

RATIONAL DESIGN AND EVALUATION OF NOVEL POLYMERIZATION INITIATORS
BASED ON AMINE-PEROXIDE REDOX REACTIONS

by

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ABSTRACT

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Thesis directed by Professor Charles Musgrave and Professor Jeffrey Stansbury

Radical polymerization accounts for 45% of all manufactured polymer, producing approximately 150 million tons of materials annually. These polymer products are ubiquitous in modern society and need continuous development of new radical initiators in order to meet the ever-changing demands for materials. In this dissertation, I focus on the design and evaluation of novel radical initiators to address persistent problems in the polymer field by discovering new mechanistic details about radical generation mechanisms that led to the improvement of various existing applications and enablement of new future applications.

In my doctoral studies, I first examined the mechanism of a well-known polymerization method that utilizes amine reductant and peroxide oxidant. Despite its extensive use since the 1950s, the initiation mechanism of amine-peroxide redox polymerizations (APRP) has been poorly understood and therefore, advances in this polymerization method have been largely incremental and empirically driven. Through a combination of computational modeling and experimental analysis, I elucidated the APRP mechanisms including its rate-determining step and derived a kinetic model that utilizes the computational calculation to predict experimental polymerization rates. This new mechanistic understanding was then applied to computationally design new amine reductant initiators with faster initiation kinetics, leading to the discovery of an initiator system that was experimentally proven to outperform current state-of-the-art amines by ~20-fold, making

it the most efficient amine redox initiator to date for use in amine-peroxide redox polymerization processes.

I then evaluated structural variations in the peroxide oxidants within the framework of APRP using my previously developed kinetic model. By improving radical and anion stabilization with increased π -electron conjugation and increasing the electrophilicity of the peroxy bond with electron-withdrawing groups, I computationally designed several new peroxides and predicted that they would exhibit improved initiation rates when compared to the commonly used benzoyl peroxide. I then developed a redox-based 3D printing process with a custom direct writing printer that used an APRP redox pair optimized using my computational modeling to exploit its extremely high reactivity.

Beyond redox initiation, I also developed a unique photoinitiator based on amine-peroxide redox initiation that enables continued polymerization after irradiation is ceased, known as dark curing. The photoactivation of this initiator creates both initiating radicals as well as the amine compounds that can react with a peroxide over an extended period. This dark curing photoinitiator achieved a remarkable 25-60% additional conversion after exposure and slightly improved mechanical properties in comparison to conventional continuous photocuring, which can contribute to the homogeneity of polymers by raising conversions in initially under-cured regions. Using laboratory experiments and computational studies, I then clarified the origin of the high initiation efficiency and showed that this photoinitiator may be the most-photon-efficient photoinitiator to date.

Lastly, I expanded dark-curing photoinitiation to absorption in the visible range with a new chromophore through a series of computational predictions, including the study of position-dependent effects of substituents, electronic transitions, and energetics. A target compound was

synthesized and optically examined to demonstrate strong visible light absorption. I then demonstrated extensive dark-curing with a high quantum yield.

All of the new initiators that I developed in my doctoral studies have unprecedented capabilities that enable innovation in polymer synthesis. For instance, bone cement adhesive polymers can be more rapidly fabricated with lower cytotoxicity from my redox initiators with higher efficiency. On the other hand, my photoinitiators can allow rapid coating of curved surfaces present in automotive or airplanes without a large oven needed for thermal curing.

Dedication

To those who have supported me.

