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Visible-Light-Sensitive Polymerizable and Polymeric Triazine-Based Photoinitiators with Enhanced Migration Stability

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Abstract: Photopolymerization has attracted great interest because of its mild reaction conditions, spatiotemporal controllability, cost efficiency, and fast speed. However, with the raising environmental awareness and the increasing attention to life and health, the leachability of photoinitiators has become a growing concern. In this research, a methacrylate functionalized triazine-based polymerizable visible light photoinitiator, 2-(((4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenoxy)carbonyl)amino)ethyl methacrylate (CT) and its reversible addition–fragmentation chain transfer (RAFT) polymerized CT (pCT) were designed as the polymerizable and polymeric photoinitiators, respectively. The photoinitiation abilities of the investigated triazine derivatives were evaluated under violet LEDs. Due to the steric effect, pCT showed slightly reduced photoinitiation ability under both LED at 400 nm and 410 nm irradiation. Nevertheless, photopolymers initiated using CT and pCT showed excellent migration stability compared to those prepared by 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MT) and 4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenol (PT). Specifically, CT and pCT-based polymers prepared under the irradiation of LED at 400 nm exhibited only 1/3-fold and 1/14-fold of photoinitiators leachability, while 1/2-fold and 1/6-fold of photoinitiator leachability were obtained compared to the MT-based photocured polymers when using LED at 410 nm. The excellent migration stability of pCT reveals potential applications in the biomedical and food packaging fields.

Keywords: triazine; polymerizable photoinitiator; polymeric photoinitiator; migration; photopolymerization



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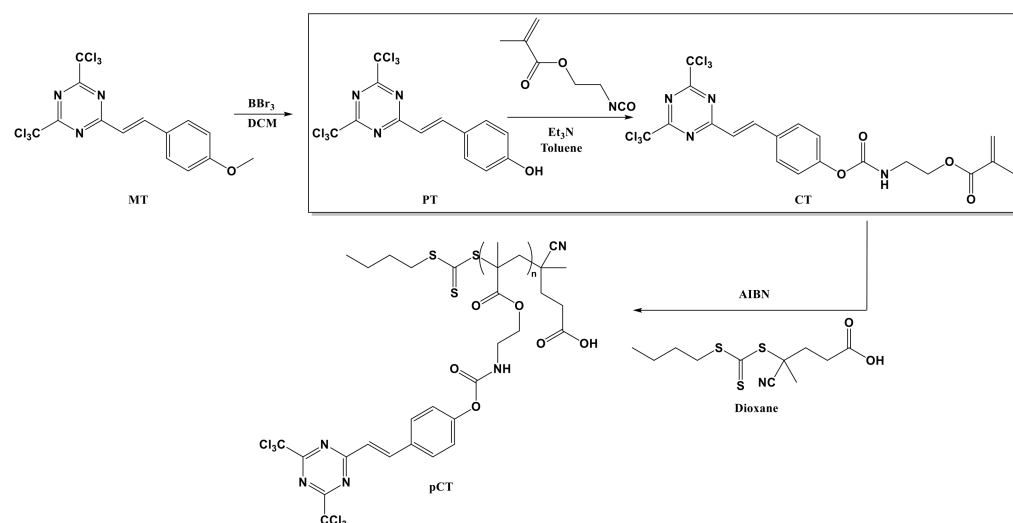
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1. Introduction

Photopolymerization has been prevalent in various fields, including 3D printing, coating, optoelectronics, dentistry, adhesive, and paints [1–8], due to its mild reaction conditions, spatiotemporal controllability, cost-efficiency, and high efficiency [9–11]. Many photocatalysts [12–14] and photoinitiators [15,16] are commercially available or have been developed to initiate photopolymerization. One of the most growing concerns in photopolymerization is the migration and leachability of photoinitiators from photocured products. Although only a small amount of photocatalysts or photoinitiators is required in photopolymerization, unconsumed photoinitiators and their photolysis fragments still remain in the photocured products, while it is even more significant for photocatalysts as they are almost not consumed at all and remain unchanged after reactions [17–20]. The residual photocatalysts or photoinitiators and fragments produced from the photolysis of photoinitiating systems can bring undesired properties of the polymers and cause migration problems. All these issues greatly limit the applications of the produced polymers on food packaging or biochemical materials due to toxicity [18,21–28]. Thus, the strategies to minimize the migration of photoinitiators have attracted much interest. One prevalent strategy is to introduce polymerizable groups such as the methacrylate group into photoinitiators, including thioxanthone, naphthalimide, and (2E,5E)-2,5-bis(4-((2-hydroxyethyl)(methyl)amino)benzylidene)cyclopentanone.

This allows the crosslinking of photoinitiators into the prepared photopolymer networks, which significantly decreases their mobility [17,18,28–34]. Another strategy is to develop the macromolecular photoinitiators from the low molecular weight photoinitiators, including bisacylphosphine oxide (BAPO), 1-hydroxy-cyclohexyl-phenylketone (HCAP), 2-hydroxy-2-methyl-1-phenyl propanone (HMPP), and naphthalimide derivatives [35–38], and the developed macromolecular photoinitiators were well-known for their low leachability due to the significantly reduced diffusion coefficient of macromolecules in both the fluid layer and polymer matrix [36–45]. However, most of them only contain a low content of photoinitiator; thus, they require high mass concentrations [35–41,43]. Alternatively, these polymeric photoinitiators work efficiently mainly under UV light irradiation, which limits their potential applications in household usage and making thick samples due to the potential harm of UV light to the human body and its poor penetration depth [46–52]. The most direct approach to solving these issues is to employ photoinitiators that are sensitive to longer wavelengths instead. In fact, there have been some visible light-sensitive macromolecular photoinitiators reported [35,53]. Specifically, a waterborne poly(ethylene glycol) substituted BAPO derivative (PEG-BAPO) was synthesized and showed a possibility of applying it to 3D printing under 460 nm LED irradiation [35]. However, it also showed a prolonged induction time of 12 s when photopolymerized with only 50 μm -thick samples, which could be ascribed to the extremely low molar extinction coefficient at 460 nm. Alternatively, a series of BAPO salts and monoacylphosphineoxide (MAPO) salts were also synthesized and investigated under visible light irradiation [53]. Nevertheless, their low molar extinction coefficients under the visible light range significantly affect their efficiency. Therefore, it is desirable and urgent to design and develop highly efficient visible-light-sensitive photoinitiators with high migration stability for photopolymerization. 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MT) has been reported as a highly efficient photoinitiator under visible light irradiation [46]. Compared to the commercially available photoinitiators, such as BAPO, 2,4,6-trimethylbenzoyl diphenyl-phosphineoxide (TPO), and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-1-butanone (BDMB), MT exhibits a higher photoinitiation ability under the irradiation of LED at 405 nm in free radical polymerization (FRP) and has been applied in 3D printing [54]. Moreover, MT, when combined with an iodonium salt and *N*-vinylcarbazole, can photoinitiate cationic polymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (EPOX) [46]. However, most photoinitiators, including MT, show poor cytocompatibility [55–57]; therefore, the investigation of the migration of photoinitiators after photopolymerization becomes significant.

