

## Yellow Triazine as An Efficient Photoinitiator for Polymerization and 3D Printing Under LEDs

H. Lai, D. Zhu, and P. Xiao\*

Dr. H. Lai, D. Zhu, Dr. P. Xiao

Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

E-mail: pu.xiao@anu.edu.au

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The search of new efficient photoinitiators for polymerization under the illumination of visible light is under extensive investigation due to their wide application in 3D printing. 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (yellow triazine, R-Cl) alone or the R-Cl/additive systems have been indicated as promising photoinitiating systems in the free radical polymerization at 405 nm in our previous study. Here further investigation of R-Cl in the polymerization of a series of difunctional (meth)acrylate monomers is described. The effect of monomers on the polymerization performance is elucidated. The interplay of functional group, double bond concentration and fluidity determine the polymerization rate and final conversions. Remarkably, R-Cl shows better photoinitiating ability than well-known commercial photoinitiator BAPO in the polymerization of Bis-GMA/TEGDMA blend and EB605 under LED at 400 nm. The optimum concentrations of R-Cl in the photopolymerization of TetEGMA and DPGDA monomers are revealed, the results of which are used to guide the 3D printing of DPGDA.

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## 1. Introduction

Three-dimensional (3D) printing based on photopolymerization technology has received tremendous attention in advanced manufacturing owing to the high resolution and the potential to fabricate complex geometry.<sup>[1]</sup> In printing processes, monomers undergo polymerization reactions in the presence of suitable photoinitiators (PIs) and light irradiation with certain wavelength.<sup>[1c, 2]</sup> PIs are the components in 3D printing resins generating initiating species upon light exposure which affect mainly the cure speed and cost.<sup>[3]</sup> Several PIs have been developed and reported for 3D printing.<sup>[1c, d], [4]</sup> Among them, bisacylphosphine oxide (BAPO) and 2,4,6-trimethylbenzoyl-diphenylphosphineoxide (TPO) represent excellent Type I PIs which have been widely used in industry.<sup>[5]</sup> However, they are mainly used under UV light irradiation. The search for new Type I PIs under visible light for 3D printing is under extensive investigation due to the deeper penetration, higher safety and more efficient energy utilization of visible light.<sup>[2a-d], [4, 6]</sup> These emerging Type I PIs include germanium compounds,<sup>[6c, 7]</sup> lithium acylphosphinate salt,<sup>[8]</sup> and 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (yellow triazine, R-Cl, Figure S1).<sup>[9]</sup>

R-Cl exhibits a maximum ground state light absorption at 373 nm in acetonitrile.<sup>[9]</sup> The absorption spectrum goes up to 450 nm which renders this substance a yellow appearance.<sup>[9]</sup> The rapid homolytic ability of C-Cl bond under violet light irradiation makes R-Cl a potent PI for free radical polymerization. The superior performance of R-Cl compared to BAPO and TPO in photopolymerization at 405 nm has been demonstrated in our previous work.<sup>[9], [10]</sup> The efficient photoinitiation ability under visible LED encourage us to further explore its potential application as a Type I PI in 3D printing. However, some issues remain to be clarified before the real employment, including the applicability of R-Cl in different monomers and the dosage of R-Cl for efficient photopolymerization and 3D printing. The disclosure of the monomer scope that R-Cl can be applied to relies on the interpretation of the photopolymerization efficiency-monomer structure relationships. The optimum concentration to achieve efficient photocuring still needs to be assessed, as a higher polymerization efficiency is not simply in line with a higher PI concentration.<sup>[11], [12]</sup> An insufficient dosage of PI would diminish the polymerization rate and conversion. However, the existence of excessive PI would increase cost and generate excessive radicals to terminate the propagation.<sup>[13]</sup>

Therefore, the aim of this study is to further assess the photoinitiating efficiency of R-Cl in different monomer systems with different concentrations and in 3D printer with LED at 405 nm as irradiation source. To this end, the performance of R-Cl in various monomers was estimated under standard polymerization conditions by evaluating the polymerization rate and final conversion of monomers. The influences of monomer properties on the performance of R-Cl was thus elucidated. The efficiency for R-Cl in free radical photopolymerization was compared with commercial Type I PI BAPO. Moreover, the versatility of R-Cl in cationic polymerization was also estimated. In addition, the optimum concentrations in the photocuring formulations were determined by varying the concentration in the formula. The results obtained were further used to guide the formula preparation in 3D printing under low intensity LED.

