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The Influence of the Photoinitiating System on Residual Monomer Contents and Photopolymerization Rate of a Model Pigmented UV/LED Nail Gel Formulation

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Abstract

This study investigates the influence of photoinitiating systems on the degree of methacrylate group conversion and the rate of polymerization in UV/LED-curable nail gel formulations. Camphorquinone and Eosin Y, commonly used in medical and dental applications, were evaluated in bimolecular systems with onium and iodonium salts, thiols, and amines as co-initiators. Real-time FT-IR spectroscopy was employed to monitor polymerization under dual-LED irradiation (365 nm and 405 nm). The results demonstrate that the tested systems, inspired by photocurable medical products, exhibit significant potential for application in highly pigmented nail gels, achieving efficient curing with low residual monomer content.

Keywords: urethane acrylates; camphorquinone; Eosin-Y; UV/LED nail gel formulations; photocurable coatings; photopolymerization

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1. Introduction

The application of photopolymerization processes requires a suitable initiating system which, in cosmetic applications such as nail polishes, must meet additional criteria. These include high efficiency in curing highly pigmented and thick layers that impede light penetration throughout the depth of the coating, as well as compatibility with low-intensity light sources. Inadequate curing of photopolymerizable lacquers—manifested by insufficient conversion of unsaturated bonds—leads to the presence of unreacted methacrylate groups, which may result in coating defects and elicit allergic responses.

Photopolymerization, a process where liquid monomers and oligomers are rapidly transformed into solid polymers upon exposure to ultraviolet (UV) or visible light, has found extensive application in various fields, including dentistry, coatings, 3D printing, adhesives, and cosmetics [1–4]. In the cosmetic industry, particularly in nail embellishment, UV/LED-curable formulations have revolutionized the durability, appearance, and functionality of nail products. The development of photo-curable nail polishes occurred in the 20th century and was inspired by dentist F. Slack, who used dental acrylate to fix his nail [5]. Currently, these systems offer fast curing times, excellent film properties, and enhanced resistance to mechanical and chemical damage, making them a preferred choice over traditional nail gels [1]. The total market for nail gels was about USD 55.6 million in 2023. The forecast for the year 2030 foresees the growth of the market up to USD 88 million [5]. Several innovative UV-curable nail coating formulations have been introduced, demonstrating

the commitment of both researchers and industry to technological advancement. Current research in this area includes, among others, nail gels formulations incorporating photoreactive bio-based components [1], aqueous polyurethane dispersions [6], photochromic compounds [7], peelable layers utilizing a thermoset 3D polymer network dispersed in a solvent-soluble resin matrix [8], and hybrid organic-inorganic (OIH) systems [9]. However, the primary goal of using UV-curable nail lacquers remains to achieve decorative and esthetic effects. Therefore, the most significant technological challenge today lies in achieving efficient photopolymerization in highly pigmented systems.

The safety assessment of UV gel nails involves evaluating any residual components that may leach from insufficiently cured gels [10]. This may result from suboptimal electromagnetic radiation intensity, inadequate photoinitiator type or concentration, and high pigmentation, all of which can impact the curing process [11,12]. Factors such as oxygen inhibition, vitrification, shadow zones, and coating shrinkage must also be considered [13]. Gel nail polishes, commonly referred to as gel manicures, are complex formulations composed of oligomers (typically urethane or polyester acrylates), reactive diluents (e.g., methacrylates), photoinitiators, pigments, and various additives [14]. These products are applied in layers (base coat, color coat, and top coat), each of which is cured using UV or LED lamps to form a durable polymeric network [1].

The curing process is typically initiated by type I (cleavage) or type II (hydrogen abstraction) photoinitiators, whose selection and concentration significantly influence both the polymerization rate and the level of unreacted monomers in the final film [15–17]. Despite the advantages of gel nail systems, several challenges persist in formulating effective and safe products [18,19]. One critical issue is the presence of residual monomers post-curing, which may lead to allergic reactions, such as allergic contact dermatitis, as well as other dermatological complications [20]. This problem is exacerbated in pigmented formulations, where pigments can absorb or scatter light, reducing the efficiency of photoinitiator activation and thus inhibiting complete polymerization. Achieving uniform curing in heavily pigmented systems remains a major technological hurdle. Current trends in cosmetic formulations emphasize not only improved performance (e.g., faster curing, higher gloss, and better durability) but also the reduction in harmful substances and enhancement of biocompatibility [11,21].

In this context, understanding the interplay between photoinitiator systems and formulation variables (such as pigment content and monomer structure) is essential for optimizing both curing kinetics and product safety. This study investigates how the type and concentration of photoinitiating systems affect the residual monomer content and photopolymerization rate in a model pigmented UV/LED-curable gel nail formulation. The results aim to contribute to the development of high-performance, low-toxicity nail gel products.

2. Materials and Methods

2.1. Materials

Two dyes that differ in the chemical structure and photoactivated characteristics were tested as light absorbers in two component photoinitiating systems. They were Camphorquinone (CQ) and Eosin-Y (EO), respectively. All of the used reagents were commercially available and were not further purified. The role of coinitiators was played by new onium salt, i.e., N-ethoxy-4-(3-phenylpropyl)pyridinium hexafluorophosphate (C0), and commercially available compounds, namely bis(4-tert-butylphenyl)iodonium p-toluenesulfonate (C1), diphenyliodonium hexafluorophosphate (C2), and diphenyliodonium chloride (C3). Commercially available thiol and amine components, i.e., Ebecryl LED 02 (L02; Allnex, Bergen, The Netherlands), Ebecryl LED 03 (L03; Allnex, The Netherlands)

and triethylamine (TEA; Sigma Aldrich, Darmstadt, Germany), were used as co-initiating additives. The chemical structures and characteristics of the photoinitiating systems components are presented in Tables 1 and 2.

Table 1. Chemical structures of dye sensitizers and absorption characteristics.

