Lovell, L.G.; Lu, H.; Elliott, J.E.; Stansbury, J.W.; Bowman, C.N. The effect of cure rate on the mechanical properties of dental resins. *Dent. Mater.* 2001, 17, 504-511. [CrossRef]

88. Stansbury, J.W. Dimethacrylate network formation and polymer property evolution as determined by the selection of monomers and curing conditions. *Dent. Mater.* 2012, 28, 13–22. [CrossRef]

89. Zandinejad, A.A.; Atai, M.; Pahlevan, A. The effect of ceramic and porous fillers on the mechanical properties of experimental dental composites. *Dent. Mater.* 2006, 22, 382–387. [CrossRef]

90. Lee, J.H.; Um, C.M.; Lee, I. Rheological properties of resin composites according to variations in monomer and filler composition. *Dent. Mater.* 2006, 22, 515–526. [CrossRef] [PubMed]

91. Leprince, J.G.; Palin, W.M.; Hadis, M.A.; Devaux, J.; Leloup, G. Progress in dimethacrylate-based dental composite technology and curing efficiency. *Dent. Mater.* 2013, 29, 139–156. [CrossRef] [PubMed]

92. Buruiana, T.; Melinte, V.; Stroea, L.; Buruiana, E.C. Urethane dimethacrylates with carboxylic groups as potential dental monomers. Synthesis and properties. *Polyim.* 2009, 41, 978–987. [CrossRef]

93. Nguyen, J.F.; Migonney, V.; Ruse, N.D.; Sadoun, M. Properties of experimental urethane dimethacrylate-based dental resin composite blocks obtained via thermo-polymerization under high pressure. *Dent. Mater.* 2013, 29, 535–541. [CrossRef]

94. Polydorou, O.; König, A.; Hellwig, E.; Kümmere, K. Uthene dimethacrylate: A molecule that may cause confusion in dental research. *J. Biomed. Mater. Res. Part B Appl. Biomater.* 2009, 91, 1–4. [CrossRef]

95. Sideridou, I.; Tserki, V.; Papanastasiou, G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials* 2003, 24, 655–665. [CrossRef]

96. Charton, C.; Falk, V.; Marchal, P.; Pla, F.; Colon, P. Influence of Tg, viscosity and chemical structure of monomers on shrinkage stress in light-cured dimethacrylate-based dental resins. *Dent. Mater.* 2007, 23, 1447–1459. [CrossRef]

97. Ellakwa, A.; Cho, N.; Lee, I.B. The effect of resin matrix composition on the polymerization shrinkage and rheological properties of experimental dental composites. *Dent. Mater.* 2007, 23, 1229–1235. [CrossRef]

98. Gonçalves, F.; Pfeifer, C.S.; Ferracane, J.L.; Braga, R.R. Contraction stress determinants in dimethacrylate composites. *J. Dent. Res.* 2008, 87, 367–371. [CrossRef]

99. Gonulves, F.; Kawano, Y.; Pfeifer, C.; Stansbury, J.W.; Braga, R.R. Influence of BisGMA, TEGDMA, and BisEMA contents on viscosity, conversion, and flexural strength of experimental resins and composites. *Eur. J. Oral Sci.* 2009, 117, 442–446. [CrossRef]

100. Pfeifer, C.S.; Silva, L.R.; Kawano, Y.; Braga, R.R. Bis-GMA co-polymerizations: Influence on conversion, flexural properties, fracture toughness and susceptibility to ethanol degradation of experimental composites. *Dent. Mater.* 2009, 25, 1136–1141. [CrossRef]

101. Cramer, N.B.; Stansbury, J.W.; Bowman, C.N. Recent advances and developments in composite dental restorative materials. *J. Dent. Res.* 2011, 90, 402–416. [CrossRef] [PubMed]

102. Price, R.B.; Rizkalla, A.S.; Hall, G.C. Effect of stepped light exposure on the volumetric polymerization shrinkage and bulk modulus of dental composites and an unfilled resin. *Am. J. Dent.* 2000, 13, 176–180. [PubMed]

103. Sheth, J.J.; Fuller, J.L.; Jensen, M.E. Cusp deformation and fracture resistance of teeth with dentin adhesives and composites. *J. Prostheth. Dent.* 1988, 60, 560–569. [CrossRef]

104. Schoepfl, S.; Catel, Y.; Moszner, N.; Gorsche, C.; Liska, R. Enhanced reduction of polymerization-induced shrinkage stress: Via combination of radical ring opening and addition fragmentation chain transfer. *Polym. Chem.* 2019, 10, 1357–1366. [CrossRef]