## 2. Results and discussion

### 2.1. Effect of monomers on the photopolymerization performance

The FRPs of various monomers in laminate in the presence of R-CI were conducted under three different LED irradiations (400 nm, 410 nm and 445 nm). The conversion-time profiles under 400 nm LED irradiation are depicted in **Figure 1** and Figure S3. The physical parameters of the investigated monomers including viscosity and double bond concentrations are listed in Table 1 (other parameters including molecular weight can be seen in Table S1), wherein final conversion (C) and the maximum polymerization rate of each polymerization are also summarized. As shown in Table 1, the photocuring of HDDA resulted in lowest C among all the investigated acrylate monomers with ether groups. This is probably caused by the existence of higher oxygen concentration in HDDA initially dissolved during the sample preparation. As the photocuring of all sample were carried out in laminate, the dissolved oxygen in air-saturated samples influenced the chain propagation. Previous studies on the measurement of the dissolved oxygen concentration in acrylate monomers indicated that the presence of the ether linkage decreased the oxygen solubility.<sup>[15]</sup> Thus, a higher oxygen concentration would exist in HDDA formulation than ether containing monomers. The ether groups were also found to be advantageous in reducing oxygen inhibition due to the presence of abstractable hydrogen,<sup>[16]</sup> which is also true for hydroxyl groups which is present in Bis-GMA monomer.<sup>[17]</sup> The abstractable hydrogens can reinitiate the polymerization by reacting with peroxy radicals *via* a mechanism similar to Type II initiators. Therefore, the absence of ether group in HDDA ruled out the reinitiation once radicals were terminated. Higher concentration of dissolved oxygen and lack of reinitiation resulted in lowest C of HDDA. The reduction of oxygen inhibition effect is substantiated by higher C of TPGDA than DPGDA due to the higher viscosity and higher ether content in TPGDA (Table 1). The polymerization of ethylene ether monomer series (*i.e.* DEGDA, TetEGDA, PEGDA575 and PEGDA700) also supported that monomers with higher viscosity and higher

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ether content resulted in higher Cs (Table 1). All the photopolymerizations of the investigated monomers resulted in higher Cs at LED@410 nm than those at LED@400 nm (see Table 1) due to the much higher light intensity ( $110 \text{ mW cm}^{-2}$ ) of LED@410 nm than that of LED@400 nm ( $6.5 \text{ mW cm}^{-2}$ ). The polymerization at LED@445 nm showed lower polymerization efficiency (Table 1) than those at LED@400 nm, which can be ascribed to the much lower absorption of R-Cl at 445 nm despite of the stronger light intensity ( $80 \text{ mW cm}^{-2}$ ) than LED@400 nm. The Cs of monomers polymerized at LED@410 nm and LED@445 nm follow the similar trend to those at LED@400 nm. The Cs for the polymerizations of acrylates under LED@410 nm and LED@445 nm fell into the rule that monomers with higher ether content and higher viscosity resulted in higher Cs. The polymerization of methacrylates (TEGDMA, TEGDMA/Bis-GMA blend and EB605) resulted in much lower C than acrylates (Table 1). This can be ascribed to the lower reactivity of methacrylates than that of acrylates and the stiffer chain or network formed by methacrylates, which leads to the termination of propagating chain with lower conversion.<sup>[18], [19]</sup> The conversion (66%) in photopolymerization of TEGDMA/Bis-GMA blend under 410 nm was comparable with that previously achieved under LED@405 nm (64%,  $\sim 110 \text{ mW cm}^{-2}$ ), which demonstrates that the photopolymerization with R-Cl is quite reproducible.<sup>[9]</sup>