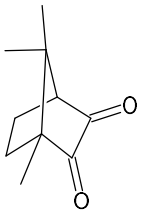
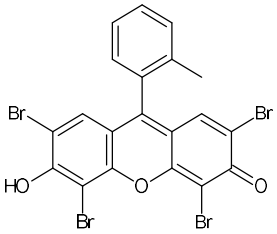
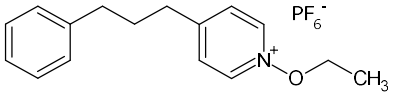
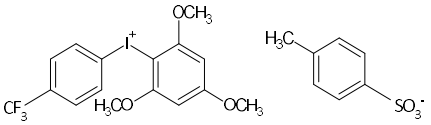
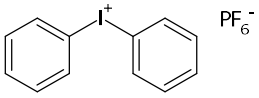
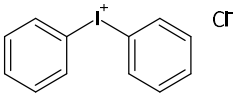
Symbol	Chemical Name	Structure	Absorption Range [nm]	Absorbance Maximum [nm]
CQ	Camphorquinone		360–510 [22]	468 [22]
EO	Eosin-Y		300−700 [23]	515 [23]

Table 2. Chemical structures of coinitiators.

Symbol	Chemical Name	Structure	Absorbance Maximum [nm]
C0	N-ethoxy-4-(3-phenylpropyl)pyridinium hexafluorophosphate		256
C1	[3-(trifluoromethyl)phenyl](2,4,6-trimethoxyphenyl)iodonium p-toluenesulfonate		202 [24]
C2	diphenyliodonium hexafluorophosphate		400 [25]
C3	diphenyliodonium chloride		214, 226 [26]

A photoreactive system (NG) based on a urethane acrylate oligomer (80 wt.%; Ebecryl 8209, Allnex, Netherlands), 2-hydroxyethyl methacrylate (10 wt.%; Sigma Aldrich, Germany), ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (as a type I photoinitiator, 3 wt.%; TPO-L; IGM Resins, Waalwijk, The Netherlands), and titanium dioxide pigment (10 wt.%; Grupa Azoty, Police, Poland) was used for the experiments. Two-component photoinitiating systems were added to the pigmented photoreactive mixture of oligomers and monomers. The formulation composition is presented in Table 3. Homogeneous samples were subjected to photopolymerization kinetics studies in the form of thin films obtained using a slot applicator (250 µm). The research was conducted using a dual LED lamp (Indigo Nails, Łódź, Poland), which contained two types of LEDs: 365 and 405 nm, the absorption characteristics are presented in the results.

Table 3. Composition of coating compositions containing photoinitiating dye systems.

Sample Name	NG [wt.%]	CQ [wt.%]	EO [wt.%]	Coinitiator	
				Name	[wt.%]
CQ-0	100	-	-	-	-
CQ-0.3	100	0.3	-	-	-
CQ-0.6	100	0.6	-	-	-
CQ-2.5	100	2.5	-	-	-
CQ-5	100	5	-	-	-
EO-0	100	-	-	-	-
EO-0.3	100	-	0.3	-	-
EO-0.6	100	-	0.6	-	-
EO-2.5	100	-	2.5	-	-
EO-5	100	-	5	-	-
CQ-C0	100	5	-	C0	3
CQ-C1	100	5	-	C1	3
CQ-C2	100	5	-	C2	3
CQ-C3	100	5	-	C3	3
CQ-L02	100	5	-	L02	3
CQ-L03	100	5	-	L03	3
CQ-TEA	100	5	-	TEA	3
EO-C0	100	5	-	C0	3
EO-C1	100	5	-	C1	3
EO-C2	100	5	-	C2	3
EO-C3	100	5	-	C3	3
EO-L02	100	5	-	L02	3
EO-L03	100	5	-	L03	3
EO-TEA	100	5	-	TEA	3

NG-pigmented UV nail gel (80 wt.% urethane actylate, 10 wt.% 2-hydroxyethyl methacrylate, 3 wt.% ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (as a type I photoinitiator), and 10 wt.% titanium dioxide pigment), CQ-Camphorquinone; EO-Eosin-Y, C0-N-methoxy-4-(3-phenylpropyl)pyridinium hexafluorophosphate; C1-bis(4-tert-butylphenyl)iodonium p-toluenesulfonate; C2-diphenyliodonium hexafluorophosphate; C3-diphenyliodonium chloride; L02-thiol additive; L03-amine additive; TEA-triethylamine.

2.2. Methods

Characteristics of the photopolymerization process was determined using the Fourier-transformed infrared (FTIR) spectroscopy in the attenuated total reflectance mode (ATR) on Nicolet iS5 instrument (Thermo Electron Corporation, Waltham, MA, USA). For each sample, the average of sixteen scans was in the range of 4000–400 cm^{-1} and the resolution of 4 cm^{-1}. The series real-time IR (RT-IR) was used to determine the conversion of unsaturated chemical bonds. This spectroscopic technique permits in situ monitoring of the chemical processes via mimicking the disappearance of the characteristic bands of the reactive compounds subjected to UV exposure. The photoreactive polymer films (250 um in thickness) were placed at the measuring site of a FTIR-ATR spectrometer and exposed to a source of UV/LED radiation (dual LED lamp; 36 W; 365 and 405 nm) and an IR analysis light beam. The absorbance change in the acrylate double bond (C=C) peak area was correlated to the extent of polymerization and analyzed using the Omnic program version 7.3. The degree of conversion (DC) can be expressed by the following relations: $DC\ (\%) = (A_0 - A_t) \cdot 100 / A_0$, where A_0 is the initial peak area before irradiation and A_t is the peak area at time t. The photopolymerization rate (R_p) was calculated by the following relations: $R_p = dDC/dt$, where t is the time of irradiation.

3. Results and Discussion

Free radical photopolymerization is an example of a photochemical chain reaction and consists of three main stages: initiation, propagation and termination [27]. This process leads to the formation of oligomers or polymers and has practical applications in cosmetic products, such as protective, decorative, and therapeutic nail coatings [28–30]. The typical composition of light-curable nail polish formulations includes urethane methacrylate or epoxy methacrylate oligomers, methacrylate monomers, photoinitiators, pigments, and various additives that enhance properties such as product rheology. Depending on the structure of the radical photoinitiator, free radicals can be generated via homolytic photodissociation of the photoinitiator molecule—these are classified as Type I photoinitiators. This group includes the following, among others: hydroxyketones and acylphosphine oxidesperoxides [31]. Alternatively, free radicals may be generated through the use of Type II photoinitiators, wherein the excited state of the photoinitiator molecule interacts with a suitable co-initiator, such as an electron donor or acceptor, or a hydrogen donor, to produce reactive radicals or radical ions [32]. This study focuses on Type II photoinitiators, which are less commonly employed in nail lacquers, in part due to the complexity of their reaction mechanisms and the necessity for carefully tailored formulations designed to meet specific functional requirements of the final product. Currently, multi-component photoinitiating systems based on electron transfer and hydrogen abstraction mechanisms are emerging as promising alternatives for such applications.