Herein, we reported a polymerizable MT derivative and a polymeric MT derivative with high efficiency and migration stability. Specifically, the polymerizable MT derivative, 2-(((4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenoxy)carbonyl)amino)ethyl methacrylate (CT) was synthesized by first forming 4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenol (PT) by the demethylation of MT, followed by the coupling of PT with 2-isocyanatoethyl methacrylate. Subsequently, CT underwent RAFT polymerization to generate polymerized CT (pCT), a polymeric photoinitiator with high triazine content, as shown in Scheme 1. The light absorption properties of the synthesized triazine derivatives were fully studied. The photoinitiation abilities of these triazine derivatives were investigated under the irradiation of LED at 400 nm and 410 nm by the photopolymerization of trimethylolpropane triacrylate (TMPTA) via real-time Fourier transform infrared spectroscopy (RT-FTIR). Furthermore, the migration stability of the residual photoinitiators from photocured samples was discussed.



Scheme 1. Synthetic route for PT, CT, and pCT.

2. Results and Discussion

2.1. Synthesis and Characterization of Triazine Derivatives

Triazine (MT) was first demethylated by boron tribromide (BBr_3) to yield 4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenol (PT). PT was subsequently coupled with 2-isocyanatoethyl methacrylate to form polymerizable 2-(((4-(2-(4,6-bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenoxy)carbonyl)amino)ethyl methacrylate (CT). Finally, CT was RAFT polymerized to yield a polymeric photoinitiator, pCT. The successful synthesis of CT was confirmed with nuclear magnetic resonance (^1H NMR and ^{13}C NMR), as shown in Figure 1. Specifically, H1, H4, and H5 proton signals in Figure 1a suggested the introduction of the methacrylate group, while the carbonyl group signal of C12 in Figure 1b indicated the formation of the carbamate.

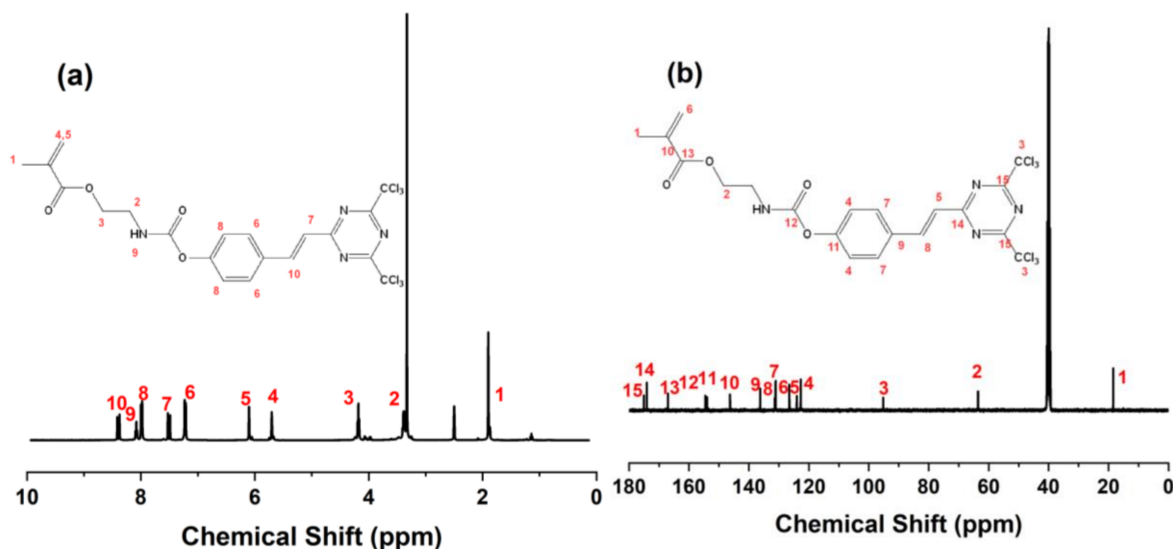


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of CT in $\text{DMSO}-d_6$ (400 MHz).

The prepared CT was also characterized using Fourier-transform infrared spectroscopy (FTIR). As shown in Figure 2, the presence of the characterization bands at 3417 and 1703 cm^{-1} of CT were attributed to the N-H and C=O stretching, respectively [58]. This again confirmed the successful synthesis of CT from PT. Finally, the RAFT polymerized CT (pCT) was examined to have M_n of 5240 g/mol , M_w of 6840 g/mol , and a polydispersity index (PDI) of 1.305 using the GPC measurements (Figure 3). The triazine content of pCT

was calculated via the equation: $MT\ wt\% = \frac{(M_n - M_{CTPA})}{M_n} \times \frac{M_{MT}}{M_{CT}} = 72\ wt\%$, where M_{CTPA} , M_{MT} , and M_{CT} are the molecular weight of CTPA, MT, and CT, respectively.

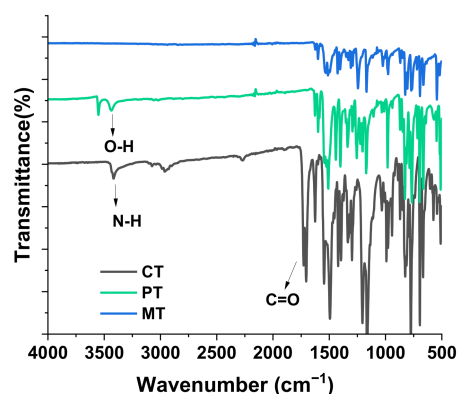


Figure 2. FTIR spectra of CT, PT, and MT.

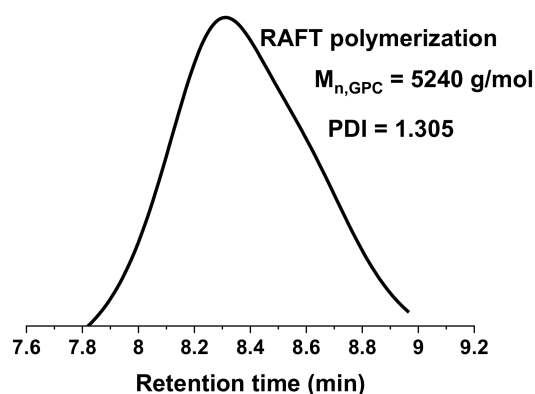


Figure 3. GPC elution profile of pCT synthesized by RAFT polymerization.