105. Braga, R.R.; Ballester, R.Y.; Ferracane, J.L. Factors involved in the development of polymerization shrinkage stress in resin-composites: A systematic review. *Dent. Mater.* 2005, 21, 962–970. [CrossRef]

106. Vitale, A.; Sangermano, M.; Bongiovanni, R.; Burtscher, P.; Moszner, N. Visible light curable restorative composites for dental applications based on epoxy monomer. *Materials* 2014, 7, 554–562. [CrossRef]

107. Oxman, J.D.; Jacobs, D.W. Ternary Photoinitiator System for Curing of Epoxy Resins. WO 1998047046 A1, 22 October 1998.
108. Hamano, N.; Chiang, Y.C.; Nyamaa, I.; Yamaguchi, H.; Ino, S.; Hickel, R.; Kunzelmann, K.H. Repair of silorane-based dental composites: Influence of surface treatments. *Dent. Mater.* **2012**, *28*, 894–902. [CrossRef]
109. Hamano, N.; Chiang, Y.C.; Nyamaa, I.; Yamaguchi, H.; Ino, S.; Hickel, R.; Kunzelmann, K.H. Repair of silorane-based dental composites. *Dent. Mater.* **2005**, *21*, 68–74. [CrossRef]
110. Nuyken, O.; Böchner, R.; Erdmann, C. Oxetane photopolymerization—A system with low volume shrinkage. *Macromol. Symp.* **1996**, *107*, 125–138. [CrossRef]
111. Moszner, N.; Salz, U. Composites for Dental Restoratives. In *Polymers for Dental and Orthopedic Application*, 1st ed.; Salz, U., Shalaby, W.S., Eds.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2006; pp. 13–68.
112. Eick, J.D.; Kotha, S.P.; Chappelow, C.C.; Kilway, K.V.; Giese, G.J.; Glaros, A.G.; Pinzino, C.S. Properties of silorane-based dental resins and composites containing a stress-reducing monomer. *Dent. Mater.* **2007**, *23*, 1011–1017. [CrossRef]
113. Neumann, M.G.; Miranda, W.G.; Schmitt, C.C.; Rueggeberg, F.A.; Correa, I.C. Molar extinction coefficients of dental photoinitiators and light curing units. *J. Dent.* **2005**, *33*, 525–532. [CrossRef]
114. Eick, J.D.; Kostoryz, E.L.; Rozzi, S.M.; Jacobs, D.W.; Oxman, J.D.; Chappelow, C.C.; Glaros, A.G.; Yourtee, D.M. In vitro biocompatibility of oxirane/polyl dental composites with promising physical properties. *Dent. Mater.* **2002**, *18*, 413–421. [CrossRef]
115. Nie, J.; Andrzejewska, E.; Rabek, J.F.; Lindén, L.Å.; Scigalski, F.; Wrzyszczynski, A. Effect of peroxides and hydroperoxides on the camphorquinone-initiated photopolymerization. *Macromol. Chem. Phys.* **1999**, *200*, 1692–1701. [CrossRef]
116. Schneider, L.F.J.; Cavalcante, L.M.; Silikas, N. Shrinkage stresses generated during resin-composite applications: A review. *J. Dent. Biomech.* **2010**, *2010*, 131630. [CrossRef] [PubMed]
117. Li, M.; Mondrinos, M.J.; Chen, X.; Gandhi, M.R.; Ko, F.K.; Lelkes, P.I. Elastin Blends for Tissue Engineering Scaffolds. *J. Biomed. Mater. Res. Part A* **2006**, *79*, 963–973. [CrossRef]
118. Wei, J.; Lu, R.; Liu, F. Novel, highly efficient macrophotoinitiator comprising benzophenone, coinitiator amine, and thio moieties for photopolymerization. *Polym. Adv. Technol.* **2010**, *21*, 656–662. [CrossRef]
119. Cook, W.D. Photopolymerization kinetics of dimethacrylates using the camphorquinone-amines photoinitating systems for the initiation of free radical polymerization. *Dent. Mater.* **1992**, *33*, 600–609. [CrossRef]
120. Bi, Y.; Neckers, D.C. A Visible Light Initiating System for Free Radical Promoted Cationic Polymerization. *Macromolecules* **1994**, *27*, 3683–3693. [CrossRef]
121. Nie, J.; Bowman, C.N. Synthesis and photopolymerization of N,N′-dimethyl-N,N′-di(methacryloxy ethyl)-1,6-hexanediamine as a polymerizable amine coinitiator for dental restorations. *Biomaterials* **2002**, *23*, 1221–1226. [CrossRef]
122. Guo, X.; Peng, Z.; Spencer, P.; Wang, Y. Effect of initiator on photopolymerization of acidic, aqueous dental model adhesives. *J. Biomed. Mater. Res. Part A* **2009**, *90*, 1120–1127. [CrossRef] [PubMed]
123. Wei, J.; Liu, F. Novel highly efficient macrophotoinitiator comprising benzophenone, coinitiator amine, and thio moieties for photopolymerization. *Macromolecules* **2009**, *42*, 5486–5491. [CrossRef]
124. Decker, C.; Jenkins, A.D. Kinetic Approach of o2 Inhibition in Ultraviolet and Laser-Induced Polymerizations. *Macromolecules* **1985**, *18*, 1241–1244. [CrossRef]
125. Lin, Y.; Stansbury, J.W. Kinetics studies of hybrid structure formation by controlled photopolymerization. *Polymer* **2003**, *44*, 4781–4789. [CrossRef]
126. Ogliari, F.A.; Ely, C.; Petzhold, C.L.; Demarco, F.F.; Piva, E. Onium salt improves the polymerization kinetics in an experimental dental adhesive resin. *J. Dent.* **2007**, *35*, 583–587. [CrossRef]
131. Brömme, T.; Schmitz, C.; Moszner, N.; Burtscher, P.; Strehmel, N.; Strehmel, B. Photochemical Oxidation of NIR Photosensitizers in the Presence of Radical Initiators and Their Prospective Use in Dental Applications. *ChemistrySelect* **2016**, *1*, 524–532. [CrossRef]