Thanks to modern technologies such as light-emitting diodes (LEDs), various light sources for curing nail lacquers are now readily available. Traditional light-induced polymerizations typically employed light sources emitting in the range of approximately 150–400 nm, often requiring high-energy ultraviolet (UV) radiation with wavelengths of 254 nm or shorter [33]. However, the advent of new photoinitiators featuring functional groups that can be excited by light in the 350–700 nm range has enabled the use of new photoreactive formulations that can be cured using LED lamps. Among available light sources, UV lamps emit polychromatic radiation, whereas laser diodes offer monochromatic light. The main advantages of LEDs include: (i) low heat generation (absence of IR emission); (ii) low energy consumption; (iii) reduced operational costs, minimal maintenance, a lifespan of approximately 50,000 h and portability. LED technology continues to evolve and holds significant promise for future applications. In the present study, a dual-LED lamp was used, emitting electromagnetic radiation at two wavelengths: 365 nm and 405 nm (Figure 1). In addition to the selection of an appropriate light source, the choice of a suitable photoinitiator is essential for initiating the polymer coating formation reaction. In addition to acylphosphine oxide, among the photoinitiators of polymerization are dye-based photoinitiating systems. These photoinitiators are characterized by the presence of an organic dye that exhibits sensitivity to light at specific wavelengths [34]. In this study, Camphorquinone and Eosin Y were evaluated as representative dye-based photoinitiators. Furthermore, the use of co-initiators absorbing in the far-ultraviolet region, such as commonly used iodonium salts, causes a change in absorption because absorption of the dye and coinitiator are overlapping. These systems are particularly suited for highly pigmented formulations, such as light-curable nail lacquers.

Urethane methacrylate oligomers constitute the primary component of photoreactive nail gel formulations, as their unique chemical structure-featuring polyol segments (so-called “soft segments”) and urethane segments (so called “hard segments”) provides an optimal balance of flexibility and hardness, making them ideally suited for use as coatings for nail plates. The kinetics of photopolymerization was tested on photoreactive pigmented compositions based on the urethane methacrylate oligomers and methacrylate monomers and titanium dioxide as pigment (10 wt.%). The results are presented in Figures 2–5 in

the form of the degree of conversion of unsaturated bonds C=C monitored on the basis of the disappearance of the 810 cm^{-1} peak and the rate of changes occurring during LED lamp irradiation. The aim of the study is to develop highly efficient photoinitiating systems for the radical polymerization of methacrylates in pigmented formulations. The research employed a system consisting of a photosensitizer as the radiation absorber and a co-initiator as the source of radicals.

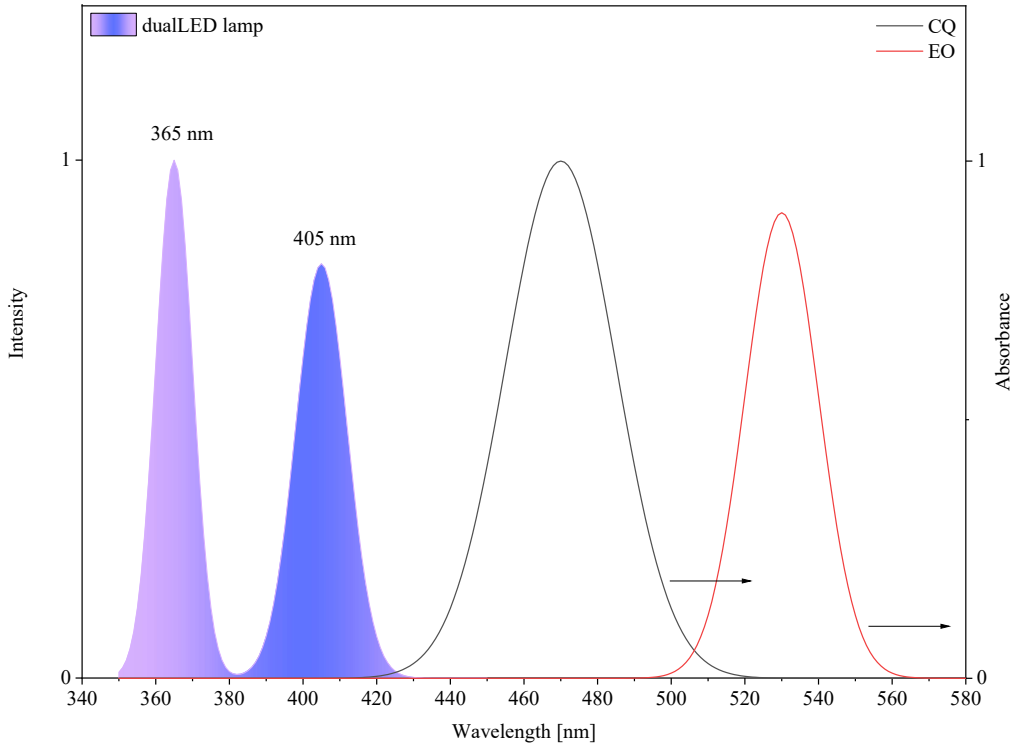


Figure 1. The electromagnetic radiation emission spectrum of the dual LED lamp and the radiation absorption range of Camphoquinone and Eosin Y.