2.2. Light Absorption Properties of MT, PT, CT, and pCT

The light absorption spectra of the investigated triazine derivatives in DMF are shown in Figure 4. To compare the light absorption properties of pCT with small molecule triazine derivatives, the equivalent concentration of triazine moiety of pCT was applied. Their light absorption maxima (λ_{max}) and extinction coefficients at the maximum absorption (ϵ_{max}) are summarized in Table 1. Compared to the maximum absorption peak of MT ($\lambda_{max} = 380\ nm$), the maximum light absorption of PT is slightly red-shifted ($\lambda_{max} = 385\ nm$), possibly due to the hydrogen bonding and the basic condition of *N,N*-dimethylformamide (DMF) [59]. Specifically, the phenol hydroxyl group of PT could form hydrogen bonds with DMF and could also be ionized in basic DMF, resulting in the bathochromic shift. In contrast, those of CT and pCT were both blue-shifted ($\lambda_{max} = 350\ nm$), which can be attributed to the fact that the substituents with low electron-donating abilities lead to the hypsochromic shift [60]. The order of maximum absorption peak follows the order of electron-donating abilities: CT and pCT: $-O(CO) < MT: -OMe < PT: -OH$. Interestingly, even though the molar extinction coefficient of pCT ($24,900\ M^{-1}\ cm^{-1}$) is slightly lower than that of CT ($29,900\ M^{-1}\ cm^{-1}$), the light absorption of pCT is extended up to 460 nm (Figure 4). With the light absorption profiles of the synthesized triazine derivatives and the knowledge of the photoinitiation mechanism [48], the following studies were performed under the irradiation of LED at 400 nm or LED at 410 nm (Table 1).

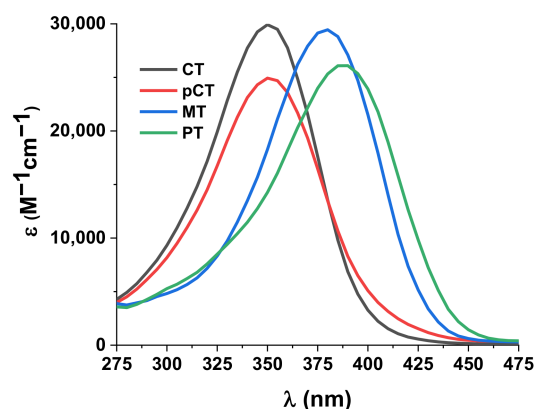


Figure 4. UV–Vis absorption spectra of CT, pCT, MT, and PT in DMF.

Table 1. The maximum absorption wavelengths $\lambda_{\max}$, extinction coefficients $\epsilon_{\max}$ at $\lambda_{\max}$, $\epsilon_{400\text{ nm}}$ at 400 nm, and $\epsilon_{410\text{ nm}}$ at 410 nm of MT, PT, CT, and pCT in DMF.

Photoinitiators	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ($\text{M}^{-1}\text{ cm}^{-1}$)	$\epsilon_{400\text{ nm}}$ ($\text{M}^{-1}\text{ cm}^{-1}$)	$\epsilon_{410\text{ nm}}$ ($\text{M}^{-1}\text{ cm}^{-1}$)
MT	380	29,400	21,500	14,000
PT	385	26,000	23,900	19,000
CT	350	29,900	3300	1500
pCT	350	24,900	5100	3100

2.3. Photoinitiation Abilities of Triazine Derivatives

With the knowledge of the fact that the free radicals generated from the self-cleavage of MT are the active species for the initiation of the following polymerization of trimethylolpropane triacrylate (TMPTA) [46], the photoinitiation ability of MT is efficient for the free radical polymerization of acrylates under the irradiation of LED at 400 nm in terms of the final double bond conversion (35.6%) and maximum rate of photopolymerization ($R_{p,\max}$: 4.21 s^{-1}) (Figure 5a and Table 2). Furthermore, the higher intensity violet LED at 410 nm (110 mW cm^{-2}) improves the photopolymerization of TMPTA in the presence of MT (Figure 5b), in line with the results reported previously [42,46,54]. To evaluate the effect of modification of MT structure on their photoinitiation abilities, the photopolymerization of TMPTA was carried out in laminate under both LED at 400 nm and LED at 410 nm (Figure 5 and Table 2). The demethylated triazine derivative, PT, showed similar final double bond conversions (36.2% and 46.4%) compared with MT (35.6% and 45.0%) (Table 2) upon exposure to LED at 400 nm and LED at 410 nm, respectively; nonetheless, it showed diminished $R_{p,\max}$ to 3.31 s^{-1} and 7.34 s^{-1} . However, the polymerizable and the polymeric triazine derivatives, CT and pCT, exhibited reduced photoinitiation abilities in terms of both final double bond conversions and the $R_{p,\max}$ to different extents (Figure 5a and Table 2). Specifically, CT and pCT reduced the final double bond conversions to 15.3% and 24.9% upon exposure to LED at 400 nm, respectively (Table 2). This trend is in accordance with the discussed light absorption of the investigated triazine and its derivatives at 400 nm above, except for pCT (Table 1). As shown in Figure 5a, the overall slope of the TMPTA photopolymerization profile of pCT (red) revealed that the rate of polymerization was adversely affected by its nature as the polymeric photoinitiator. Specifically, the triazine moieties pendants on the chain of the pCT induced a huge steric effect, which restricted the mobility of the generated free radicals; hence, this significantly sacrificed the photoinitiation ability of corresponding photoinitiators [61]. Nevertheless, the slower polymerization rate in the pCT-based formula allowed the active species produced by pCT to release into the uncured resin gradually and resulted in a higher final double bond conversion of 24.9% compared to that produced by CT. In contrast, the $R_{p,\max}$ of pCT is higher under LED at 410 nm than under LED at 400 nm (Table 2). This can be ascribed to the concentrated free radicals generated by pCT under LED at 410 nm compared to that under LED at 400 nm due to light intensity. Therefore, the distribution of active species in the uncured resin was

promoted by the radical concentration gradient. The accelerated $R_{p,max}$ of pCT (2.97 s^{-1}) under LED at 410 nm compared to LED at 400 nm (0.18 s^{-1}) resulted in faster gelation of the monomers, of which the formed network subsequently reduced the mobility of residual active species and limited the diffusion of active species into the uncured sample; hence, the final double bond conversion of TMPTA cannot reach a higher plateau. (Figure 5b).