The polymerization rates of different monomers were affected by the interplay of viscosities, double bond concentration and oxygen inhibition. The enlargement of monomer molecules increases the viscosity and dilutes the double bond in the formulation (Table 1). Increased monomer viscosity can reduce oxygen diffusion into samples at the initial stages, thus facilitating polymerization. On the contrary, it can also hamper the freedom of double bonds and propagating radicals, hence slows polymerization. Therefore, the polymerization of TPGDA is slower than DPGDA (with polymerization rates of  $9.32$  and  $13.21 \text{ s}^{-1}$ , respectively, Table 1 & Figure S3 (a)). The polymerization rates of DEGDA, TetEGDA, PEGDA575 and PEGDA700 showed a first increasing then decreasing tendency with the elongation of spacer. Polymerization rate was facilitated by reduction of oxygen inhibition moving from DEGDA to PEGDA700 due to impeded fluidity and increased concentration of ether group,

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while dilution of double bond and impeded fluidity slower the chain propagation and deteriorate the polymerization rate. The interplay of these factors leads to the peaking of polymerization rate at TetEGDA with rate of  $14.84 \text{ s}^{-1}$  (Table 1). All methacrylate systems studied showed maximum polymerization rate no greater than  $7 \text{ s}^{-1}$ , lower than those of the investigated acrylates due to the lower reactivity of methacrylates and considerably higher viscosity (Figure 1 & Table 1).

## 2.2. Comparison of photoinitiating efficiency with commercial photoinitiator BAPO

The photoinitiating efficiency of R-Cl was also compared with that of a reference commercial Type I PI BAPO. As presented in Figure S4, R-Cl performed better in the polymerization of Bis-GMA/TEGDA blend (dental resin) and EB605 under LED@400 nm, giving higher polymerization rates and Cs. The polymerization of dental resin and EB605 by R-Cl resulted in Cs of 53% and 58%, respectively, whereas 47% and 50% conversions for dental resin and EB650 were attained using BAPO as the PI.

## 2.3. Cationic photopolymerization

In addition, the efficiency of R-Cl to initiate the cationic photopolymerization of tri(ethylene glycol) divinyl ether (DVE-3, Figure S5) was also evaluated. Specifically, R-Cl/diphenyliodonium hexafluorophosphate (Iod) system can initiate the polymerization of DVE-3 under LED@400 nm but with lower final conversion (Figure S5). However, upon the addition of N-vinyl carbazole (NVK), the R-Cl/Iod/NVK PI system could form high reactive NVK based cations to trigger the polymerization of DVE-3 under LED@400 nm.<sup>[9]</sup> An exposure time of 5 mins resulted in a C of 82% and a fully cured film. These results indicate that R-Cl was a versatile PI for both FRP and cationic polymerization.

## 2.4. Effect of concentrations of yellow triazine on the photopolymerization performance

A sufficient presence of PI is required to overcome oxygen inhibition and maintain a fast photocuring.<sup>[20]</sup> However, an overloading of PIs would leave unreacted PI remained in the cured sample, which increases the cost and sometimes the potential migration issue. The excessive PIs at the surface will also hinder the transmission of light into deeper layer and reduce the polymerization therein.<sup>[13]</sup> Therefore, significant termination would occur when PIs are overdosed due to the biradical coupling, resulting in limited increase in Cs.<sup>[21]</sup> The polymerization profiles of TetEGDA containing between 0.01 and 0.5 wt% R-Cl under LED@400 nm is recorded in Figure 2 & S6. Table S2 gives the polymerization rates and Cs. It is apparent that the polymerization rates and Cs decreased with reduced PI concentrations. However, the maximum rates and final conversions were not drastically impaired when the PI concentration reduced from 0.5 wt% to 0.1 wt% (Figure 2 & Table S2). A concentration of 0.1 wt% is enough to get a satisfactory Cs as 0.5 wt%. A significant depletion of polymerization performance was observed when the dosage was reduced to 0.01 wt%, which was too low to fully cure the sample, leading to a 43% Cs and a tacky sample. These results demonstrated that R-Cl is an efficient initiator in the radical polymerization of TetEGDA even at a low dosage of 0.1wt%. Usually, ~1-5 wt% of Type I PI was loaded in 3D printing in previous reports.<sup>[22]</sup> Our results suggest that a much less PI can be added for efficient photopolymerization, which can save the cost for 3D printing and avoid the aforementioned issues. The minimum concentration for maintaining a good photocuring is dependent on type of PI and monomer reactivity. As shown in Figure 2(b), the reduction of R-Cl concentration has a more pronounced effect on the polymerization of DPGDA. The final conversions dropped from 81% to 56% in polymerization of DPGDA compared with TetEGDA (88% to 77%) when R-Cl concentration reduced from 0.5 wt% to 0.1 wt% (Table S2). It is therefore necessary to systematically investigate the optimum PI concentration for a given system prior to the real application of developed resins.