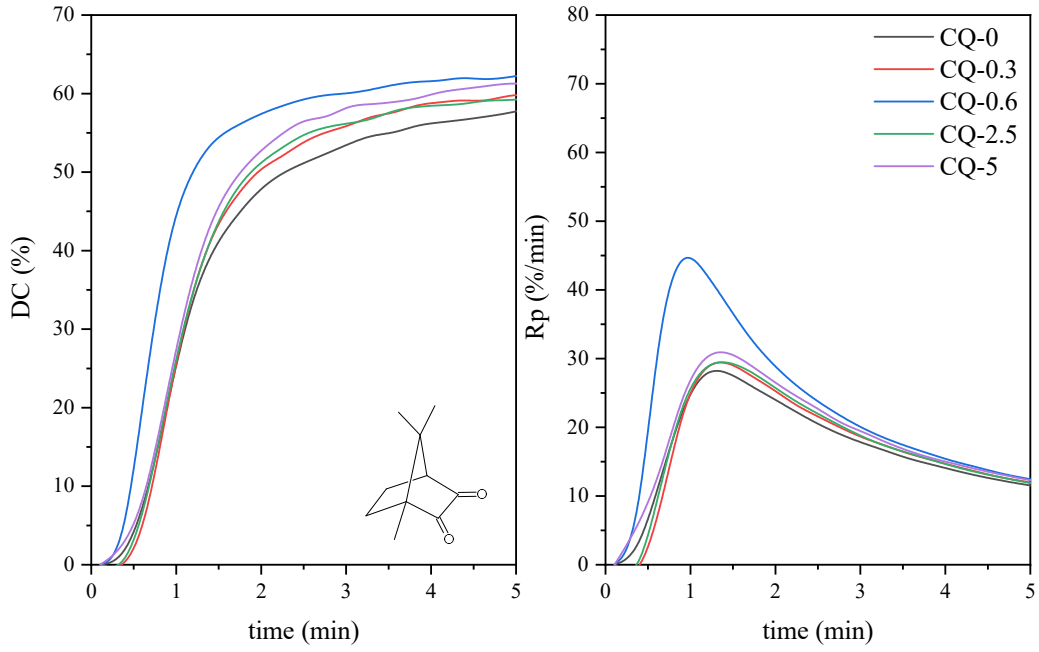


Figure 2. Conversion of unsaturated double bonds (DC) and the rate of the photopolymerization process (R_p) of the formulation with CQ (the studies were performed using the FTIR-ATR technique and a dual LED lamp, 365 nm and 405 nm).

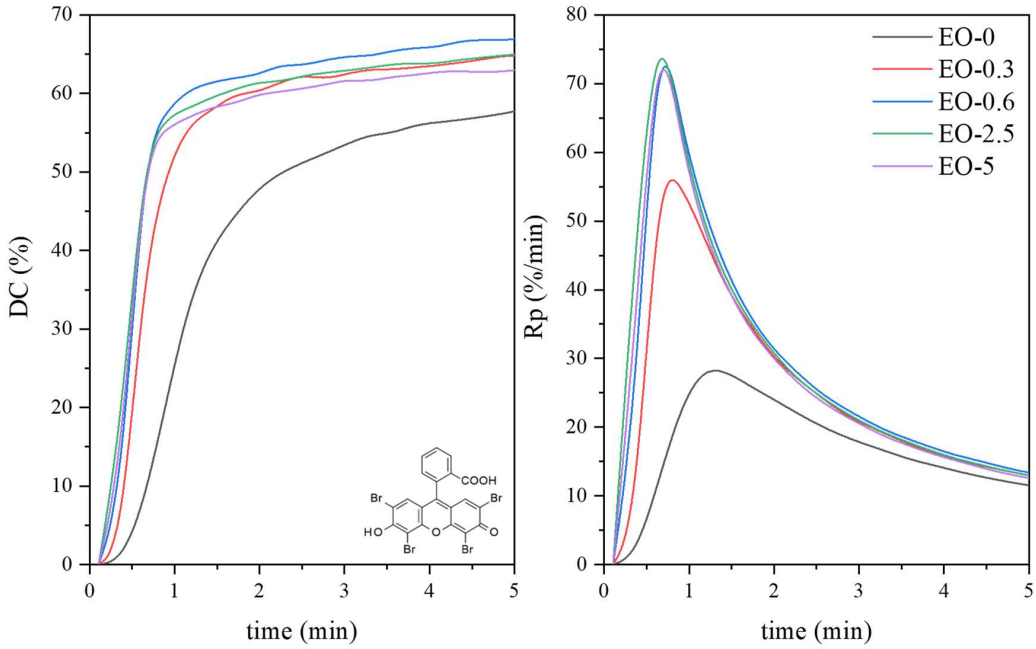


Figure 3. Conversion of unsaturated double bonds (DC) and the rate of the photopolymerization process (R_p) of the formulation with EO (the studies were performed using the FTIR-ATR technique and a dual LED lamp, 365 nm and 405 nm).

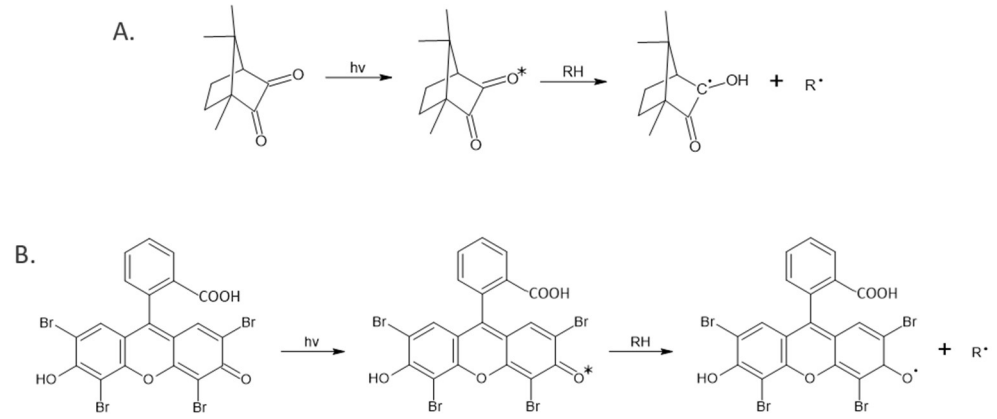


Figure 4. (**A**) The one-compound photoinitiating systems based on CQ, (**B**) The one-compound photoinitiating systems based on Eosin Y.

First, compositions using Camphorquinone (CQ) at various concentrations (up to 5 wt.%) were tested. The starting composition (without CQ, i.e., CQ-0) achieved the lowest degree of conversion of unsaturated double bonds (55% C=C conversion). The presence of CQ in the varnish composition increased the acrylate double bond conversion (up to 62%) and increased the photopolymerization rate (from R_p = 27 to R_p = 45 %/min). Interestingly, an improvement in the curing process was observed only up to a concentration of 0.6 wt.% CQ in the polymerization system. For the remaining concentrations used, only a slight change was observed (Figure 2).

In turn, the use of Eosin Y resulted in significant changes in the efficiency of the photopolymerization process of pigmented nail polish systems. The highest conversion was achieved when the Eosin Y content in the formulation was as low as 0.6% by weight (DC = 67%). The process proceeded at an extremely high rate, reaching R_p = 56%/min for 0.3% by weight EO, and exceeding R_p = 70%/min for higher concentrations. The reaction proceeds immediately after the lamp is turned on.