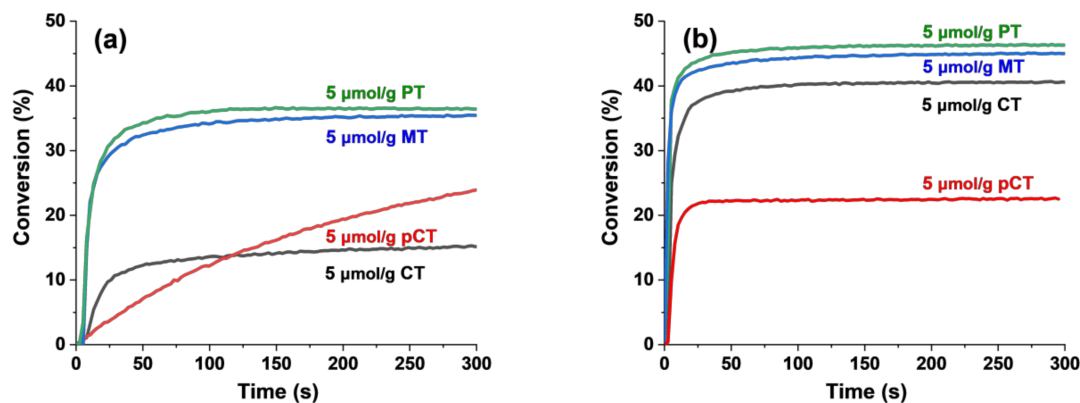


Figure 5. Photopolymerization profiles (double bond conversion vs. time) of TMPTA in laminate upon exposure to (a) LED at 400 nm and (b) LED at 410 nm in the presence of triazine derivative-based photoinitiators (molar concentrations of all triazine moieties are $5.0\text{ }\mu\text{mol/g}$).

Table 2. Double bond conversions and polymerization rates of TMPTA in the presence of triazine derivatives (MT, PT, CT, and pCT) upon exposure to the LED at 400 nm (6.4 mW cm^{-2}) and LED at 410 nm (110 mW cm^{-2}) for 300 s.

Photoinitiators ^a	LED at 400 nm		LED at 410 nm	
	C^b	$(R_p/[C=C]) \times 100^c$	C^b	$(R_p/[C=C]) \times 100^c$
MT	35.6%	4.21 s^{-1}	45.0%	10.91 s^{-1}
PT	36.2%	3.31 s^{-1}	46.4%	7.34 s^{-1}
CT	15.3%	0.83 s^{-1}	40.5%	5.59 s^{-1}
pCT	24.9%	0.18 s^{-1}	22.5%	2.97 s^{-1}

^a Contains equal molar concentration of the triazine moiety ($5\text{ }\mu\text{mol/g}$). ^b Final double bond conversions of TMPTA after photopolymerization for 300 s. ^c Maximum rates of photopolymerization, calculated from the maximum of the first derivative of the double bond conversions versus time curves during photopolymerization.

Additionally, the effect of light intensity and triazine moiety concentrations was investigated. As aforementioned, the increasing intensity of LED promoted the polymerization of TMPTA in the presence of identical photoinitiating systems in terms of both final double bond conversions and the $R_{p,max}$ (Table 2). Moreover, except for the $1.0\text{ }\mu\text{mol/g}$ pCT formulation, the increased amount of triazine moiety from 1.0 to $10.0\text{ }\mu\text{mol/g}$ resulted in the increased final double bond conversion for both pCT and CT under the irradiation of LED at 410 nm (Figure 6). The distinctive TMPTA photopolymerization profile of $1.0\text{ }\mu\text{mol/g}$ pCT (Figure 6a) is attributed to the aforementioned steric effect.

2.4. Migration of Photoinitiators from Photocured Samples

Residual photoinitiators and photolysis fragments tend to migrate to the surface of the photocured samples, which limits their application in biochemical materials [18,21–28]. The migration stabilities of photocured samples (41.5 mg) were investigated by comparing the light absorption at the absorption maxima (λ_{max}) of each sample in their leaching solution (4 mL) as illustrated in Figure 7. Although the photoinitiation abilities of CT and pCT were reduced (Figure 5), their migration stabilities were significantly enhanced compared to MT (Table 3). Specifically, when irradiated by LED at 400 nm, PT showed the highest leachability (72.88%), possibly due to the strong hydrogen bonding interaction with the solvent, which increased its solubility, while CT (13.35%) and pCT (2.88%) showed a

1/3-fold and a 1/14-fold leachability, respectively, compared to MT (41.03%). When irradiated by LED at 410 nm, the polymers were crosslinked higher compared to that of using LED at 400 nm; thus, the migration stabilities of all the samples were enhanced, especially for PT (11.91%) and MT (3.75%). However, the trend remained the same as those with LED at 400 nm. Specifically, CT (1.55%) and pCT (0.61%) showed a 1/2-fold and a 1/6-fold leachability, respectively, compared to MT (3.75%).

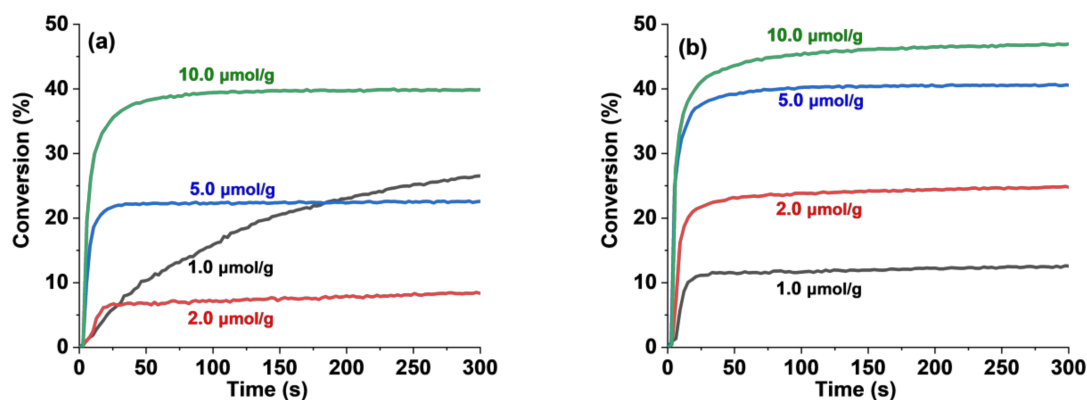


Figure 6. Photopolymerization profiles (double bond conversion vs. time) of TMPTA obtained in laminate in the presence of diverse equivalent triazine moiety concentration (a) pCT and (b) CT upon exposure to LED at 410 nm.