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Chapter 1. Introduction

1.1 Polymerization

Polymerization processes involve chemical reactions that convert many small molecules (monomers) into larger molecules (polymers). These polymers are one of the most important materials in the modern world as they offer a readily accessible means to enable a tremendous array of diverse applications based on the wide range of properties that can be intentionally designed. Polymerization can occur via various reaction mechanisms depending on functional groups of monomers, which can be categorized into two main classes: step-growth and chain-growth. In step-growth polymerization, each reaction combines two molecules of some length to form a larger molecule with the combined length. The average molar mass increases slowly and the high molecular weight polymer molecules are formed only in the late stage of polymerization (>95%). The step-growth polymerization includes examples such as polyesters that are formed by reactions between alcohol and carboxylic acid (and other routes) as well as polyurethanes that are formed by reactions between isocyanate and alcohol. On the other hand, chain-growth polymerization proceeds via the addition of a monomer to a growing polymer chain with a transferable reactive center. The addition of a monomer is usually rapid and high molecular weight chains are formed throughout the polymerization process since chain birth, growth and death typically occur in a largely independent fashion for a given chain. The monomers for the chain-growth polymerization commonly have carbon-carbon double or triple bonds that can react with radical or ionic reactive centers. During each addition, the π bond in a monomer is broken and the two electrons rearrange to form a linkage to the growing chain and a new propagating center. Chain-growth polymerization includes polyethylene with ethylene monomers, polypropylene with

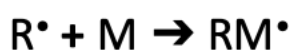
propylene monomers, poly-vinyl-chloride with vinyl chloride monomer, polystyrene with styrene monomer. and polyacrylate with acrylate monomers.

1.2. Radical Chain-growth Polymerization

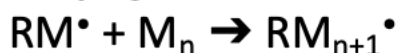
Radical polymerization represents the most investigated and utilized approach for polymer synthesis with 40-45% of the ~300 million metric tons of annual worldwide industrial polymer production based on this chemistry. Radical polymerization's predominance is due to its facile and flexible reaction conditions, its compatibility with solvents and water, as well as its tolerance for a tremendous variety of functional comonomers.¹ Due to the unpaired electron, the radical reactive centers react with monomers rapidly through the three-staged mechanism: chain initiation, chain propagation, and chain termination, where a chain transfer may also be present (**Figure 1.1**). In chain initiation, an initiator creates radical reactive centers ($R^{\bullet}$) that add to a monomer (M), activated by heat, light, or mixing. In chain propagation, the initial monomer that acquired a reactive center from the added initiator reacts with another monomer, the process of which would repeat with a number of monomers. Each addition leads to a new polymer molecule (RM_n) with extension by one repeat unit and a new reactive center. In chain termination, two propagating chains react with each other and quench the two radical reactive centers. Combination termination joins two chain radicals together while disproportionation occurs when an atom (typically hydrogen) is transferred from one radical chain to another resulting in two inert polymeric chains. All three stages occur simultaneously during polymerization. In some instances, chain transfer can occur that terminates the reactive center of a polymer chain and initiates the formation of another chain with a new reactive center. On the other hand, a slower but more controlled variant called controlled radical polymerization absence of termination reaction.

Acrylate and methacrylate are one of the most common monomer structures that contains ester groups conjugated with a reactive carbon-carbon double bond. A (meth)acrylate can undergo chain-growth polymerization with itself to form a homopolymer such as poly(methyl methacrylate) or with another monomer to form co-polymer such as poly(methyl methacrylate-co-phenyl methacrylate). Multifunctional monomers are used as a cross-linker to form a unified polymer network (thermoset), instead of covalently independent polymer chains (thermoplastic).

Initiation

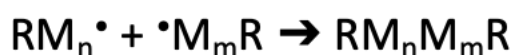


Propagation



Termination

combination



disproportionation

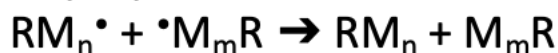


Figure 1.1. Radical polymerization mechanism. An initiator generates a radical reactive center ($\text{R}^\bullet$), activated by a stimulus (e.g. heat, light, chemical potential). $\text{R}^\bullet$ adds to a monomer (M) with sequential continued monomer addition until termination or chain transfer ends growth of the polymer chain (RM_n)

1.3. Light-activated radical initiation

Numerous radical polymerization methods have been developed. In many cases, the initiation process may differ considerably while the subsequent propagation and termination reactions effectively remain unchanged if the same experimental conditions including monomers are used. Three types of radical initiators are generally used. Thermal initiators are activated by heating until

a bond of the initiator is homolytically cleaved, producing two radicals. Redox initiators are activated when reductants and oxidants are mixed, which exchange an electron and generate two radicals that may present different reactivities towards monomers. Photoinitiators are activated by electromagnetic irradiation at appropriate wavelength with the result that the absorbed energy promotes photolysis of labile covalent bond within the initiator (Type I) or precipitates bimolecular hydrogen abstraction (Type II) (**Figure 1.2**), although some photoinitiating mechanisms do not fall into this dichotomy.

