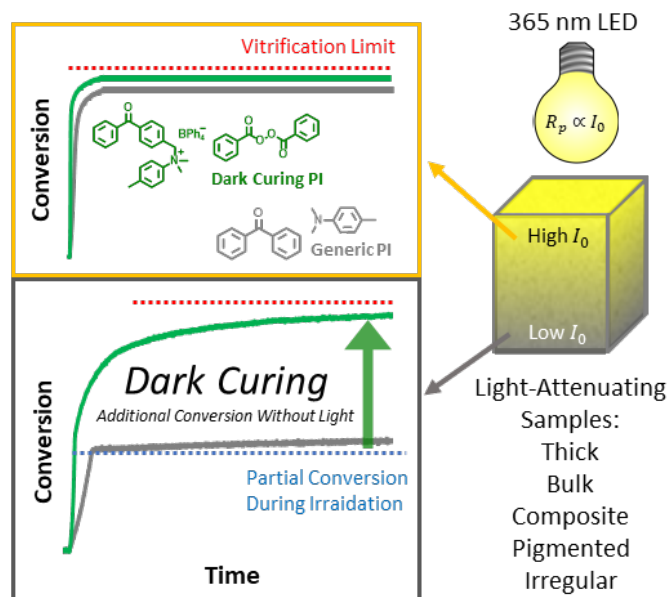


# Solvent-Free Radical Photopolymerization with Dark Curing

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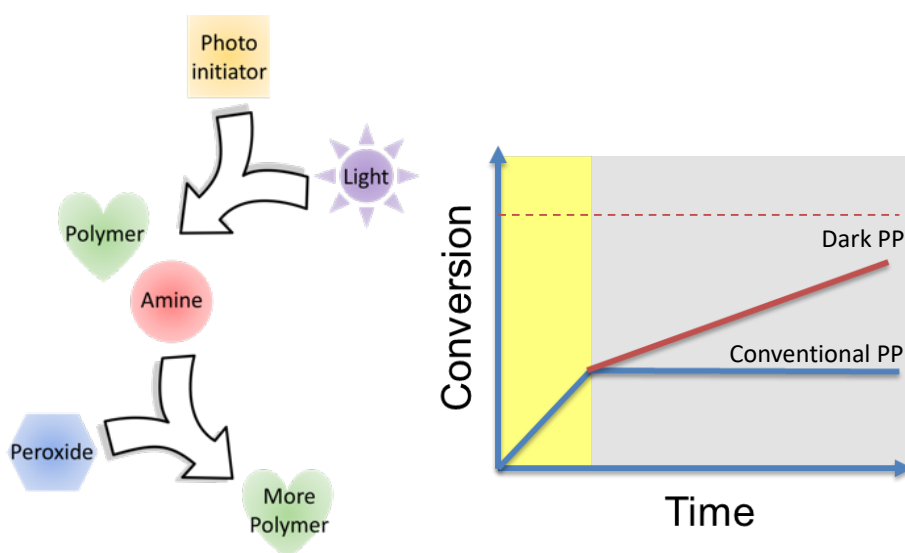
## Introduction

Radical-mediated photopolymerization (RPP) suffers from quick termination of reactive centers. As a result, irradiance and duration of irradiation must be carefully determined to ensure the full polymerization of resins. Otherwise, the final product may suffer from various issues, including poor mechanical properties. On the other hand, observation of tack-free surface of a photopolymer does not necessarily indicate sufficient cure throughout the resin. In some cases, unintended post-conversion that brings up the conversion may occur with trapped radicals persisting in vitrified regions, yet does not contribute to significant additional conversion and property change.<sup>1-3</sup> As a result, under-cured regions occur in light-attenuating systems and result in compromised polymer properties.<sup>4,5</sup> While cationic photopolymerization may be used to circumvent these issues, RPP provides a wider range of monomer choice and resultant polymer properties.<sup>6</sup> Therefore, we set out to develop radical-based dark-curing photoinitiation in bulk. We report here the novel radical dark-curing photoinitiators that does not require thermal assistance to induce rapid photopolymerization and concurrent post-conversion to near-vitrification limit after a brief irradiation. This new type of photoinitiator can not only enhance existing photocuring processes but also enable new applications by elevating the conversions of initially under-cured regions from inadequate photopolymerization.