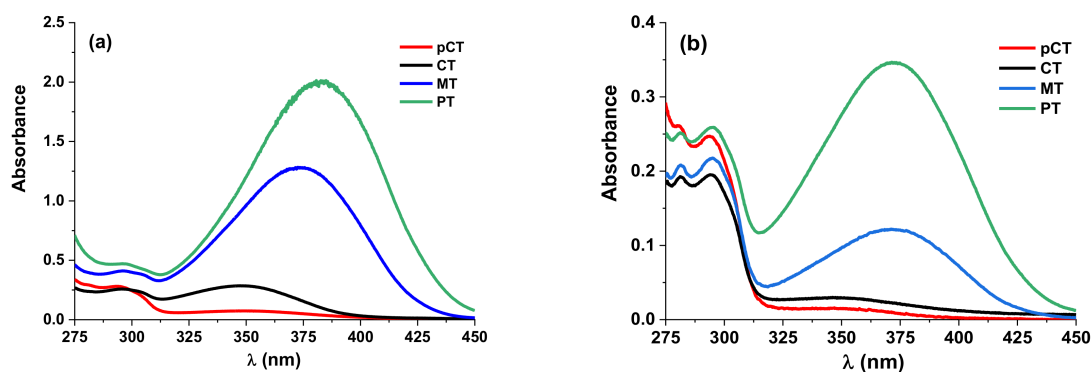


Figure 7. UV–Vis absorption spectra of photoinitiators extracted with DMF for 20 h from the photopolymers prepared by the photopolymerization of TMPTA under the irradiation of (a) LED at 400 nm and (b) LED at 410 nm in the presence of 10.0 μmol/g triazine moiety of MT, PT, CT, and pCT in TMPTA.

Table 3. The migration ratio of photoinitiators from photocured samples.

Photoinitiators	LED at 400 nm	LED at 410 nm
MT	41.03%	3.75%
PT	72.88%	11.91%
CT	13.35%	1.55%
pCT	2.88%	0.61%

3. Materials and Methods

3.1. Materials

Unless specified, all the chemicals were used as received. Trimethylolpropane triacrylate (TMPTA), 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MT), boron tribromide (BBr_3 , 1 M in heptane), dichloromethane (DCM; anhydrous), hexane, ethyl acetate (EA), absolute ethanol, toluene, triethylamine (TEA), azobisisobutyronitrile (AIBN), 2-isocyanatoethyl methacrylate, *N,N*-dimethylformamide (DMF), dimethylacetamide (DMA),

acetonitrile (ACN), and dioxane were all purchased from Sigma-Aldrich. Deuterated dimethyl sulfoxide (DMSO- d_6) was obtained from Cambridge Isotope Laboratories, Andover, MA, USA.

3.2. Synthesis

3.2.1. 4-(2-(4,6-Bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenol (PT)

The synthesis of PT followed the literature [42]. Briefly, to the solution of 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (MT) (1 g, 2.2 mmol) in 100 mL of DCM at $-78\text{ }^{\circ}\text{C}$, BBr_3 (60 mL, 1 mol/L, 60 mmol) was added dropwise. The resultant mixture was allowed to warm to room temperature ($\sim 18\text{ }^{\circ}\text{C}$) overnight and stirred for 1 day. The reaction mixture was then quenched by ice water (300 mL) and extracted by DCM. The organic layer was combined, dried with anhydrous sodium sulfate, and concentrated under vacuum, affording a yellow solid without further purification (780 mg, 80% yield).

3.2.2. Polymerizable

2-(((4-(2-(4,6-Bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenoxy)carbonyl)amino)ethyl Methacrylate (CT)

To the solution of 4-(2-(4,6-Bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenol (PT) (780 mg, 1.8 mmol) and TEA (0.5 mL, 3.6 mmol) in 20 mL toluene protected with N_2 , the solution of 2-isocyanatoethyl methacrylate in 10 mL toluene was added at room temperature. The resultant mixture was then stirred at $60\text{ }^{\circ}\text{C}$ for 18 h. The solvent was removed under vacuum and the residue was purified by a silica column (10% EA/Hexane) to give a pale-yellow solid (700 mg, 66% yield).

^1H NMR (400 MHz, DMSO- d_6) δ 8.40 (d, $J = 15.8\text{ Hz}$, 1H), 8.08 (s, 1H), 7.99 (d, $J = 8.6\text{ Hz}$, 2H), 7.51 (d, $J = 15.9\text{ Hz}$, 1H), 7.22 (d, $J = 8.5\text{ Hz}$, 2H), 6.12–6.08 (m, 1H), 5.70 (t, $J = 1.9\text{ Hz}$, 1H), 4.18 (s, 2H), 3.39 (d, $J = 5.6\text{ Hz}$, 2H), 1.90 (s, 3H).

3.2.3. Polymerized

2-(((4-(2-(4,6-Bis(trichloromethyl)-1,3,5-triazin-2-yl)vinyl)phenoxy)carbonyl)amino)ethyl Methacrylate (pCT)

The RAFT reagent 4-cyano-4-(propylthiocarbonothioylthio)pentanoic acid (CPPA) was synthesized as previously reported [62]. CT (234 mg, 0.4 mmol), CPPA (5.5 mg, 0.02 mmol), and the thermal initiator AIBN (0.2 M, 55 μL , 0.01 mmol) were mixed in a 10 mL flask to make the ratio of [CT]: [CPPA]: [AIBN] to 20: 1: 0.5. The mixture with N_2 protection was degassed via freeze-pump-thaw cycles at least 3 times, and then heated to $60\text{ }^{\circ}\text{C}$ and stirred for 10 h. The resulting polymer was purified with a short column to remove unpolymerized CT with (EA/DCM = 10%).

3.3. Irradiation Sources

Two LEDs with different emission wavelengths and light intensities were used as irradiation devices for photopolymerization reactions: LEDs with emission wavelengths centered at 400 nm (6.4 mW cm^{-2}) and 410 nm (110 mW cm^{-2}).

3.4. Characterizations

3.4.1. Fourier-Transform Infrared Spectroscopy

Infrared spectra of MT, PT, and CT were acquired using a Spectrum Two Fourier transform infrared (FTIR) spectrometer (Perkin Elmer, Waltham, MA, USA) fitted with attenuated total reflectance (ATR) accessory scans, with an average over the range of $500\text{--}4000\text{ cm}^{-1}$ at the resolution of 4 cm^{-1} .

3.4.2. Ultraviolet-Visible (UV-vis) Measurements

Ultraviolet-visible (UV-Vis) measurements were conducted on a Varian Cary 50 Bio UV-Vis spectrometer from Agilent Technologies, Selangor, Malaysia.

3.4.3. Gel Permeation Chromatography Analysis

Gel permeation chromatography (GPC) eluent profile of pCT was characterized using a 1260 Agilent Infinity GPC at 30 °C, with DMA as the eluent and polystyrene as the standard.

3.4.4. NMR Spectroscopy

All the characterization experiments utilized Ascend™ 400 MHz NMR from Bruker BioSpin AG, Fällanden, Switzerland. Chemical shifts were standardized using DMSO, $\delta = 2.50$ ppm.