132. Münchow, E.A.; Valente, L.L.; Peralta, S.L.; Fernández, M.R.; Lima, G.D.S.; Petzhold, C.L.; Piva, E.; Ogliari, F.A. 1,3-Diethyl-2-thiobarbituric acid as an alternative coinitiator for acidic photopolymerizable dental materials. *J. Biomed. Mater. Res. Part B Appl. Biomater.* **2013**, *101*, 1217–1221. [CrossRef]

133. Bowen, R.L.; Cobb, E.N.; Rapson, J.E. Adhesive Bonding of Various Materials to Hard Tooth Tissues: Improvement in Bond Strength to Dentin. *J. Dent. Res.* **1982**, *61*, 1070–1076. [CrossRef]

134. Ikemura, K.; Endo, T. A review of our development of dental adhesives—Effects of radical polymerization initiators and adhesive monomers on adhesion. *Dent. Mater. J.* **2010**, *29*, 109–121. [CrossRef] [PubMed]

135. Ali Tehfe, M.; El-Roz, M.; Lalev, J.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P. Bifunctional co-initiators: A new strategy for the design of efficient systems in radical photopolymerization reactions under air. *Eur. Polym. J.* **2012**, *48*, 956–962. [CrossRef]

136. Asmusseen, S.; Valio, C. Light absorbing products during polymerization of methacrylate monomers photoinitiated with phenyl-1,2-propanedione/amine. *J. Photochem. Photobiol. A Chem.* **2009**, *202*, 228–234. [CrossRef]

137. Dart, E.C.; Cantwell, J.B.; Traynor, J.R.; Jaworzyzn, J.F.; Nemeck, J. Method of Repairing Teeth Using a Composition Which Is Curable by Radiation with Visible Light. U.S. Patent 4,089,763, 17 March 1976.

138. Dressano, D.; Palialol, A.R.; Xavier, T.A.; Braga, R.R.; Oxman, J.D.; Watts, D.C.; Marchi, G.M.; Lima, A.F. Effect of diphenyliodonium hexafluorophosphate on the physical and chemical properties of ethanolic solvated resins containing camphorquinone and 1-phenyl-1,2-propanedione sensitizers as initiators. *Dent. Mater.* **2016**, *32*, 756–764. [CrossRef]

139. Sun, G.J.; Chae, K.H. Properties of 2,3-butanedione and 1-phenyl-1,2-propanedione as new photosensitizers for visible light cured dental resin composites. *Polymer* **2000**, *41*, 6205–6212. [CrossRef]

140. Brandt, W.C.; Silva, C.G.; Frollini, E.; Souza-Junior, E.J.C.; Sinhoreti, M.A.C. Dynamic mechanical thermal analysis of composite resins with CQ and PPD as photo-initiators photoactivated by QTH and LED units. *J. Mech. Behav. Biomed. Mater.* **2013**, *24*, 21–29. [CrossRef]

141. Kunio, I.; Takeshi, E. A review of the development of radical photopolymerization initiators used for designing light-curing dental adhesives and resin composites. *Dent. Mater. J.* **2010**, *29*, 481–501. [CrossRef]