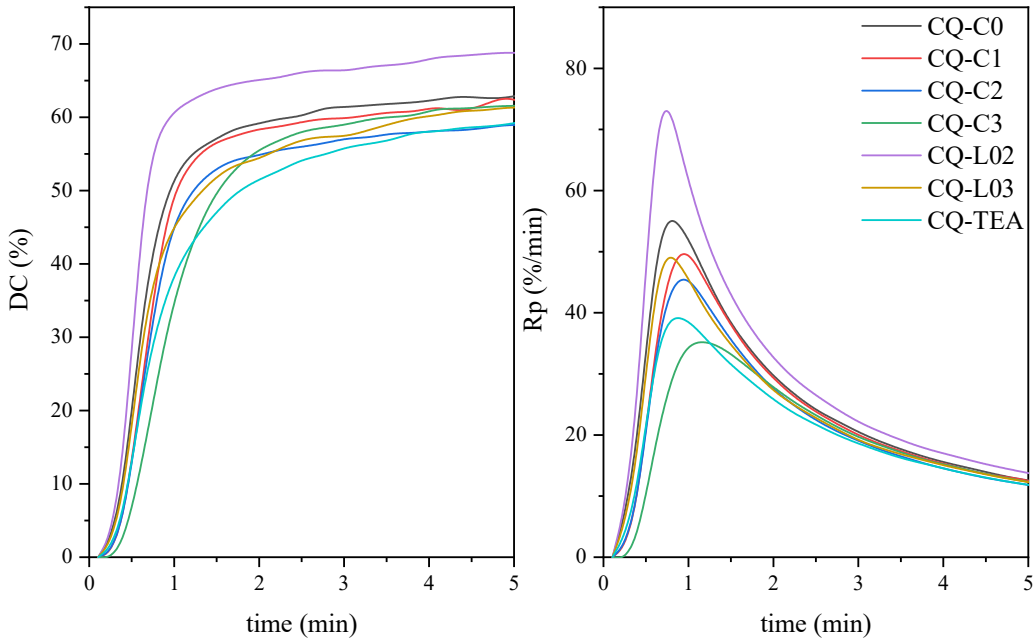


Figure 5. DC and R_p of the formulation with CQ and coinitiators (the studies were performed using the FTIR-ATR technique and a dual LED lamp, 365 nm and 405 nm).

Currently, photopolymerizable nail decoration products are expected to exhibit high opacity, enabling their use as single-layer coatings. Such coatings, in addition to being highly pigmented, must also cure within a short time frame—significantly faster than their conventional solvent-based counterparts, which typically require several minutes to cure process. The photopolymerization of highly pigmented systems poses a significant challenge due to the limited penetration of electromagnetic radiation through thicker layers and the absorption of light by the pigments. The formulation of nail lacquers requires comprehensive knowledge of safe cosmetic ingredients, as well as expertise in polymer chemistry, photopolymerization, materials engineering, and coating technologies. Highly pigmented, light-curable systems are also used in dentistry. Polymerization of dental resins is generally initiated by the Camphorquinone (CQ)/amine photoinitiating system, which produces free radicals upon exposure to radiation in the 450–500 nm range [35]. During LED irradiation, CQ absorbs light and its α-dicarbonyl chromophore forms an excited singlet state that transitions into an excited triplet state. This excited triplet interacts with oxidizable co-initiators, leading to the formation of radicals and the decomposition of CQ into colorless products (Figure 4) [36]. The presence of a light-absorbing photoinitiator in a photopolymerizable resin inevitably causes a reduction in light intensity along the radiation path and often limits the curing depth in the sample intended for polymerization [37]. However, when the photoinitiator undergoes photobleaching, its absorbance decreases and light attenuation is reduced, allowing deeper light penetration as the initiator is consumed [38]. Consequently, Camphorquinone is considered a suitable photoinitiator, particularly for the photopolymerization of thick and highly pigmented coatings.

Alternative photoinitiating systems have been proposed for use in the formulation of nail polish resins. One of the primary objectives is the selection of an appropriate co-initiator for a bimolecular system based on Camphorquinone (CQ). To this end, onium and iodonium salts, as well as thiol and amine additives, were investigated. According to literature, in order to accelerate the polymerization reaction, CQ is most commonly used in combination with various amines, such as N,N-dimethyl-p-toluidine, 2-ethyl dimethylbenzoate, N-phenylglycine, and others [39–42]. As previously demonstrated, CQ without co-initiator in the photoinitiation system, is capable of initiating polymerization, although only with

limited efficiency and at a relatively low rate, providing only marginal improvement in the reduction in residual monomer content. Below, several types of CQ/co-initiator systems are presented. Studies on highly pigmented nail lacquer compositions have shown improved conversion of unsaturated double bonds and enhanced polymerization rates across all tested systems. Notably, the system incorporating a thiol-based co-initiator yielded the most favorable results (CQ-L02; degree of conversion, DC = 67%; polymerization rate, Rp = 73 %/min). The use of onium and iodonium salts, as well as amines, led to a reduction in residual monomers and an increase in the photopolymerization rate under dual-LED lamp exposure, relative to the base composition (CQ-0).

Eosin Y is employed as a photoinitiator due to its excellent spectroscopic properties, which make it well-suited for use with visible light sources and safe for biological systems. Eosin Y is a representative example of a Type II photoinitiator, which requires a second component—typically an electron donor—to initiate polymerization. A common example of such a co-initiator is an amine, such as triethanolamine, which undergoes reduction during the reaction [27]. As illustrated in Figure 4, upon absorption of light, Eosin Y is excited to its triplet state, where it acts as an electron acceptor from, for instance, an amine. In the photoinitiating systems based on Eosin Y, the same co-initiators were used as in the previously discussed CQ-based systems. All tested formulations containing such additives exhibited enhanced conversion of unsaturated double bonds and higher rates of photopolymerization (Figure 6). The highest degree of conversion was achieved with the use of an iodonium salt (EO-C3; DC = 65%), as well as with the additive bis(4-tert-butylphenyl)iodonium p-toluenesulfonate (EO-C0; DC = 65%), which also yielded the highest polymerization rate (R_p = 74%/min).