3.5. Photopolymerization Experiments

Photopolymerization of TMPTA in the presence of the investigated triazine-derived photoinitiators under the irradiation of LED at 400 nm (6.4 mW cm^{-2}) and 410 nm (100 mW cm^{-2}) was investigated using a real-time Fourier transform infrared spectroscopy INVENIO® (RT-FTIR) manufactured by Bruker. The free radical photopolymerization of TMPTA was conducted in laminate. Specifically, formulations were added in between two polypropylene films with a volume of samples of approximately 15 μL . The film was then sandwiched between two BaF_2 windows and placed on a measuring holder. The evolution of the double bond of TMPTA was at the band of 1620 cm^{-1} . Conversions of functional groups of monomers (C) during the photopolymerization processes were calculated via the equation: $C = (A_0 - A_t)/A_0 \times 100\%$, where A_0 and A_t are the peak areas at the characterized band of TMPTA before irradiation and at time t irradiation, respectively.

3.6. Migration Test

The samples were prepared upon exposure to LED at 410 nm or LED at 400 nm in the presence of equal triazine moiety ($10 \mu\text{mol/g}$) with a thickness of 0.3 mm. The resultant samples were washed with ethanol to remove the unpolymerized monomer and immersed in DMF (4 mL) for 20 h. The leaching solution was measured using a UV–Vis spectrometer to determine the migration stability of the investigated photoinitiators. The calibration curves were plotted using their UV–Vis spectra with different equivalent concentrations of triazine moieties (Figures S1–S4).

4. Conclusions

In summary, we prepared three triazine derivatives to investigate their photoinitiation abilities and migration stabilities. The blue-shifted light absorptions were found for the polymerizable and the RAFT polymerized triazine derivatives (CT and pCT), which reduced the photoinitiation abilities of both CT and pCT for the photopolymerization of TMPTA under the irradiation of LED at 400 nm compared to MT, while PT showed comparable photoinitiation efficiency to MT. In contrast, PT and CT kept comparable photoinitiation efficiency for the photopolymerization of TMPTA under the irradiation of LED at 410 nm compared to MT. Nevertheless, the migration stability of the photoinitiators was significantly enhanced in the photocured polymers photoinitiated by CT and pCT compared to that photoinitiated by MT under both LED at 400 nm and LED at 410 nm. Therefore, the discovery of the exceeding migration stabilities of CT and pCT can expand their applications in various areas, especially in the food packing or biochemical fields.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12111305/s1>, Figure S1: (a) UV-vis spectra of different concentrations of CT and (b) calibration curve of CT (absorbance at 350 nm vs concentration) in DMF; Figure S2: (a) UV-vis spectra of pCT with different concentrations of triazine moiety and (b) calibration curve of triazine moiety (absorbance at 350 nm vs concentration of triazine moiety) in DMF; Figure S3: (a) UV-vis spectra of different concentrations of MT and (b) calibration curve of MT (absorbance at 380 nm vs concentration) in DMF; Figure S4: (a) UV-vis spectra of different concentrations of PT and (b) calibration curve of PT (absorbance at 385 nm vs concentration) in DMF. Table S1: Migration concentrations of photoinitiators from the photocured samples in DMF.

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References

- Xiao, P.; Zhang, J.; Dumur, F.; Tehfe, M.A.; Morlet-Savary, F.; Graff, B.; Gigmès, D.; Fouassier, J.P.; Lalevée, J. Visible light sensitive photoinitiating systems: Recent progress in cationic and radical photopolymerization reactions under soft conditions. *Prog. Polym. Sci.* **2015**, *41*, 32–66. [\[CrossRef\]](#)
- Cataldi, A.; Corcione, C.E.; Frigione, M.; Pegoretti, A. Photocurable resin/nanocellulose composite coatings for wood protection. *Prog. Org. Coat.* **2017**, *106*, 128–136. [\[CrossRef\]](#)
- Yagci, Y.; Jockusch, S.; Turro, N.J. Photoinitiated Polymerization: Advances, Challenges, and Opportunities. *Macromolecules* **2010**, *43*, 6245–6260. [\[CrossRef\]](#)
- Leibfarth, F.; Mattson, K.; Fors, B.P.; Collins, H.A.; Hawker, C.J. External Regulation of Controlled Polymerizations. *Angew. Chem. Int. Ed.* **2013**, *52*, 199–210. [\[CrossRef\]](#)
- Liu, C.; Li, T.; Zhang, J.; Chen, S.; Xu, Z.; Zhang, A.; Zhang, D. Preparation and properties of phosphorous–nitrogen containing UV-curable polymeric coatings based on thiol–ene click reaction. *Prog. Org. Coat.* **2016**, *90*, 21–27. [\[CrossRef\]](#)
- Chiulan, I.; Heggset, E.B.; Voicu, Ş.I.; Chinga-Carrasco, G. Photopolymerization of Bio-Based Polymers in a Biomedical Engineering Perspective. *Biomacromolecules* **2021**, *22*, 1795–1814. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, Z.; Guo, Y.; Cai, S.; Yang, J. Three-Dimensional Printing of Liquid Crystal Elastomers and Their Applications. *ACS Appl. Polym. Mater.* **2022**, *4*, 3153–3168. [\[CrossRef\]](#)
- Ligon, S.C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117*, 10212–10290. [\[CrossRef\]](#)
- 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. [\[CrossRef\]](#)
- Anastasakis, A.; Nikolaou, V.; Zhang, Q.; Burns, J.; Samanta, S.R.; Waldron, C.; Haddleton, A.J.; McHale, R.; Fox, D.; Percec, V.; et al. Copper(II)/Tertiary Amine Synergy in Photoinduced Living Radical Polymerization: Accelerated Synthesis of ω -Functional and α,ω -Heterofunctional Poly(acrylates). *J. Am. Chem. Soc.* **2014**, *136*, 1141–1149. [\[CrossRef\]](#)
- Lee, E.K.; Park, C.H.; Lee, J.; Lee, H.R.; Yang, C.; Oh, J.H. Chemically robust ambipolar organic transistor array directly patterned by photolithography. *Adv. Mater.* **2017**, *29*, 1605282. [\[CrossRef\]](#) [\[PubMed\]](#)
- Kütahya, C.; Wang, P.; Li, S.; Liu, S.; Li, J.; Chen, Z.; Strehmel, B. Carbon Dots as a Promising Green Photocatalyst for Free Radical and ATRP-Based Radical Photopolymerization with Blue LEDs. *Angew. Chem. Int. Ed.* **2020**, *59*, 3166–3171. [\[CrossRef\]](#)
- Shanmugam, S.; Boyer, C. Organic photocatalysts for cleaner polymer synthesis. *Science* **2016**, *352*, 1053–1054. [\[CrossRef\]](#) [\[PubMed\]](#)
- Theriot, J.C.; Lim, C.-H.; Yang, H.; Ryan, M.D.; Musgrave, C.B.; Miyake, G.M. Organocatalyzed atom transfer radical polymerization driven by visible light. *Science* **2016**, *352*, 1082–1086. [\[CrossRef\]](#)
- Liao, W.; Liao, Q.; Xu, C.; Wu, X.; Xiong, Y.; Li, Z.; Tang, H. Structural Effects of Cinnamoyl-Indanone-Based Photobleachable Free Radical Visible Initiators. *ACS Appl. Polym. Mater.* **2022**, *4*, 6466–6476. [\[CrossRef\]](#)
- Chi, T.; Somers, P.; Wilcox, D.A.; Schuman, A.J.; Johnson, J.E.; Liang, Z.; Pan, L.; Xu, X.; Boudouris, B.W. Substituted Thioxanthone-Based Photoinitiators for Efficient Two-Photon Direct Laser Writing Polymerization with Two-Color Resolution. *ACS Appl. Polym. Mater.* **2021**, *3*, 1426–1435. [\[CrossRef\]](#)
- Huang, X.; Zhang, Y.; Shi, M.; Zhang, Y.; Zhao, Y. Study on a polymerizable visible light initiator for fabrication of biosafety materials. *Polym. Chem.* **2019**, *10*, 2273–2281. [\[CrossRef\]](#)
- Wu, Q.; Wang, X.; Xiong, Y.; Yang, J.; Tang, H. Thioxanthone based one-component polymerizable visible light photoinitiator for free radical polymerization. *RSC Adv.* **2016**, *6*, 66098–66107. [\[CrossRef\]](#)
- Liska, R. Industrial Photoinitiators: A Technical Guide by W. Arthur Green. *ChemPhysChem* **2011**, *12*, 1389. [\[CrossRef\]](#)
- Ay, E.; Raad, Z.; Dautel, O.; Dumur, F.; Wantz, G.; Gigmès, D.; Fouassier, J.-P.; Lalevée, J. Oligomeric Photocatalysts in Photoredox Catalysis: Toward High Performance and Low Migration Polymerization Photoinitiating Systems. *Macromolecules* **2016**, *49*, 2124–2134. [\[CrossRef\]](#)
- Johns, S.; Jickells, S.; Read, W.; Castle, L. Studies on functional barriers to migration. Components from cartonboard to food during frozen storage and microwave heating. *Packag. Technol. Sci.* **2000**, *13*, 99–104. [\[CrossRef\]](#)
- Papilloud, S.; Baudraz, D. Analysis of food packaging UV inks for chemicals with potential to migrate into food simulants. *Food Addit. Contam.* **2002**, *19*, 168–175. [\[CrossRef\]](#) [\[PubMed\]](#)