142. Van Landuyt, K.L.; Snauwaert, J.; De Munck, J.; Peumans, M.; Yoshida, Y.; Poitevin, A.; Coutinho, E.; Suzuki, K.; Lambrechts, P.; Van Meerbeek, B. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* **2007**, *28*, 3757–3785. [CrossRef]

143. Wu, N.; Zhang, Y.; Wang, Y. Photo-polymerization efficiency of self-etch dental adhesives composed of camphorquinone or trimethylbenzoyl-diphenyl-phosphate oxide. *Int. J. Adhes. Adhes.* **2013**, *45*, 53–58. [CrossRef]

144. Tomal, W.; Ortyl, J. Water-soluble photoinitiators in biomedical applications. *Polymers* **2020**, *12*, 1073. [CrossRef]

145. Albuquerque, P.P.A.C.; Moreira, A.D.L.; Moraes, R.R.; Cavalcante, L.M.; Schneider, L.F.J. Color stability, water sorption and solubility of dental composites formulated with different photoinitiator systems. *J. Dent.* **2013**, *41*, e67–e72. [CrossRef] [PubMed]

146. Moszner, N.; Salz, U.; Zimmermann, J. Chemical aspects of self-etching enamel-dentin adhesives: A systematic review. *Dent. Mater.* **2005**, *21*, 895–910. [CrossRef] [PubMed]

147. Meereis, C.T.W.; Leal, F.B.; Lima, G.S.; De Carvalho, R.V.; Piva, E.; Ogliari, F.A. BAPO as an alternative photoinitiator for the radical polymerization of dental resins. *Dent. Mater.* **2014**, *30*, 945–953. [CrossRef] [PubMed]

148. Popal, M.; Volk, J.; Leyhausen, G.; Geurtsen, W. Cytotoxic and genotoxic potential of the type I photoinitiators BAPO and TPO on human oral keratinocytes and V79 fibroblasts. *Dent. Mater.* **2018**, *34*, 1783–1796. [CrossRef] [PubMed]

149. Ganster, B.; Fischer, U.K.; Moszner, N.; Liska, R. New photocleavable structures, 4a acylgermane-based photoinitiator for visible light curing. *Macromol. Rapid Commun.* **2008**, *29*, 57–62. [CrossRef]

150. Ganster, B.; Fischer, U.K.; Moszner, N.; Liska, R. New photocleavable structures. *Macromolecules* **2008**, *41*, 2394–2400. [CrossRef]
151. Ely, C.; Ottoboni, T.D.; Kumagai, R.Y.; de Souza, N.A.; da Ramos, T.S.; Arrais, C.A.G.; Piva, E.; Reis, A.F. Bond Strength of Methacrylate-based Blends Containing Elastomeric Monomers and Alternative Initiators after Thermomechanical Cycling. J. Adhes. Dent. 2019, 21, 281–286. [CrossRef]

152. Moszner, N.; Fischer, U.K.; Ganster, B.; Liska, R.; Rheinberger, V. Benzyol germanium derivatives as novel visible light photoinitiators for dental materials. Dent. Mater. 2008, 24, 901–907. [CrossRef]

153. Hayashi, T.; Maeda, K. Preparation of a New Phototropic Substance. Bull. Chem. Soc. Jpn. 1960, 33, 565–566. [CrossRef]

154. Li, Y.H.; Chen, Y.C. Triphenylamine-hexaarylbiimidazole derivatives as hydrogen-acceptor photoinitiators for free radical photopolymerization under UV and LED light. Polym. Chem. 2020, 11, 1504–1513. [CrossRef]

155. Berdzinski, S.; Strehmel, N.; Lindauer, H.; Strehmel, V.; Strehmel, B. Extended mechanistic aspects on photoinitiated polymerization of 1,6-hexanediol diacrylate by hexaarylbisimidazoles and heterocyclic mercapto compounds. Photochem. Photobiol. Sci. 2014, 13, 789–798. [CrossRef] [PubMed]

156. Berdzinski, S.; Horst, J.; Straßburg, P.; Strehmel, V. Recombination of lophyl radicals in pyrrolidinium-based ionic liquids. ChemPhysChem 2013, 14, 1899–1908. [CrossRef]

157. Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. The first in situ direct observation of the light-induced radical pair from a hexaarylbimidazolyl derivative by X-ray crystallography. J. Am. Chem. Soc. 1999, 121, 8106–8107. [CrossRef]

158. Ahn, D.; Sathe, S.S.; Clarkson, B.H.; Scott, T.F. Hexaarylbimidaizoles as visible light thiol-ene photoinitiators. Dent. Mater. 2015, 31, 1075–1089. [CrossRef]