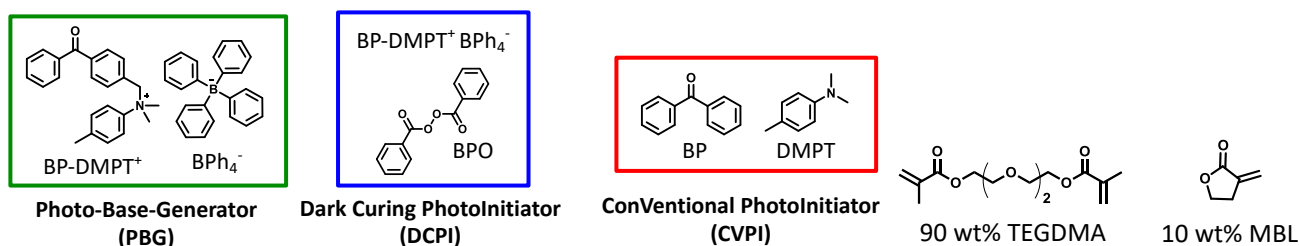
## Results and Discussion

### Dark-curing photoinitiator design

Our dark-curing photoinitiator (DCPI) was designed to induce rapid photopolymerization concurrent during irradiation as well as unhindered extensive post-polymerization by in situ generation of redox initiators that persist until encountering a counter redox partner, which juxtaposes against limited lifetimes of excited photoinitiators and radicals. Therefore, the resultant polymerization scheme is following (**Figure 1**): light activates DCPI that generates radicals and polymer as well as amine reductant; amine reductant diffuses to undergo redox reaction with peroxide oxidants that generates radicals and polymer over extended periods. The intended result of such DCPI is that when the light is shuttered, conversion continues while conventional photoinitiator (CVPI) is terminated quickly. Our DCPI was designed with UV-absorbing benzophenone-chromophore and conveniently synthesized in two steps with isolation achieved by recrystallization (**Figure 2**).<sup>7</sup>



**Figure 1.** Polymerization scheme of dark-curing photoinitiator and its intended polymerization profile.

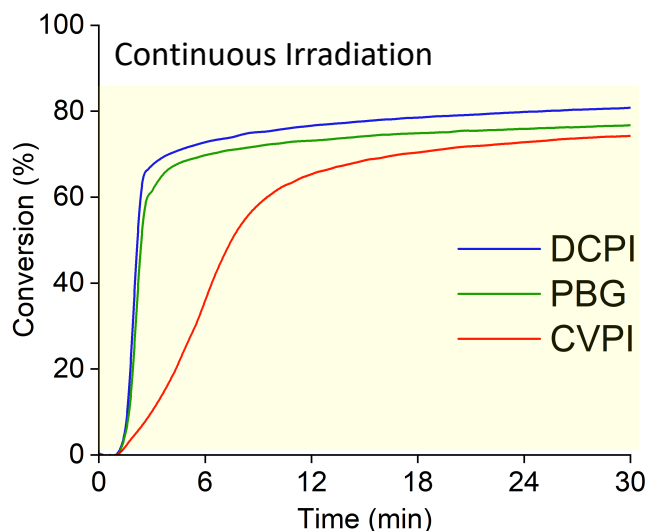


**Figure 2.** Molecular structures of photo-base-generator (PBG), dark-curing photoinitiator (DCPI), and conventional photoinitiator (CVPI), and methacrylate resins used in the study.

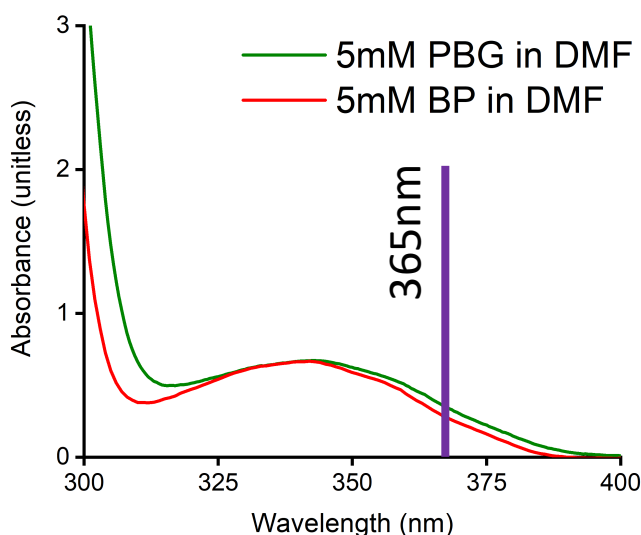
### Performance of dark-curing photoinitiator against conventional photoinitiator