23. Sanches-Silva, A.; Pastorelli, S.; Cruz, J.; Simoneau, C.; Castanheira, I.; Paseiro-Losada, P. Development of an Analytical Method for the Determination of Photoinitiators Used for Food Packaging Materials with Potential to Migrate into Milk. *J. Dairy Sci.* **2008**, *91*, 900–909. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Pastorelli, S.; Sanches-Silva, A.; Cruz, J.M.; Simoneau, C.; Losada, P.P. Study of the migration of benzophenone from printed paperboard packages to cakes through different plastic films. *Eur. Food Res. Technol.* **2008**, *227*, 1585–1590. [\[CrossRef\]](#)
25. Rodriguez-Bernaldo De Quirós, A.R.-B.; Paseiro-Cerrato, R.; Pastorelli, S.; Koivikko, R.; Simoneau, C.; Paseiro-Losada, P. Migration of Photoinitiators by Gas Phase into Dry Foods. *J. Agric. Food Chem.* **2009**, *57*, 10211–10215. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Sanches-Silva, A.; Andre, C.; Castanheira, I.; Cruz, J.M.; Pastorelli, S.; Simoneau, C.; Paseiro-Losada, P. Study of the Migration of Photoinitiators Used in Printed Food-Packaging Materials into Food Simulants. *J. Agric. Food Chem.* **2009**, *57*, 9516–9523. [\[CrossRef\]](#)
27. Shen, D.-X.; Lian, H.-Z.; Ding, T.; Xu, J.-Z.; Shen, C.-Y. Determination of low-level ink photoinitiator residues in packaged milk by solid-phase extraction and LC-ESI/MS/MS using triple-quadrupole mass analyzer. *Anal. Bioanal. Chem.* **2009**, *395*, 2359–2370. [\[CrossRef\]](#)
28. Qi, Y.; Zhang, X.; Huang, X.; Zhang, Y.; Shi, M.; Zhao, Y. High-efficient lignin-based polymerizable macromolecular photoinitiator with UV-blocking property for visible light polymerization. *Int. J. Biol. Macromol.* **2022**, *204*, 234–244. [\[CrossRef\]](#)
29. Xiao, P.; Dumur, F.; Frigoli, M.; Tehfe, M.-A.; Graff, B.; Fouassier, J.P.; Gigmes, D.; Lalevée, J. Naphthalimide based methacrylated photoinitiators in radical and cationic photopolymerization under visible light. *Polym. Chem.* **2013**, *4*, 5440–5448. [\[CrossRef\]](#)
30. Wei, J.; Wang, B. A Highly Efficient Polymerizable Photoinitiator Comprising Benzophenone, Thio Moieties, and N-Arylmaide. *Macromol. Chem. Phys.* **2011**, *212*, 88–95. [\[CrossRef\]](#)
31. Liang, S.; Yang, Y.; Zhou, H.; Li, Y.; Wang, J. Novel polymerizable HMPP-type photoinitiator with carbamate: Synthesis and photoinitiating behaviors. *Prog. Org. Coat.* **2017**, *110*, 128–133. [\[CrossRef\]](#)
32. Wang, J.; Yang, J.; Atif, M.; Bongiovanni, R.; Li, G.; Xue, Z.; Yang, X. One-component photoinitiator based on benzophenone and sesamol. *Polym. Adv. Technol.* **2018**, *29*, 2264–2272. [\[CrossRef\]](#)
33. Kreutzer, J.; Yagci, Y. One-component, double-chromophoric thioxanthone photoinitiators for free radical polymerization. *J. Polym. Sci. Part A Polym. Chem.* **2017**, *55*, 3475–3482. [\[CrossRef\]](#)
34. Hutchison, J.B.; Stark, P.F.; Hawker, C.J.; Anseth, K.S. Polymerizable Living Free Radical Initiators as a Platform To Synthesize Functional Networks. *Chem. Mater.* **2005**, *17*, 4789–4797. [\[CrossRef\]](#)
35. Wang, J.; Stanic, S.; Altun, A.A.; Schwentenwein, M.; Dietliker, K.; Jin, L.; Stampfl, J.; Baudis, S.; Liska, R.; Grützmacher, H. A highly efficient waterborne photoinitiator for visible-light-induced three-dimensional printing of hydrogels. *Chem. Commun.* **2018**, *54*, 920–923. [\[CrossRef\]](#)
36. Sandmeier, M.; Paunović, N.; Conti, R.; Hofmann, L.; Wang, J.; Luo, Z.; Masania, K.; Wu, N.; Kleger, N.; Coulter, F.B.; et al. Solvent-Free Three-Dimensional Printing of Biodegradable Elastomers Using Liquid Macrophotoinitiators. *Macromolecules* **2021**, *54*, 7830–7839. [\[CrossRef\]](#)
37. Deng, L.; Tang, L.; Qu, J. Synthesis and photopolymerization of novel UV-curable macro-photoinitiators. *Prog. Org. Coat.* **2020**, *141*, 105546. [\[CrossRef\]](#)
38. Yang, J.; Liao, W.; Xiong, Y.; Wang, X.; Li, Z.; Tang, H. A multifunctionalized macromolecular silicone-naphthalimide visible photoinitiator for free radical polymerization. *Prog. Org. Coat.* **2018**, *115*, 151–158. [\[CrossRef\]](#)
39. Gacal, B.; Akat, H.; Balta, D.K.; Arsu, N.; Yagci, Y. Synthesis and Characterization of Polymeric Thioxanthone Photoinitiators via Double Click Reactions. *Macromolecules* **2008**, *41*, 2401–2405. [\[CrossRef\]](#)
40. Wang, C.; Venditti, R.A. UV Cross-Linkable Lignin Thermoplastic Graft Copolymers. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1839–1845. [\[CrossRef\]](#)
41. Zhou, J.; Allonas, X.; Ibrahim, A.; Liu, X. Progress in the development of polymeric and multifunctional photoinitiators. *Prog. Polym. Sci.* **2019**, *99*, 101165. [\[CrossRef\]](#)
42. Peng, X.; Zhang, J.; Stachurski, Z.H.; Holl, M.M.B.; Xiao, P. Visible-Light-Sensitive Triazine-Coated Silica Nanoparticles: A Dual Role Approach to Polymer Nanocomposite Materials with Enhanced Properties. *ACS Appl. Mater. Interfaces* **2021**, *13*, 46033–46042. [\[CrossRef\]](#)
43. Fan, Y.; Song, Y.; He, N.; Cheng, F.; Jiao, X.; Lai, G.; Hua, X.; Yang, X. High Efficiency and Low Migration Hyperbranched Silicone Contain Macrophotoinitiators for UV-Cured Transparent Coatings. *Polymers* **2020**, *12*, 3005. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Nugent, L.J.; Jain, R.K. Extravascular diffusion in normal and neoplastic tissues. *Cancer Res.* **1984**, *44*, 238–244. [\[PubMed\]](#)
45. Radomsky, M.L.; Whaley, K.J.; A Cone, R.; Saltzman, W.M. Macromolecules released from polymers: Diffusion into unstirred fluids. *Biomaterials* **1990**, *11*, 619–624. [\[CrossRef\]](#)
46. Zhang, J.; Xiao, P.; Morlet-Savary, F.; Graff, B.; Fouassier, J.P.; Lalevée, J. A known photoinitiator for a novel technology: 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine for near UV or visible LED. *Polym. Chem.* **2014**, *5*, 6019–6026. [\[CrossRef\]](#)
47. Fouassier, J.-P.; Lalevée, J. *Photoinitiators for Polymer Synthesis: Scope, Reactivity, and Efficiency*, 1st ed; Wiley-VCH: Weinheim, Germany, 2012. [\[CrossRef\]](#)
48. Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Carl Hanser Verlag GmbH & Co.: Munich, Germany, 1995.
49. Crivello, J. *Photoinitiators for Free Radical Cationic and Anionic Photopolymerization*; John Wiley & Sons: Chichester, UK, 1998.
50. Dietliker, K. *A Compilation of Photoinitiators Commercially Available for UV Today*; SITA: London, UK, 2002.