159. Chen, Y.C.; Kuo, Y.T.; Ho, T.H. Photo-polymerization properties of type-II photoinitiator systems based on 2-chlorohexaaryl biimidazole (o-Cl-HABI) and various N-phenylglycine (NPG) derivatives. Photochem. Photobiol. Sci. 2019, 18, 190–197. [CrossRef]

160. Wu, X.; Wang, Y.; Liu, J.; He, S.; Zhang, L.; Polymers, F. Improved Crack Growth Resistance and Its Molecular Origin of Natural Rubber/Carbon Black by Nanodispersed Clay. Polym. Eng. Sci. 2012, 52, 1027–1036. [CrossRef]

161. Shi, Y.; Yin, J.; Kaji, M.; Yori, H. Photopolymerization of acrylate derivatives initiated by hexaarylbimidazole with ether groups. Polym. Int. 2006, 55, 330–339. [CrossRef]

162. West, R. The polysilane high polymers. J. Organomet. Chem. 1986, 300, 327–346. [CrossRef]

163. Wolff, A.R.; West, R. Photoinitiation of vinyl polymerization by polysilanes. Appl. Organomet. Chem. 1987, 1, 7–14. [CrossRef]

164. Yagci, Y.; Kmienik, I.; Schnabel, W. Long wavelength photoinitiated cationic polymerization using diphenyliodonium salt and catena-poly (phenyl-4-phenylphenylsilicon). Polymer 1993, 34, 426–428. [CrossRef]

165. Gilman, H.; Atwell, W.H.; Sen, P.K.; Smith, C.L. Branched-chain organic polysilanes containing the silicon-hydrogen group. J. Organomet. Chem. 1965, 4, 163–167. [CrossRef]

166. Kanabus-Kaminska, J.M.; Hawari, J.A.; Griller, D.; Chatgilialoglu, C. Reduction of Silicon-Hydrogen Bond Strengths. J. Am. Chem. Soc. 1987, 109, 5267–5268. [CrossRef]

167. Chatgilialoglu, C.; Griller, D.; Lesage, M. Tris(trimethylsilyl)silane. A new reducing agent. J. Org. Chem. 1988, 55, 3641–3642. [CrossRef]

168. Lalevée, J.; Blanchard, N.; El-Roz, M.; Graff, B.; Allonas, X.; Fouassier, J.P. New photoinitiators based on the silyl radical chemistry: Polymerization ability, ESR spin trapping, and laser flash photolysis investigation. Macromolecules 2008, 41, 4180–4186. [CrossRef]

169. Lalevée, J.; Dirani, A.; El-Roz, M.; Allonas, X.; Fouassier, J.P. Silanes as new highly efficient co-initiators for radical polymerization in aerated media. Macromolecules 2008, 41, 2003–2010. [CrossRef]

170. Lalevée, J.; Blanchard, N.; Chan, A.C.; El-Roz, M.; Souane, R.; Graff, B.; Allonas, X.; Fouassier, J.P. Silyl radical chemistry and conventional photoinitiators: A route for the design of efficient systems. Macromolecules 2009, 42, 6031–6037. [CrossRef]

171. Chatgilialoglu, C.; Lalevée, J. Recent applications of the (TMS)₃SiH radical-based reagent. Molecules 2012, 17, 527–555. [CrossRef]

172. Matsumura, S.; Hiji, A.R.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z.; Holdcroft, S.; Hay, A.S. Stability and Utility of Pyridyl Disulfide Functionality in RAFT and Conventional Radical Polymerizations. J. Polym. Sci. Part A Polym. Chem. 2008, 46, 7207–7224. [CrossRef]
173. Abedin, F.; Ye, Q.; Song, L.; Ge, X.; Camarda, K.; Spencer, P. E. Tris(trimethylsilyl)silyl versus tris(trimethylsilyl)germyl: Radical reactivity and oxidation ability. J. Organomet. Chem. 2008, 693, 3643–3649. [CrossRef] [PubMed]

174. Lalevée, J.; Allonas, X.; Fouassier, J.P. Tris(trimethylsilyl)isilane (TTMSS)-derived radical reactivity toward alkenes: A combined quantum mechanical and laser flash photolysis study. J. Org. Chem. 2007, 72, 6434–6439. [CrossRef]

175. Lalevée, J.; Tehfe, M.A.; Morlet-Savary, F.; Graff, B.; Allonas, X.; Fouassier, J.P. Radical photopolymization reactions under air upon lamp and diode laser exposure: The input of the organosilane radical chemistry. Prog. Org. Coatings 2011, 70, 83–90. [CrossRef]