## 2.5. Application of yellow triazine as photoinitiator in 3D printing

The efficiency of R-Cl as PI in real application was demonstrated by the photopolymerization of DPGDA in 3D printing. The UV-Vis spectrum of R-Cl exhibits an apparent overlap with the emission wavelength of the light source of the 3D printer, *i.e.* LED@405 nm (Figure S7). The concentration study above has indicated that a low dosage of R-Cl (0.1 wt%) in the formulation is enough for a complete photocuring of TetEGDA and TPGDA. As shown in Figure 3, the sharp edge can be seen in the Mayan pyramid printed with 0.1 wt% of R-Cl as PI [Figure 3 (a)], however, the object was obtained with an irregular and coarse edge with 0.05 wt% of R-Cl [Figure 3 (b)]. In addition, a sphinx can also be properly 3D printed with 0.1 wt% of R-Cl [Figure 3 (c)]. Moreover, the 3D printed Mayan Pyramid exhibited obvious edge defects initiated with 0.1% BAPO (Figure S8). The better performance of R-Cl in 3D printing is in agreement with the superior photoinitiating efficiency of R-Cl under LED@400 nm.

## 3. Conclusion

In summary, R-Cl was investigated as PI for the photopolymerization of a range of different monomers. It was found that in the polymerization of ether groups containing acrylate monomers, monomers with higher viscosity and higher ether content resulted in higher Cs. The polymerization rate was determined by the interplay of double bond concentration, viscosity of monomers and functional group. Moreover, R-Cl behaved more efficiently in the photopolymerization of Bis-GMA/TEGDMA blend and EB605 than BAPO under LED@400 nm. In addition, R-Cl based PI system can be used for cationic polymerization. The potent initiating efficiency of R-Cl allows it to work