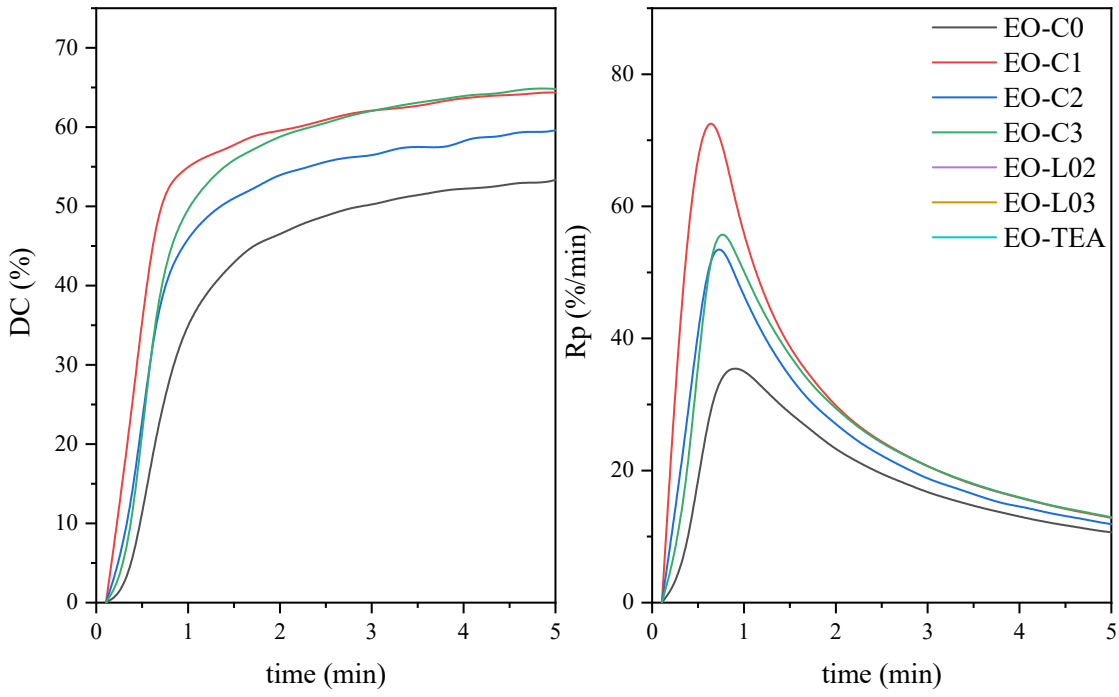


Figure 6. DC and R_p of the formulation with EO and coinitiators (the studies were performed using the FTIR-ATR technique and a dual LED lamp, 365 nm and 405 nm).

Camphorquinone (1,7,7-trimethylbicyclo [2.2.1]heptane-2,3-dione, CQ) belongs to the class of aliphatic α-diketones. It is well-documented in the literature and widely used as a photoinitiator for visible-light-induced photocrosslinking processes [43]. As mentioned above, the intrinsic efficiency of this photoinitiator is limited. However, the incorporation of electron/proton donors or reducing agents significantly enhances its performance, resulting

in an effective photoinitiating system. Such combinations are extensively employed for the crosslinking of methacrylate-based dental polymers. Indeed, numerous studies have investigated the photoinitiation mechanism of the CQ–amine system. Nevertheless, an interesting alternative involves the use of onium salts, iodonium salts, and thiols as co-initiators. Similar relationships have been observed in the case of binary photoinitiating systems based on Eosin Y.

It is well known that the initiation of the polymerization reaction by means of dyeing photoinitiating systems is based on the photoinduced electron transfer (PET) between their components [34]. The photoinitiating systems we propose, based on dyes in combination with onium or iodonium salts, initiate chain reactions also via intermolecular photoinduced electron transfer (PET) processes. It should be emphasized that the photoinitiation mechanism involving squaraine dyes as photosensitizers, paired with appropriate onium or iodonium salts as co-initiators, has been investigated and elucidated by our research group, as detailed in previous studies [34]. A general schematic of the free radical generation mechanism in a binary photoinitiating system composed of a dye acting as a photosensitizer and the onium or iodonium salts used in this study is presented below (Figure 7). As confirmed by the results of photopolymerization kinetics studies on methacrylate formulations intended for use as nail lacquers, such systems—utilizing Camphorquinone or Eosin Y—represent an excellent alternative for the polymerization of highly pigmented formulations under LED irradiation.

Another co-initiator used in the studied systems was a thiol, acting as an electron/proton donor. Thiols react with the radical species generated upon excitation of CQ (or EO), forming a new, highly reactive thiyl radical (Figure 8). This species can initiate the polymerization of double bonds much more efficiently than conventional amine-derived radicals. While pigments inherently limit the penetration of electromagnetic radiation, the thiol-based mechanism compensates for this drawback by enabling rapid and efficient radical generation. The CQ-thiol system, in particular, facilitates faster consumption of Camphorquinone, thereby reducing absorbance within the layer and allowing deeper light penetration into the material. Due to the higher polymerization rate and more effective radical transfer, the content of unreacted methacrylate groups is significantly reduced. Comparable effects were also observed in the EosinY-thiol system.

As well-established in the literature, amines are commonly employed as co-initiators to accelerate the polymerization process. The resulting aminoalkyl radicals are capable of initiating polymerization. The efficiency of this process depends on the spatial structure of the amine-derived radicals, which must effectively approach the reactive unsaturated bond in the monomer. It is widely accepted that the formation of aminoalkyl radicals occurs via a photoinduced electron transfer (PET) mechanism. Upon absorption of electromagnetic radiation, Camphorquinone (CQ) typically transitions into two possible excited states (Figure 9): (i) the singlet state, which does not involve spin inversion of the electron, and (ii) the triplet state, which plays a crucial role in free radical generation and is characterized by a very short half-life [43]. A similar mechanism governs the radical formation in binary photoinitiating systems composed of Eosin Y and amines. After light absorption, Eosin Y is excited to its triplet state and subsequently acts as an electron acceptor from the amine. This electron transfer generates an Eosin Y radical anion and an amine radical cation. Through subsequent proton transfer from the amine radical cation, two neutral radicals are formed: the amine radical and the Eosin Y radical [27].