176. 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. Prog. Org. Coat. 2011, 70, 23–31. [CrossRef]

177. Chatgilialoglu, C. Organosilanes as Radical-Based Reducing Agents in Synthesis. Acc. Chem. Res. 1992, 25, 188–194. [CrossRef]

178. Bouzrati-Zerelli, M.; Kirschner, J.; Fik, C.P.; Maier, M.; Dietlin, C.; Morlet-Savary, F.; Fouassier, J.P.; Becht, J.M.; Klee, J.E.; Lalevée, J. Silyl Glyoxylates as a New Class of High Performance Photoinitiators: Blue LED Induced Polymerization of Methacrylates in Thin and Thick Films. Macromolecules 2017, 50, 6911–6923. [CrossRef]

179. Kirschner, J.; Bouzrati-Zerelli, M.; Fouassier, J.P.; Becht, J.M.; Klee, J.E.; Lalevée, J. Silyl glyoxylates as high-performance photoinitiators for cationic and hybrid polymerizations: Towards better polymer mechanical properties. J. Polym. Sci. Part A Polym. Chem. 2019, 57, 1420–1429. [CrossRef]

180. Kirschner, J.; Baralle, A.; Graff, B.; Becht, J.M.; Klee, J.E.; Lalevée, J. 1-Aryl-2-(trisopropylsilyl)ethane-1,2-diones: Toward a New Class of Visible Type I Photoinitiators for Free Radical Polymerization of Methacrylates. Macromol. Rapid Commun. 2019, 40, 2–7. [CrossRef]

181. Kirschner, J.; Paillard, J.; Graff, B.; Becht, J.M.; Klee, J.E.; Lalevée, J. 2-Oxo-2(tert-butyldimethylsilyl)Acetid Acid (DKSi-COOH) as a New Water-Soluble Visible Light Type I Photoinitiator for Free Radical Photopolymerization. Macromol. Chem. Phys. 2020, 221, 5–9. [CrossRef]

182. Hayakawa, T.; Horie, K. Effect of water-soluble photoinitiator on the adhesion between composite and tooth substrate. Dent. Mater. 1992, 8, 351–353. [CrossRef]

183. Breloy, L.; Losantos, R.; Sampedro, D.; Marazzi, M.; Malval, J.-P.; Heo, Y.; Akimoto, J.; Ito, Y.; Brezová, V.; Versace, D.-L. Allyl amino-thioxanthone derivatives as highly efficient visible light H-donors and co-polymerizable photoinitiators. Polym. Chem. 2020, 11, 4297–4312. [CrossRef]

184. Ely, C.; Schneider, L.F.J.; Ogiari, F.A.; Schmitt, C.C.; Corrêa, I.C.; Lima, G.D.S.; Samuel, S.M.W.; Piva, E. Polymerization kinetics and reactivity of alternative initiators systems for use in light-activated dental resins. Dent. Mater. 2012, 28, 1199–1206. [CrossRef]

185. Kabatc, J.; Ortyl, J.; Kostrzewska, K. New kinetic and mechanistic aspects of photosensitization of iodonium salts in photopolymerization of acrylates. RSC Adv. 2017, 7, 41619–41629. [CrossRef]

186. Baralle, A.; Garra, P.; Morlet-Savary, F.; Dietlin, C.; Fouassier, J.P.; Lalevée, J. Polymeric Iodonium Salts to Trigger Free Radical Photopolymerization. Macromol. Rapid Commun. 2020, 41. [CrossRef] [PubMed]

187. Abedin, F.; Ye, Q.; Spong, L.; Ge, X.; Camarda, K.; Spencer, P. Effect of Partition of Photo-Initiator Components and Addition of Iodonium Salt on the Photopolymerization of Phase-Separated Dental Adhesive. JOM 2016, 68, 1090–1099. [CrossRef]

188. Shiraiishi, A.; Ueda, Y.; Schläfner, M.; Schmitz, C.; Brömme, T.; Oprych, D.; Strehmel, B. Nir-sensitized photopolymerization with iodonium salts bearing weak coordinating anions. J. Photopolym. Sci. Technol. 2016, 29, 609–615. [CrossRef]

189. Cook, W.D.; Chen, F. Enhanced visible radiation photopolymerization of dimethacrylates with the three component thioxanthone (CPTXO)-amine-iodonium salt system. Polym. Chem. 2015, 6, 1325–1338. [CrossRef]

190. Podsidił, R.; Maruszewska, A.; Michalski, R.; Marcinek, A.; Kolińska, J. Naphthoylbenzimidazolone dyes as electron transfer photosensitizers for iodonium salt induced cationic photopolymerizations. Dye. Pigment. 2012, 95, 252–259. [CrossRef]