under a low concentration. With the guidance from the concentration study, a low dosage of R-Cl (0.1 wt%) was used in the 3D printing of DPGDA. Our results indicate that R-Cl can be used as efficient PI for 3D printing under LED@405 nm.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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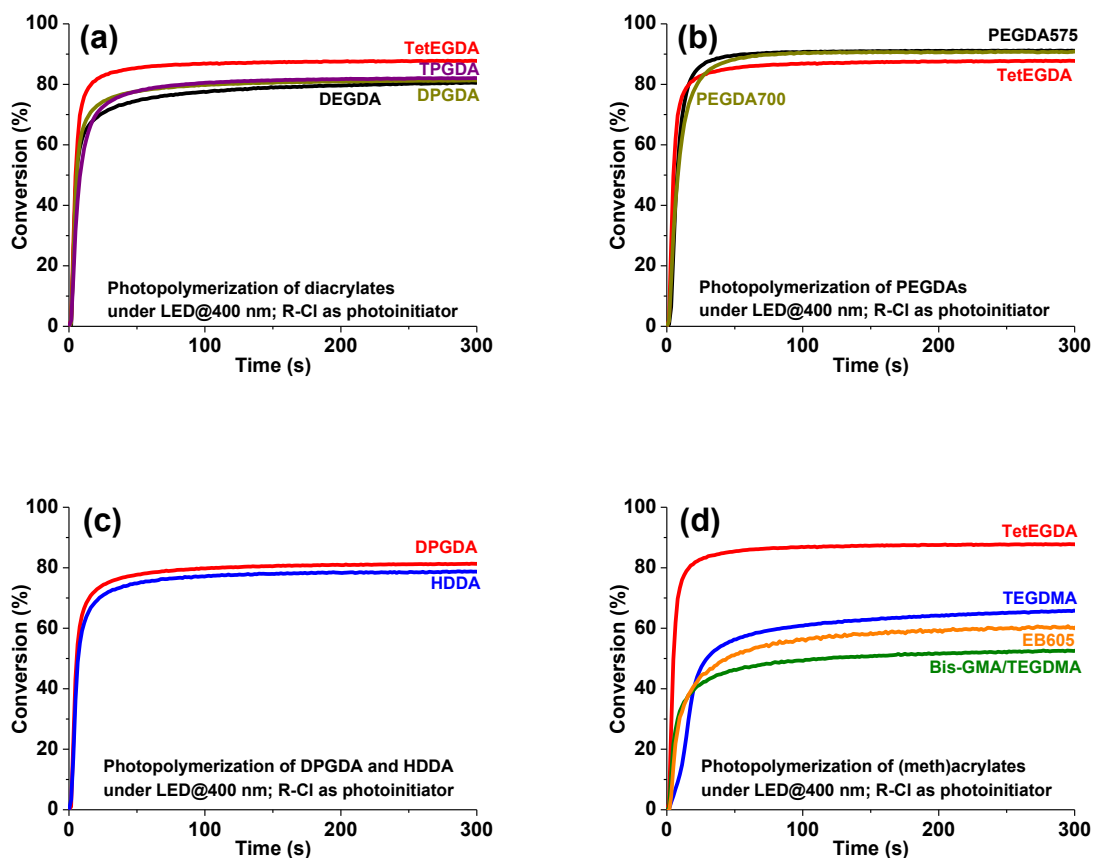


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**Figure 1.** Photopolymerization profiles (double bond conversions vs time) of (a) TetEGDA, TPGDA, DPGDA and DEGDA; (b) TetEGDA, PEGDA575 and PEGDA700; (c) DPGDA and HDDA; (d) TetEGDA, TEGDMA, EB605, Bis-GMA/TEGDMA blend in laminate in the presence of R-CI (0.5 wt%) as the photoinitiator upon exposure to LED@400 nm for 300 s.

**Table 1.** Properties, polymerization rates and double bond conversions of photopolymerization of different di(meth)acrylates obtained in laminate in the presence of R-Cl (0.5 wt%) as the photoinitiator upon exposure to various LEDs for 300 s.

Monomer	$\eta^a)$ (mPa·s)	[C=C] <sup>b)</sup> (mol L <sup>-1</sup> )	$(R_{p@400\text{ nm}}/[C=C]) \times 100^c)$ (s <sup>-1</sup> )	Double bond conversions		
				LED@400 nm	LED@410 nm	LED@445 nm
HDDA	9	8.93	10.22	79%	82%	76%
DPGDA	5-15	8.75	13.21	81%	84%	79%
TPGDA	10-15	6.86	9.32	82%	84%	82%
DEGDA	12	10.46	13.82	80%	83%	78%
TetEGDA	20	7.34	14.84	88%	89%	83%
PEGDA575	57	3.90	10.78	91%	91%	88%
PEGDA700	-	3.20	8.78	91%	89%	88%
TEGDMA	11	7.61	3.28	60%	60%	61%
Bis- GMA/TEGDMA	2000	-	6.63	53%	61%	48%
EB605	6000- 9000	-	5.49	60%	66%	53%

<sup>a)</sup> viscosities of monomers;

<sup>b)</sup> double bond concentrations of monomers;

<sup>c)</sup> maximum rates of photopolymerization under LED@400 nm.