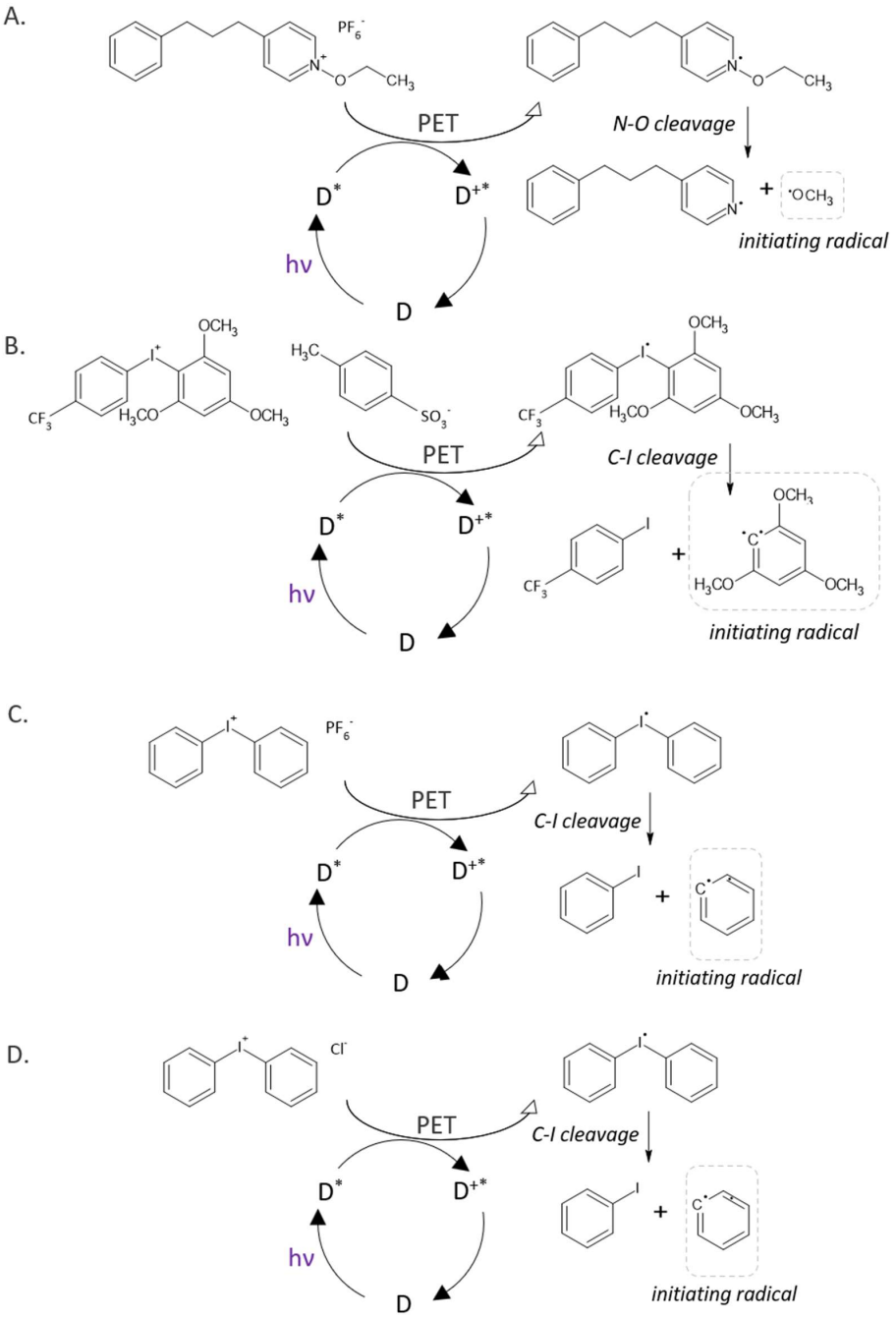


Figure 7. Mechanism of photoinitiation of the polymerization reaction using two-component systems: dye (D) + onium or iodonium salt ((**A**)C0; (**B**) C1; (**C**) C2; (**D**) C3) [34].

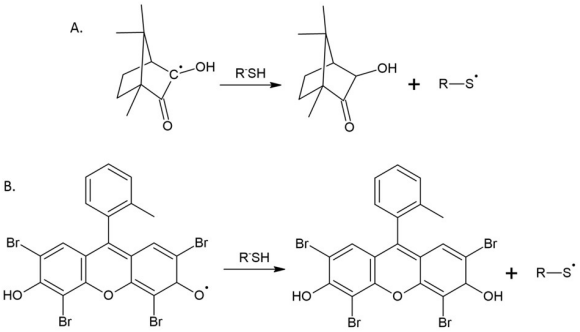


Figure 8. Mechanism of free radical generation in a photoinitiating system composed of Camphorquinone (**A**) and Eosin Y (**B**) with thiols.

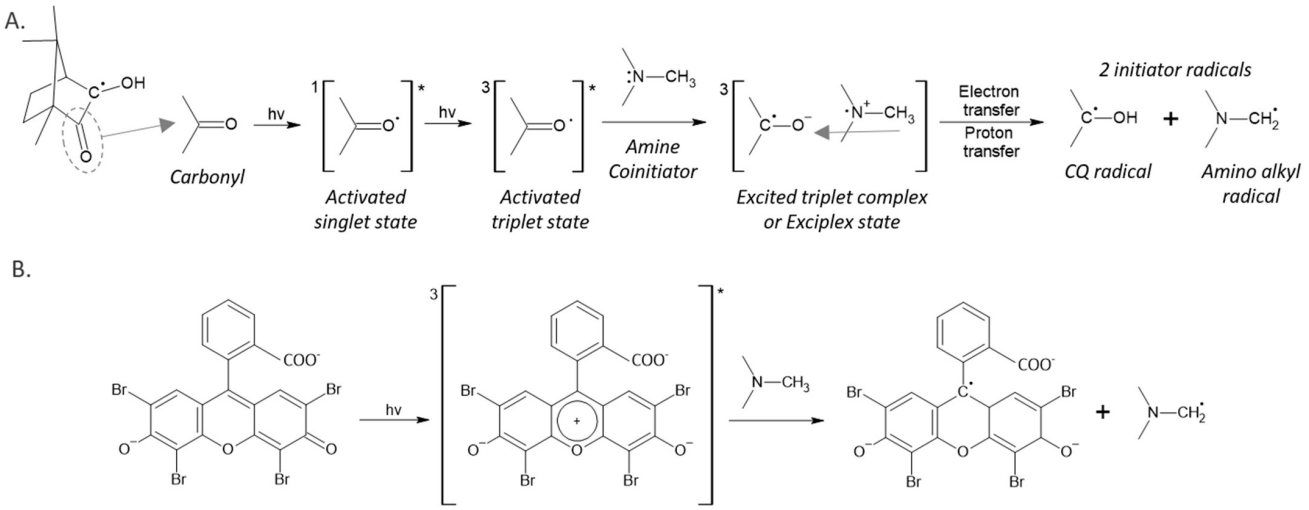


Figure 9. Mechanism of free radical generation in a photoinitiating system composed of Camphorquinone (**A**) and Eosin Y (**B**) with an amine [43].