191. Brömme, T.; Oprych, D.; Horst, J.; Pinto, P.S.; Strehmel, B. New iodonium salts in NIR sensitized radical photopolymerization of multifunctional monomers. RSC Adv. 2015, 5, 69915–69924. [CrossRef]
192. Asmussen, S.; Arenas, G.; Vallo, C. Photopolymerization of pyrrole/methacrylate mixtures using α-cleavage type photoinitiators in combination with iodonium salt. *Synth. Met.* 2015, 209, 304–312. [CrossRef]

193. Crivello, J.V.; Lam, J.H.W. Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization. *Macromolecules* 1977, 10, 1307–1315. [CrossRef]

194. Asmussen, S.; Arenas, G.; Vallo, C. Photopolymerization of pyrrole.

195. Topa, M.; Petko, F.; Galek, M.; Ortyl, J. Double role of diphenylpyridine derivatives as fluorescent sensors for monitoring photopolymerization and the determination of the efficiencies of the generation of superacids by cationic photoinitiators. *Sensors* 2020, 20, 3043. [CrossRef]

196. Green, W.A. *Industrial Photoinitiators*, 1st ed.; CRC Press: Boca Raton, FL, USA, 2010.

197. Dadashi-Silab, S.; Aydogan, C.; Yagci, Y. Shining a light on an adaptable photoinitiator: Advances in photopolymerizations initiated by thioxanthenones. *Polym. Chem.* 2015, 6, 6595–6615. [CrossRef]

198. Al Mousawi, A.; Dietlin, C.; Graff, B.; Morlet-Savary, F.; Toufaily, J.; Hamieh, T.; Fouassier, J.P.; Ortyl, J. One-component cationic photoinitiators based on coumarin scaffold iodonium salts as highly sensitive photoacid generators for 3D printing IPN photopolymers under visible LED sources. *Polym. Chem.* 2020, 11, 5261–5278. [CrossRef]

199. Karaca, N.; Ocal, N.; Arsu, N.; Jockusch, S. Thioxanthone-benzothiophenes as photoinitiator for free radical photoinitiating systems. *J. Photochem. Photobiol. A Chem.* 2016, 331, 22–28. [CrossRef]

200. Kamoun, E.A.; Winkel, A.; Eisenburger, M.; Menzel, H. Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application. *Arab. J. Chem.* 2016, 9, 745–754. [CrossRef]

201. Lima, A.F.; Salvador, M.V.O.; Dressano, D.; Saraceni, C.H.C.; Gonçalves, L.S.; Hadis, M.; Palin, W.M. Increased rates of photopolymerisation by ternary type II photoinitiator systems in dental resins. *J. Mech. Behav. Biomed. Mater.* 2019, 98, 71–78. [CrossRef]

202. Guo, X.; Wang, Y.; Spencer, P.; Ye, Q.; Yao, X. Effects of water content and initiator composition on photopolymerization of a model BisGMA/HEMA resin. *Dent. Mater.* 2008, 24, 824–831. [CrossRef]

203. Dressano, D.; Salvador, M.V.; Oliveira, M.T.; Marchi, G.M.; Fronza, B.M.; Hadis, M.; Palin, W.M.; Lima, A.F. Chemistry of novel and contemporary resin-based dental adhesives. *J. Mech. Behav. Biomed. Mater.* 2020, 110, 103875. [CrossRef]

204. Baena Lopes, M.; Tirado Dos Santos, A.M.; Coelho, D.; Gonini J.; Augusto, C.R.; Leitune, V.C.B.; Ogliari, F.A.; Collares, F.M. Influence of diphenyliodonium hexafluorophosphate on the bond strength and mechanical properties of model resin cements. *Int. J. Adhes. Adhes.* 2013, 47, 125–128. [CrossRef]

205. Leal, F.B.; Lima, G.S.; Collares, F.M.; Samuel, S.M.; Petzhold, C.L.; Piva, E.; Ogliari, F.A. Iodonium salt improves the dentin bonding performance in an experimental dental adhesive resin. *Int. J. Adhes. Adhes.* 2012, 38, 1–4. [CrossRef]

206. Augusto, C.R.; Leitune, V.C.B.; Ogliari, F.A.; Collares, F.M. Influence of an iodonium salt on the properties of dual-polymerizing self-adhesive resin cements. *J. Prosthet. Dent.* 2017, 118, 228–234. [CrossRef] [PubMed]

207. Chloride, D.; Padon, K.S.; Scranton, A.B. A mechanistic investigation of the three-component radical photoinitiator system Eosin Y spirit soluble, n-methyldiethanolamine. *Dent. Mater.* 2016, 32, 1226–1234. [CrossRef]