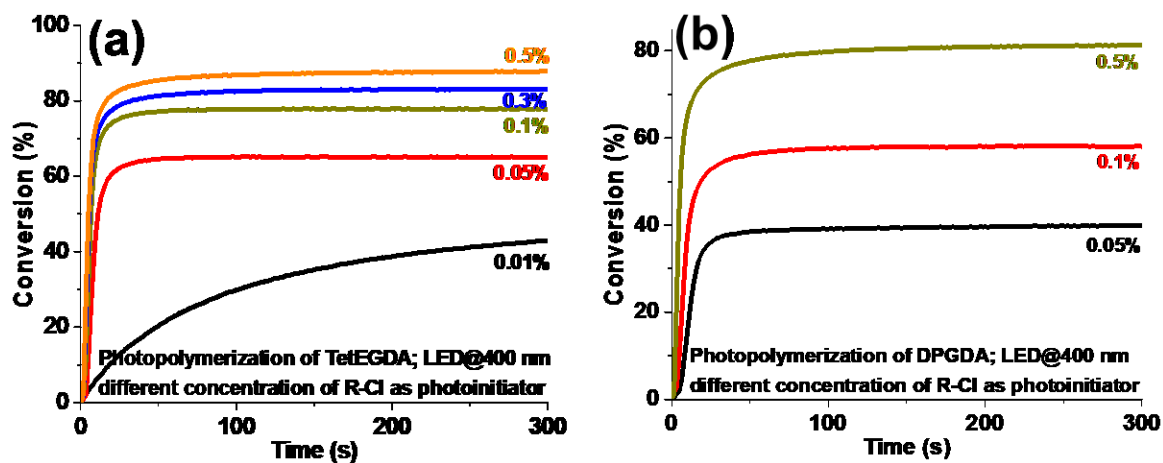
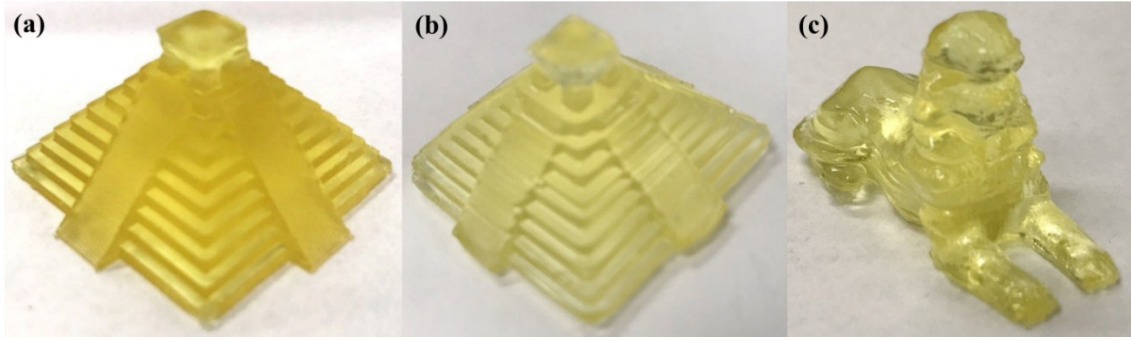


Figure 2. Photopolymerization profiles (double bond conversions vs time) of (a) TetEGDA and (b) DPGDA in laminate in the presence of different concentrations of R-Cl (0.01% ~ 0.5%, wt) as the photoinitiator upon exposure to LED@400 nm for 300 s.



**Figure 3.** 3D printed objects of (a) Mayan Pyramid ( $32 \times 32 \times 18$  mm) printed by DPGDA with 0.1 wt% R-Cl; (b) Mayan Pyramid ( $32 \times 32 \times 18$  mm) printed by DPGDA with 0.05 wt% R-Cl; (c) Sphinx ( $30 \times 9 \times 18$  mm) printed by DPGDA with 0.1 wt% R-Cl.

The effects of monomer property and concentration of photoinitiator on the photopolymerization performance initiated by 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (yellow triazine) under LED irradiations were investigated. The potent initiating efficiency of R-Cl allows a low dosage of R-Cl (0.1 wt%) to be used for efficient 3D printing of DPGDA under 405 nm irradiation.

## Photoinitiator

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