When DCPI, photo-base-generator without peroxide oxidant (PBG), and conventional photoinitiator (CVPI) were subjected to continuous irradiation with a 30 mW/cm<sup>2</sup> 365 nm LED, we did not observe any distinctive difference in the trend of their photopolymerization profiles. However, due to higher efficiency photopolymerization of DCPI and PBG, the full conversion was reached earlier than one

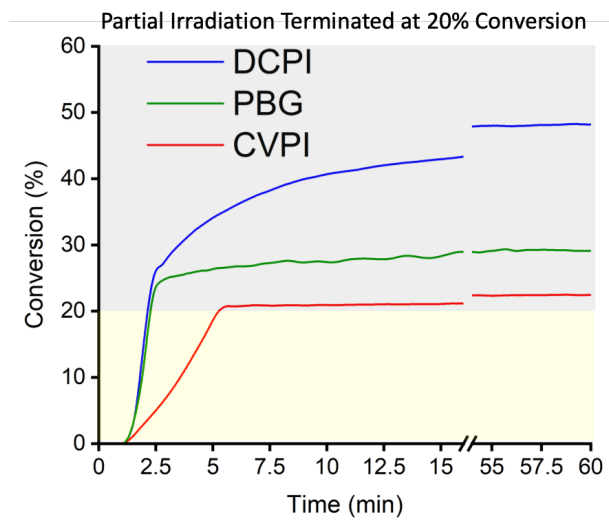
by CVPI (**Figure 3**). The higher efficiency is not due to the difference in the absorption of the light as the absorption with the same concentration is near identical (**Figure 4**). To demonstrate the unique dark-curing ability of DCPI against PBG or CVPI, we intentionally shuttered the light when conversions in respective resins reached 20%. As expected, both CVPI and PBG plateaued their conversions quickly after light was shuttered, gaining 2-5% additional post-conversion over 60 mins. Yet, DCPI continued its polymerization, achieving additional 20-25% post-conversion (**Figure 5**). This is the first demonstration of photo-activated radical polymerization that significantly extends beyond the discontinuation of irradiation without any assistance of solvent or heat. As a result, DCPI can produce more robust and homogenous materials with shorter exposure times.



**Figure 3.** photopolymerization profiles of three photoinitiators under continuous irradiation. 0.5 wt% photoinitiator concentration and 30 mW/cm<sup>2</sup> 365 nm LED.



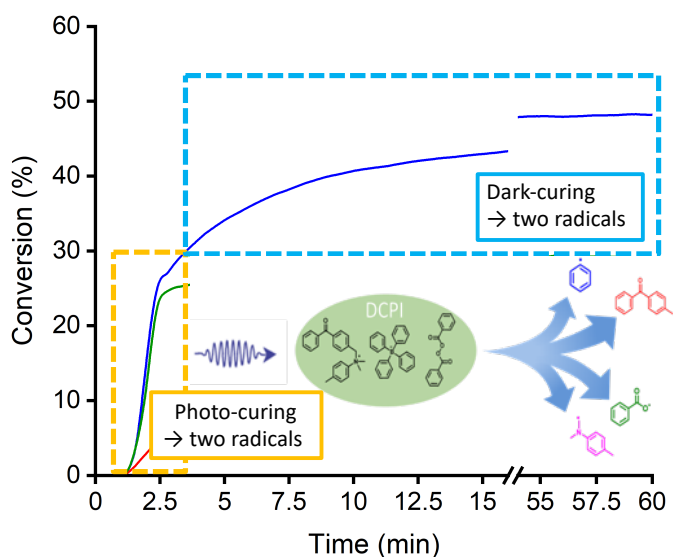
**Figure 4.** UV-Vis spectra of photo-base-generator (PBG) and benzophenone (BP) that show absorption characters of DCPI and CVPI, respectively.