51. Ullrich, G.; Ganster, B.; Salz, U.; Moszner, N.; Liska, R. Photoinitiators with functional groups. IX. Hydrophilic bisacylphosphine oxides for acidic aqueous formulations. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 1686–1700. [[CrossRef](#)]
52. Zhang, J.; Xiao, P. 3D printing of photopolymers. *Polym. Chem.* **2018**, *9*, 1530–1540. [[CrossRef](#)]
53. Benedikt, S.; Wang, J.; Markovic, M.; Moszner, N.; Dietliker, K.; Ovsianikov, A.; Grützmacher, H.; Liska, R. Highly efficient water-soluble visible light photoinitiators. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54*, 473–479. [[CrossRef](#)]
54. Lai, H.; Zhu, D.; Xiao, P. Yellow triazine as an efficient photoinitiator for polymerization and 3D printing under LEDs. *Macromol. Chem. Phys.* **2019**, *220*, 1900315. [[CrossRef](#)]
55. Fairbanks, B.D.; Schwartz, M.P.; Bowman, C.N.; Anseth, K.S. Photoinitiated polymerization of PEG-diacrylate with lithium phenyl-2,4,6-trimethylbenzoylphosphinate: Polymerization rate and cytocompatibility. *Biomaterials* **2009**, *30*, 6702–6707. [[CrossRef](#)] [[PubMed](#)]
56. Bryant, S.J.; Nuttelman, C.R.; Anseth, K.S. Cytocompatibility of UV and visible light photoinitiating systems on cultured NIH/3T3 fibroblasts in vitro. *J. Biomater. Sci. Polym. Ed.* **2000**, *11*, 439–457. [[CrossRef](#)] [[PubMed](#)]
57. Yan, J.; Lai, H.; Zeng, B.; Wang, L.; Xing, F.; Xiao, P. Photoinduced free radical-releasing systems and their anticancer properties. *Photochem. Photobiol. Sci.* **2022**, *21*, 1405–1417. [[CrossRef](#)]
58. Coates, J. *Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry*; John Wiley & Sons Ltd.: Chichester, UK, 2000.
59. Antosiewicz, J.M.; Shugar, D. UV-Vis spectroscopy of tyrosine side-groups in studies of protein structure. Part 1: Basic principles and properties of tyrosine chromophore. *Biophys. Rev.* **2016**, *8*, 151–161. [[CrossRef](#)] [[PubMed](#)]
60. Brown, R.D. Effects of Substituents on Ultra-violet Absorption Spectra. *Nature* **1952**, *169*, 286–287. [[CrossRef](#)]
61. Li, S.; Wu, F.; Li, M.; Wang, E. Host/guest complex of Me- β -CD/2,2-dimethoxy-2-phenyl acetophenone for initiation of aqueous photopolymerization: Kinetics and mechanism. *Polymer* **2005**, *46*, 11934–11939. [[CrossRef](#)]
62. Lai, H.; Zhu, D.; Peng, X.; Zhang, J.; Lalevée, J.; Xiao, P. N-Aryl glycines as versatile initiators for various polymerizations. *Polym. Chem.* **2021**, *12*, 1991–2000. [[CrossRef](#)]