Table 4 presents a comparison of the photopolymerization performance of systems based on Camphorquinone (CQ) or Eosin Y (EO) using either thiols or amines as co-initiators. The results clearly demonstrate superior photopolymerization parameters in systems employing thiols compared to their amine-based counterparts. Despite the prevalence of literature reports on CQ–amine systems, thiol-containing systems exhibit enhanced capabilities in key aspects such as radical generation efficiency, polymerization rate, and degree of conversion (DC). These advantages are supported by several well-documented mechanistic and kinetic foundations substantiated in the scientific literature. Thiol-based photoinitiating systems operate via hydrogen atom transfer (HAT), a rapid process in which the excited-state molecule of the photoinitiator (e.g., CQ or EO) abstracts a hydrogen atom from the thiol's –SH group. The resulting thiyl radical (RS•) is (i) highly reactive, (ii) less sterically hindered than aminoalkyl radicals, and (iii) more efficient in initiating the polymerization of methacrylate double bonds [44,45].

Table 4. Comparison of the properties of photoinitiating systems with thiols and amines.

Property	Camphorquinone		Eosin Y	
	+Thiol	+Amine	+Thiol	+Amine
Radical Generation Efficiency	High	Moderate	High	Moderate
Polymerization Rate (R_p)	High (up to 73 %/min)	Moderate	High (up to 70 %/min)	Moderate
Degree of Conversion (DC)	67%	50%–60%	65%	45%–55%
Light Penetration support	High	Moderate	High	Moderate
Residual monomer content	Low	Moderate	Medium	Low
Compatibility with dual-LED (365/405 nm)	High	High	Moderate	Moderate
Stability in formulation	Moderate	High	Moderate	High

Thiyl radicals exhibit different efficiency of the initiation step than aminoalkyl radicals. In addition, (i) thiyl radicals show a lower tendency for termination, (ii) which results in faster polymerization rates (Rp) and greater degrees of conversion (DC) within shorter curing times [46,47]. Moreover, thiol-based systems facilitate more rapid consumption of the photoinitiator (CQ or EO), which leads to the following: (i) photobleaching of the initiator and consequent reduction in absorption, (ii) improved light penetration through pigmented layers, and (iii) enhanced curing efficiency at greater film depths. This is

especially critical in highly pigmented nail polish formulations, where light scattering and absorption significantly hinder polymerization efficiency [48]. Although amines are inexpensive and widely used, they possess several important drawbacks: (i) chemical instability and formulation aging due to oxidation, (ii) formation of colored byproducts, and (iii) limited compatibility with modern pigments and LED systems, (iv) lower performance in highly pigmented formulations. In contrast, CQ-thiol or EO–thiol systems are more effective due to their ability to (i) generate more reactive and mobile radicals, (ii) initiate polymerization more rapidly, and (iii) perform better in optically challenging, pigment-rich systems. The findings support the rationale for using thiols as more efficient co-initiators in cosmetic applications—particularly in highly pigmented formulations cured with LED sources and dye-based sensitizers (Table 4).

To sum up, dye-based photoinitiators (CQ and EO) are suitable for LED-cured, pigmented UV nail gel systems, enabling effective initiation within the 365–405 nm range, especially when coupled with proper co-initiators. Eosin Y outperforms Camphorquinone in terms of both conversion efficiency and polymerization rate in standalone applications. Thiol-containing co-initiating systems (CQ-thiol or EO-thiol) demonstrated the most favorable photopolymerization parameters, including: higher degrees of conversion (DC up to 67%), faster polymerization rates (R_p > 70%/min), greater photoinitiator consumption, leading to deeper curing (photobleaching effect). Amines, despite their cost-effectiveness, show several drawbacks, particularly in pigmented systems, due to limited light penetration, chemical instability, and lower reactivity compared to thiyl radicals. The CQ-thiol or EO-thiol photoinitiating systems are recommended as the most efficient and practical solution for achieving fast, deep, and complete curing in modern, highly pigmented, light-curable nail gel formulations.

4. Conclusions

This study investigated the effectiveness of two-component dye-based photoinitiating systems—using Camphorquinone (CQ) and Eosin Y (EO) as photosensitizers—for initiating radical polymerization in highly pigmented nail gel formulations. The systems were examined under LED light (365 and 405 nm), focusing on their ability to enhance the degree of conversion (DC) of unsaturated methacrylate groups and the photopolymerization rate (R_p). The photoreactive formulations were based on urethane methacrylate oligomers with titanium dioxide pigment, simulating a realistic, high-opacity nail gel. Several classes of co-initiators were tested, including onium salts, iodonium salts, thiols, and amines. Real-time FTIR-ATR spectroscopy enabled precise monitoring of photopolymerization kinetics under dual-LED irradiation. Initial tests showed that both CQ and EO alone improved DC and Rp compared to the control, with Eosin Y demonstrating superior efficiency even at low concentrations. Further enhancement was achieved by introducing co-initiators. Across all tested formulations, the use of thiol-based co-initiators resulted in the highest DC (up to 67%) and fastest R_p (up to 74%/min), surpassing traditional CQ–amine systems. These results were attributed to the formation of highly reactive thiyl radicals, which are less sterically hindered and more efficient in initiating polymerization compared to aminoalkyl radicals. In comparison, amine-based systems, while widely used and economical, presented limitations including chemical instability, by-product discoloration, and suboptimal performance in pigmented matrices. Onium and iodonium salt systems showed moderate improvements but were less efficient than thiol-based systems, especially in visible-light applications. These findings provide valuable insights for the development of advanced cosmetic materials, particularly where high pigment loading and efficient curing are essential under mild, LED-based conditions. Future work could explore further

optimization of co-initiator ratios, compatibility with various pigments, and long-term stability in real product conditions.

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