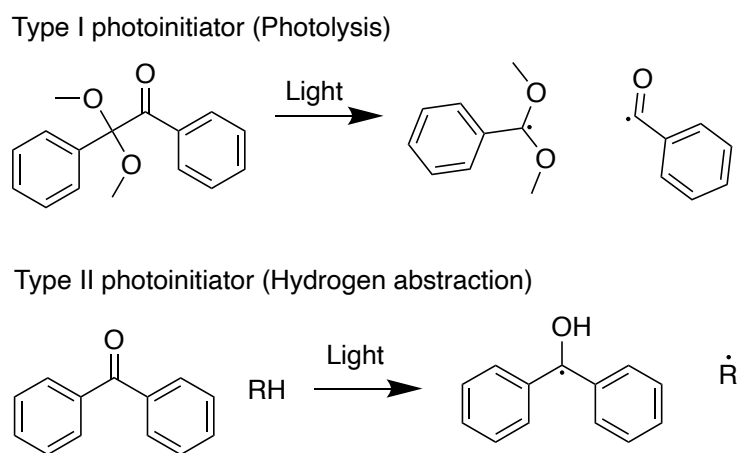


Figure 1.2. Common photoinitiation mechanisms. Type I photoinitiators undergo photolysis mechanism to produce two initiating radicals while Type II counterparts undergo hydrogen abstraction with a co-initiator (RH) to give one viable radical.

In particular, radical photopolymerization has received great attention as a green technology relative to conventional thermal polymerization and has grown rapidly by its potential to reduce energy consumption and waste (e.g. no volatile organic compounds), while increasing productivity;²⁻⁴ Radical photopolymerization provides the advantages of ambient temperature processing with fewer side reactions, and a well-controlled onset and rate of polymerization dependent on the light source and photocuring conditions. This has driven the development of a

photopolymer market currently estimated to be \$4.8 billion and projected to grow at a rate of 9.4% through 2025 to \$8.3 billion.⁵ Photopolymerization in industrial processes has greatly expanded over the past several decades, replacing many traditional thermally cured technologies that also may require solvent-based processing to aid temperature control. Most photoinitiators are activated through ultraviolet (UV) radiation. However, the development of visible photoinitiating systems introduced potential advances of safer practices. The common practice involves adding a small amount of photoinitiator(s) (0.1-5+ wt%) to a batch of neat monomer, followed by radiation of selective wavelength, commonly resulting in a highly crosslinked product. Typically, a photopolymer resin consists of a mixture of multifunctional monomers and oligomers in order to achieve the desired reactivity and polymer physical properties such as hardness, flexibility, adhesion, among many others.

1.4. Photopolymerization Applications

Photopolymerization is a widely used technology from biomedical, floor and furniture coatings, optical fiber cladding, contact lenses, automotive coating, aerospace coating, imaging applications thanks to the unique advantages of spatial and temporal controls of polymerization that thermal or redox initiations cannot provide. In dentistry, adhesives, sealant composites, protective coatings, and the dental composites utilize photopolymer resins that consist of a matrix containing methacrylate oligomers with inorganic fillers such as silicon dioxide. The dental applications of photopolymerization continued to increase its popularity with the introduction of affordable light-emitting diodes (LEDs). In medicine, photocurable adhesives are also used in the production of catheters, hearing aids, surgical masks, medical filters, and blood analysis sensors, while photocured bulk materials are used in drug delivery, tissue engineering, and cell encapsulation. In

particular, *In-vivo* photocuring provides advantages of production and implantation of a medical device with minimal invasive surgery, whereas *ex-vivo* photopolymerization allows fabrication of complex matrices along with versatility of formulation. Photopolymerization is also extensively used in 3D printing such as stereolithography, digital imaging, and 3D inkjet printing, where a 3D computer model is realized into a 3D polymer object. The image of the model is cut in slices and each slice is reconstructed through photopolymerization of the resin. Photopolymerization is also used as a photographic or printing process including the design and production of fabricated computer chips, because polymerization only occurs in regions which have been exposed to light as a photopatterning technique. Unreacted monomer can be removed from unexposed regions, leaving a relief polymeric image.