208. Sauro, S.; Vijay, S.; Deb, S. Development and assessment of experimental dental polymers with enhanced polymerisation, crosslink density and resistance to fluid permeability based on ethoxylated-Bisphenol-A-dimethacrylates and 2-Hydroxyethyl methacrylate. *Eur. Polym. J.* 2012, 48, 1466–1474. [CrossRef]

209. Bouzrati-Zerelli, M.; Maier, M.; Dietlin, C.; Fabrice, M.S.; Fouassier, J.P.; Klee, J.E.; Lalevée, J. A novel photoinitiating system producing germyl radicals for the polymerization of representative methacrylate resins: Camphorquinone/R3GeH/iodonium salt. *Dent. Mater.* 2016, 32, 1226–1234. [CrossRef]

210. Kirschner, J.; Szillat, F.; Bouzrati-Zerelli, M.; Becht, J.M.; Klee, J.E.; Lalevée, J. Iodonium sulfonates as high-performance coinitiators and additives for CQ-based systems: Toward aromatic amine-free photoinitiating systems. *J. Polym. Sci. Part A Polym. Chem.* 2019, 57, 1664–1669. [CrossRef]
211. Kirschner, J.; Paillard, J.; Bouzrati-Zerelli, M.; Becht, J.M.; Klee, J.E.; Chelli, S.; Lakhdar, S.; Lalevée, J. Aryliodonium ylides as novel and efficient additives for radical chemistry: Example in Camphorquinone (CQ)/Amine based photoinitiating systems. *Molecules* 2019, 24, 2913. [CrossRef]

212. Kirschner, J.; Szillat, F.; Bouzrati-Zerelli, M.; Becht, J.M.; Klee, J.E.; Lalevée, J. Sulfonates and sulfonates as high performance co-initiators in CQ based systems: Towards aromatic amine-free systems for dental restorative materials. *Dent. Mater.* 2020, 36, 187–196. [CrossRef]

213. Kirschner, J.; Becht, J.M.; Klee, J.E.; Lalevée, J. A New Phosphine for Efficient Free Radical Polymerization under Air. *Macromol. Rapid Commun.* 2020, 41, 2000053. [CrossRef]

214. Ogliari, F.A.; Ely, C.; Lima, G.S.; Conde, M.C.M.; Petzhold, C.L.; Demarco, F.F.; Piva, E. Onium salt reduces the inhibitory polymerization effect from an organic solvent in a model dental adhesive resin. *J. Biomed. Mater. Res.-Part B Appl. Biomater.* 2008, 86, 113–118. [CrossRef]

215. Borges, B.C.D.; de Sousa-Lima, R.X.; Moreno, G.B.P.; Moreira, D.G.L.; Oliveira, D.C.R.S.; Souza-Junior, E.J.C.; Sinhoreti, M.A.C. Polymerization and adhesion behavior of experimental dental bonding materials with different initiator systems. *J. Adhes. Sci. Technol.* 2018, 32, 239–246. [CrossRef]

216. Gonçalves, L.S.; Moraes, R.R.; Ogliari, F.A.; Boaro, L.; Braga, R.R.; Consani, S. Improved polymerization efficiency of methacrylate-based cements containing an iodonium salt. *Dent. Mater.* 2013, 29, 1251–1255. [CrossRef] [PubMed]

217. Allen, N.S. Photoinitiators for UV and visible curing of coatings: Mechanisms and properties. *J. Photochem. Photobiol. A Chem.* 1996, 100, 101–107. [CrossRef]

218. Danso, R.; Hoedebecke, B.; Whang, K.; Sarrami, S.; Johnston, A.; Flipse, S.; Wong, N.; Rawls, H.R. Development of an oxirane/acylate interpenetrating polymer network (IPN) resin system. *Dent. Mater.* 2018, 34, 1459–1465. [CrossRef] [PubMed]

219. Zhang, J.; Wang, S.; Lalevée, J.; Morlet-Savary, F.; Lam, E.S.-H.; Graff, B.; Liu, J.; Xing, F.; Xiao, P. 1,2-Diketones as photoinitiators of both cationic and free-radical photopolymerization under UV (392 nm) or Blue (455 nm) LEDs. *J. Polym. Sci.* 2020, 58, 792–802. [CrossRef]

220. Moszner, N.; Zeuner, F.; Lamparth, I.; Fischer, U.K. Benzoylgermanium derivatives as novel visible-light photoinitiators for dental composites. *Macromol. Mater. Eng.* 2009, 294, 877–886. [CrossRef]