**Figure 5.** Polymerization profiles of three photoinitiators with irradiation shuttered at 20% conversion. 0.5 wt% photoinitiator concentration and 30 mW/cm<sup>2</sup> 365 nm LED.

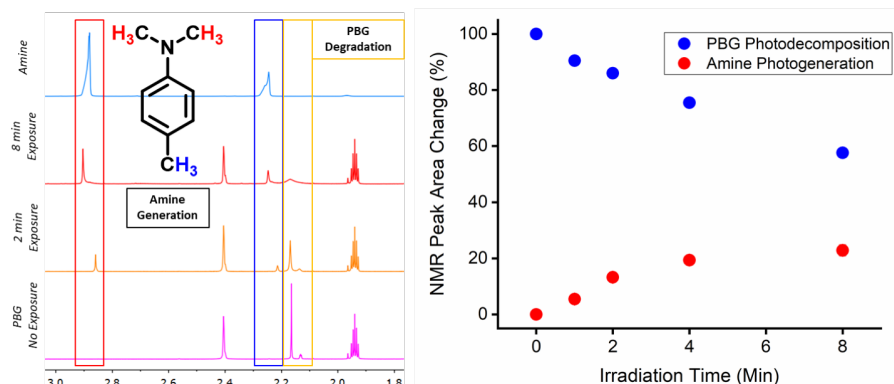
### Details about dark-curing photoinitiator mechanism

The rapid photopolymerization and extensive post-polymerization results from two separate radical generation processes that are initially activated by light. Photo-curing from the PBG moiety dominates polymerization during irradiation while dark-curing from released amine reductants reacting with formulated peroxide oxidants overtakes the polymerization after light was ceased (**Figure 6**). As such, a single photon that excites DCPI generates overall four radicals, making the most photon-efficient photoinitiators to date in comparison to one or two radicals of conventional photoinitiators. The crucial aspect of such efficiency is photo-base-generation from the PBG moiety. **Figure 7** shows a direct NMR evidence of amine generated from the PBG as well as quantitative results of the photo-base-generation. We found that the quantum yield of amine generation is ~ 30% while most commercial PBGs are much lower (less than 10%).