1.5. Current Problem of Radical Photopolymerization

Radical photopolymerization undergoes the same radical mechanism of chain initiation, chain propagation, and chain termination as those initiated by thermal or redox initiators. The major difference between these initiation methods is that irradiation can be ceased on command while other stimuli of heat or chemical mixing are not easily turned on or off. When the activating stimulus is removed, the generation of new radical species is abruptly discontinued, which prevents the chain initiation and ultimately chain propagation from occurring while the chain termination continuously occurs until all readily accessible radical reactive centers are quenched. As a result, radical photopolymerization typically undergoes nearly immediate termination of polymerization upon discontinuation of irradiation (**Figure 1.3**).

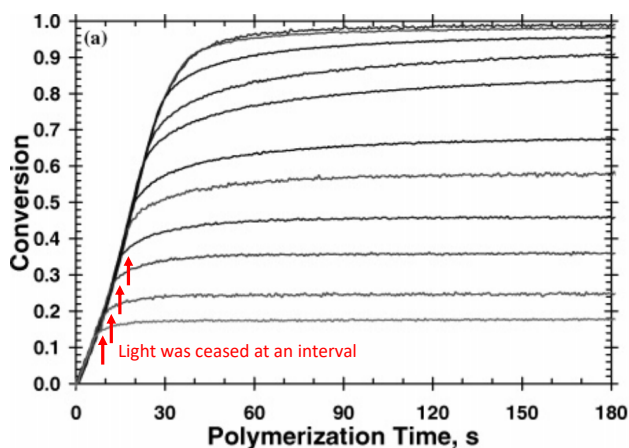


Figure 1.3. Radical photopolymerization profiles with irradiation ceased at various time intervals. The conversion plateaued within a short time due to the rapid termination of radical reactive centers, especially in the early conversion regime. Adapted from Berchtold et al. *Macromolecules*, 2005

This termination behavior gives rise to the spatial and temporal control that is highly desirable in 2D and 3D lithography. Yet, such termination behavior also restricts its broad use for a multitude of polymeric materials applications. This is because of the likelihood of producing highly heterogeneous or under-cured regions, even with careful tailoring of the photopolymerization process to its specific application. Evidence of a well-cured surface of a photopolymer does not guarantee sufficient or homogeneous through-cure, which is also challenging to verify. While trapped radicals can persist in high-conversion, vitrified regions within structurally heterogeneous photopolymer networks,⁶⁻⁸ the low mobility necessary for such radical persistence also restricts free monomer migration from adjacent domains of lower conversion, thus limiting significant post-curing potential.⁹ More critically, any low conversion regions present at the end of the irradiation interval will persist due to very efficient biradical termination that effectively arrests post-curing. As expected, under-curing contributes to

compromised properties and leachable monomer, among other issues that cannot be rectified without additional irradiation to produce new initiating radicals. This rapid termination behavior seriously limits or even precludes implementation of radical photopolymerization in applications that involve dimensionally thick or otherwise light-attenuating systems, including highly filled and pigmented materials, or curved- and irregular-surface coatings.^{10,11}

1.6 Dissertation Focus

To combat prematurely terminated polymerization and resulting poor polymer property due to inadequate irradiation, a photopolymerization method is proposed in which conversion continues beyond the cessation of irradiation, which is known as dark-curing (**Figure 1.4 (a)**). Over the past five years, a few examples of radical-based dark-curing have been demonstrated, yet they suffer from a variety of deficiencies that impose practical limitations. Our group previously reported a photoinitiating system that offered radical dark-curing to near-completion after a brief light exposure and it is the only example in the literature that is uniquely applicable in bulk conditions without any involvement of solvent. However, it suffers from heavily colored products and the absence of photopolymerization during irradiation.¹² Shanmugam et al. reported a photoinitiating system for controlled radical polymerization (CRP) that utilizes oxygen to generate radical-producing hydrogen peroxide *in situ* in an aqueous environment.¹³ Although this example is a promising green chemistry for CRP, many photopolymerization applications require significantly faster and solvent-free initiating systems. He et al. introduced a promising photoinitiation system that immediately generates radicals upon irradiation and also releases amines that react with peroxide to induce latent radical generation (**Figure 1.4 (b)**). However, only a single demonstration of the photo-activated dark-curing capability of this system was reported

in solution with ~ 50 vol% polar dimethyl sulfoxide (DMSO) solvent.^{14,15} The dark-curing strategy from these examples is possible as photo-generated redox initiators (e.g. hydrogen peroxide or amine) are relatively stable and do not undergo termination processes contrary to radicals. Hence, recognizing the unrealized potential of radical-based dark-curing photoinitiation in bulk, this thesis provides an examination of the mechanism responsible for the latent radical generation phase of the proposed dark-curing scheme (**Chapter 2** and **3**) and then using the guidance provided by the detailed reaction mechanisms and its computed energetics, and then develops improved photoinitiators that exhibit extensive dark-curing behavior accompanied by high-photon efficiency under typical photopolymer conditions (**Chapter 4** and **5**).

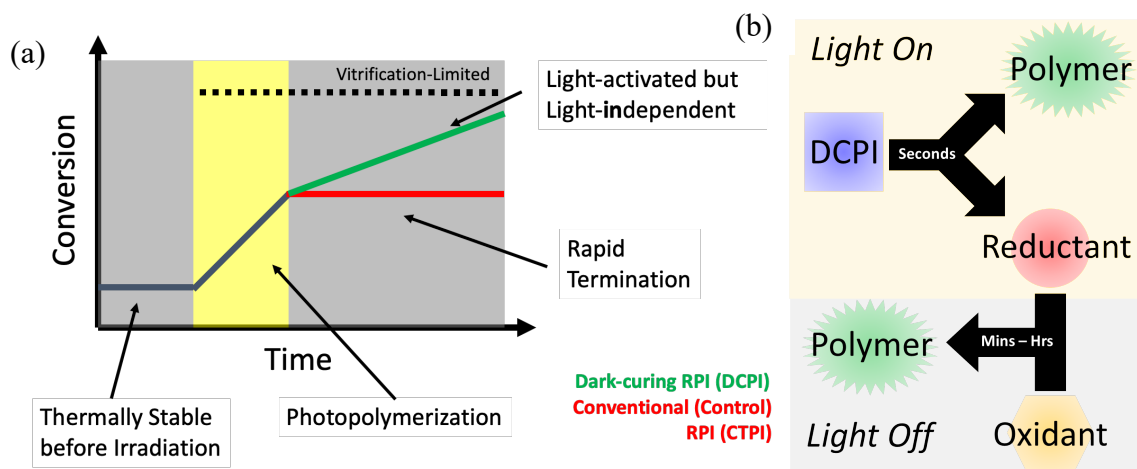


Figure 1.4. (a) Expected polymerization profiles of dark-curing photoinitiator (DCPI) in comparison to conventional photoinitiator (CTPI) (b) mechanistic scheme of dark-curing photoinitiation, where irradiation generates radicals and redox initiator that can react with a counterpart over an extended period.

Chapter 2: Rational Design of Efficient Amine Reductant Initiators for Amine-Peroxide Redox Polymerization

The work described in this chapter is adapted from a publication available at <https://pubs.acs.org/doi/abs/10.1021/jacs.8b13679>: **Kim, K.**; Singstock, N.; Childress, K.; Sinha, J.; Salazar, A.; Whitfield, S.; Holder, A.; Stansbury, J.; Musgrave, C. J. *Am. Chem. Soc.* 2019, 141, 15, 6279-6291.