**Figure 6.** DCPI mechanistic details about its polymerization profile where a single photon leads to four radicals.

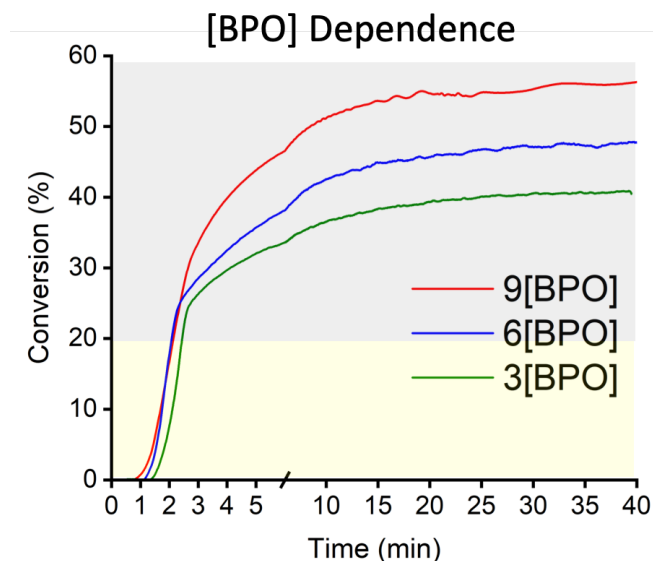
### Quantitative H NMR



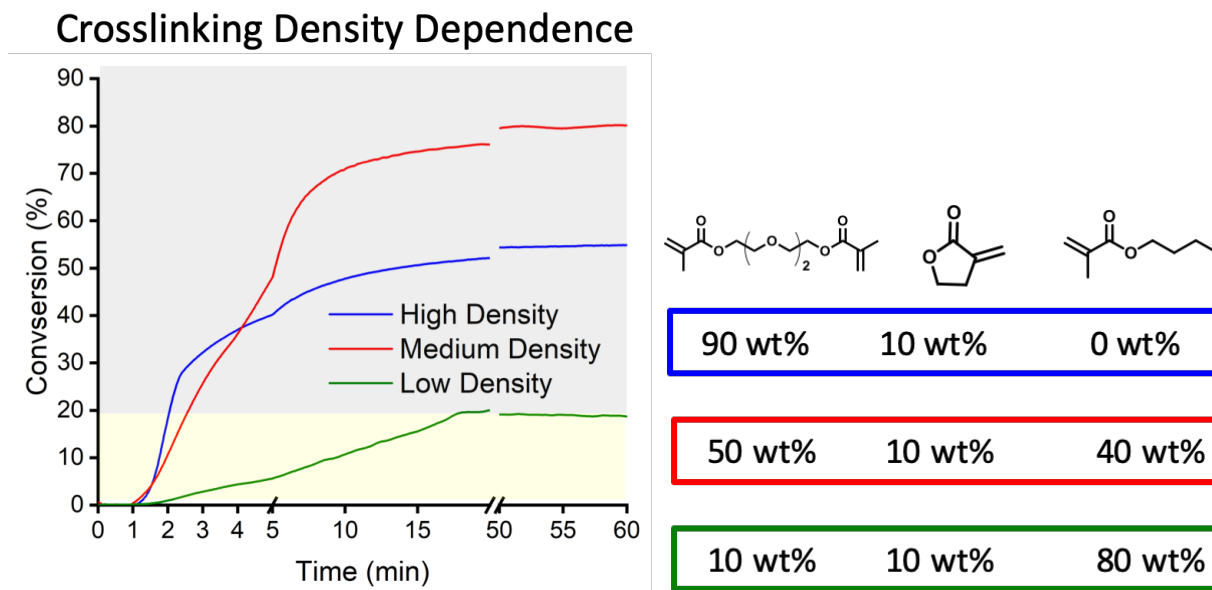
**Figure 7.** Photo-base-generation of amine from PBG and quantitative efficiency of photo-reaction.

### Dark-curing photoinitiator formulations

We studied how different formulations affected the performance of DCPI. First, we found that changing the concentration of formulated peroxide oxidant (BPO) affected the rate of dark-curing in an expected manner. Higher BPO concentrations led to greater rates of dark-curing (**Figure 8**). Changing resin conditions also resulted in a drastic difference. The resin with 90% di-methacrylate induced ~30% conversion from dark-curing when light was shuttered. When the resin was changed to 50% di-methacrylate, astounding 60% dark-curing occurred that quadruples the initial 20% conversion (**Figure 9**). When DSC thermal stability was tested of resins consisted of monomers, monomers + CVPI, monomers + PBG, monomers + DCPI, and monomers + BPO, all resins started to decompose near 90 degrees C that indicates that DCPI formulation is as stable as any other potential formulations. Lastly, **Figure 10** shows a slight coloration of polymer with the thick of 1 cm that was cured from DCPI.



**Figure 8.** Dependence of dark-curing rates on peroxide oxidant (BPO) concentrations. 3[BPO] = 0.5 wt%, 6[BPO] = 1.0 wt%, and 9[BPO] = 1.5 wt% concentrations; 30 mW/cm<sup>2</sup> 365 nm LED.



**Figure 9.** dark-curing rate dependence on crosslinking density. 1wt% photoinitiator concentration; 30 mW/cm<sup>2</sup> 365 nm LED.



**Figure 10.** slight coloration of 1 cm thick polymer sample

## Conclusion

In this contribution, we report a new class of radical photoinitiator that eliminates the temporal restriction of photo-curing by inducing second-stage-like polymerization behaviors that does not require an additional energy input. The use of this photoinitiator over conventional photoinitiators guarantees that initially incomplete polymerization can be brought to a higher conversion, whether it is due to equipment degradation, imperfect processing conditions, or resin batch variability. This autonomous post-polymerization can ensure final products are high-quality and consistent while it may allow photo-curing in new applications that are heretofore unexplored.

## Acknowledgment

NIH/NIDCR R21DE028017, the Industry/University Cooperative Research Center for the Fundamentals and Applications of Photopolymerization, and NSF Graduate Research Fellowships Program were acknowledged for funding.

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