2.1 Abstract

Amine-peroxide redox polymerization (APRP) has been highly prevalent in industrial and medical applications since the 1950s, yet the initiation mechanism of this radical polymerization process is poorly understood so that innovations in the field are largely empirically-driven and incremental. Through a combination of computational prediction and experimental analysis, we elucidate the mechanism of this important redox reaction between amines and benzoyl peroxide for the ambient production of initiating radicals. Our calculations show that APRP proceeds through S_N2 attack by the amine on the peroxide, but that homolysis of the resulting intermediate is the rate-determining step. We demonstrate a correlation between the computationally predicted initiating rate and the experimentally measured polymerization rate with an $R^2 = 0.80$. The new mechanistic understanding was then applied to computationally predict amine reductant initiators with faster initiating kinetics. This led to our discovery of *N*-(4-methoxyphenyl)pyrrolidine (MPP) as amine reductant, which we confirmed significantly outperforms current state-of-the-art tertiary aromatic amines by $\sim$ twentyfold, making it the most efficient amine-peroxide redox initiator to date. The application of amines with superior kinetics such as MPP in APRP could greatly

accelerate existing industrial processes, facilitate new industrial manufacturing methods, and improve biocompatibility in biomedical applications conducted with reduced initiator concentrations yet higher overall efficiency.

2.2 Introduction

Radical polymerization (RP) is responsible for approximately 45% of all manufactured plastics or ~100 million tons of material annually, of which RP initiated by redox initiators contributes a significant portion.^{16–19} Redox RP exploits the intrinsic chemical energy stored in a redox-active reductant-oxidant pair, which results in the unique advantages of energy-efficient room temperature (RT) activation, minimal side reactions, unrestricted product shape and size, superior mechanical properties, and applicability under a broad range of reaction conditions.^{20,21} Particularly, amine-peroxide redox polymerization (APRP) with amine reductant-peroxide oxidant pairs has the additional benefits of biocompatibility²² and facile implementation in solvent-free bulk polymerizations²³ due to the elimination of metal-ions and the neutral nature of organic initiating systems in comparison to common metallic salt redox initiators. As a result, APRP has been widely used since its discovery in the 1950s with over 18,000 APRP-related patents filed since 1975 with the majority of these filed during the last two decades.²⁴ Two areas that have exploited APRP's unique advantages are cementation processes used in dental and orthopedic applications where conditions are too restricted for thermal or photo-activation processes to be practical.^{25–32} Over the past 50 years, millions of patients have benefitted from the installation of orthopedic implants that critically rely on APRP cementation,³¹ and this reliance will grow as the market for medical polymers is forecast to exceed \$17 billion USD by 2020.³³ Beyond biomedical applications, these advantages have motivated its continuous investigation for emerging applications in frontal polymerization,³⁴ self-healing materials,^{35,36} interfacial polymerization,³⁷

adhesives,³⁸ nanocomposites,³⁹ and microfluidic chips.⁴⁰ Despite the wide success and significant impact of APRP, considerable room for further improvements still remain.

The primary disadvantage of redox RP is its generally slow initiation rates relative to other RP methods. This is because the redox RP rates are regulated by the chemical potentials of redox pairs with various intrinsic pair reactivities while thermal and photochemical polymerization rates are readily controlled by modulating external stimuli. This limitation has unfortunately precluded redox RP from being used for various emergent polymer applications such as additive manufacturing (AM), where photochemical initiation is commonly employed for *in situ* polymerization.^{41,42} The discovery of APRP redox pairs with sufficiently high initiation rates can present a new mode of chemically-induced AM *via* inkjet printing where two micro-droplet streams are mixed during patterned deposition, uniquely allowing multi-material production with locally varying composition and properties. Not only does this prospect exclude the need for the additional post-curing usually required for photochemical AM, but its established biocompatibility and metal-free chemistry also permit applications involving fabrication of customizable biomedical devices,⁴² and flexible electronic devices.^{43,44} With redox pairs having improved initiation kinetics, APRP could also enable a new manufacturing process with unprecedented energy-efficiency and environmental advantages. For example, the process of coating an aircraft fuselage involves an initial spray of a polymer-solvated solution followed by irradiation by IR heaters to accelerate organic solvent volatilization and promote further crosslinking. This process takes as much as 72 hours, which has consequently motivated manufacturers to investigate photopolymerization for coating large structures.^{45–48} Alternatively, a similar spray-coating process could be employed with APRP initiators, where two streams containing each redox component induce *in situ* RP on the surface, resulting in a cross-linked coating. This process

eliminates emissions of volatile organic compounds and the need for long curing periods while enabling the application of opaque or filled coatings where curing by photopolymerization would otherwise fail due to light-attenuation or dimensional exposure limits. Such a prospect would have substantial implications for the automotive and aerospace industries through saving significant energy and capital costs by greatly accelerating manufacturing throughput and eliminating the need for expensive curing equipment. In addition to enabling applications where fast polymerization rates are essential, the discovery of an APRP redox pair with exceptionally fast polymerization kinetics would also allow the tuning of polymerization rates to potentially lower, optimum concentrations with various concomitant aesthetic, medical, mechanical, and economic benefits, directly relevant to the currently employed applications.⁴⁹ Unfortunately, none of these opportunities are yet feasible due to the slow polymerization rates of current APRP initiators.

The principal reason for the lack of improvement in APRP polymerization kinetics is the absence of a detailed APRP initiation mechanism and its associated energetics. The mechanism of most redox initiators proceeds via an outer-sphere electron transfer (ET) from the reductant to the oxidant with ET rates that are well-characterized by Marcus theory.⁵⁰ In contrast, amine-peroxide redox pairs undergo an associative inner-sphere ET which involves the formation of a covalent bond between the reductant and oxidant. Unfortunately, the details of this process are challenging to probe experimentally as the ET rates of APRP cannot be measured readily due to its complex mechanism that involves several highly reactive intermediates. Consequently, despite a plethora of APRP kinetic studies,^{23,28,29,35,51–58} the mechanistic details of its initiation are still unclear. For instance, the rate-determining step (RDS) of APRP initiation has not yet been conclusively identified. As a result, the effort to discover more efficient amine reductants has been largely empirical and restricted by the absence of a detailed and sound fundamental framework to guide

the search for reductants through the expansive chemical space of amines. We suggest that a comprehensive and fundamental understanding of the mechanism of radical generation is crucial to fully exploiting this versatile polymerization technique with yet unrealized remarkable abilities. In this contribution, we use quantum chemistry to elucidate the details of the APRP mechanism and exploit the mechanistic insights we obtain to discover a novel amine reductant with greatly accelerated initiation kinetics. The detailed description of the elementary initiating steps we identify allowed us to derive a rate equation for the APRP initiation that accounts for all relevant reactive intermediates while also illuminating the RDS for this process. Our computational results are supported by experimental kinetic studies based on real-time Fourier-transform infrared spectroscopy (FTIR) that both confirm our proposed mechanism and the predicted associated kinetic properties. We also elucidate why primary and secondary amines fail to efficiently initiate APRP. Our study of a range of tertiary amine reductants shows how structural variations in the amine affect initiation kinetics, which we subsequently used to direct our computational search towards more effective amine species that led to the discovery of *N*-(4-methoxyphenyl)pyrrolidine (MPP) as a novel amine for accelerated APRP. We then experimentally confirmed that MPP does indeed exhibit exceptional initiation kinetics, potentially enabling various unrealized applications of APRP. This study also substantially adds to the fundamental understanding of the inner-sphere ET process between amines and peroxides beyond its use in APRP. The detailed APRP mechanism we report offers researchers valuable guidance for the development of additional APRP systems with amines that will enable practitioners to obtain optimal rates and material properties for various engineering uses, including biomedical applications, coatings, and potentially additive manufacturing as well.

2.3 Methods

2.3.1 Computational Methods

All calculations were performed within the GAUSSIAN 16 Revision A.03 software package⁵⁹ using density functional theory based on the MN15 density functional⁶⁰ and 6-31+G(d,p) basis set.⁶¹ The MN15 functional was chosen because it performed the best of 13 functionals evaluated compared to the highly accurate, but computationally demanding, CBS-QB3^{62,63} and CCSD(T)^{64–66} methods with an RMS error of 1.4 kcal/mol for reaction and activation energies relative to the CBS-QB3^{62,63} method (see **SI1**). The accuracy of this functional likely results from its ability to simultaneously describe both single- and multi-reference systems.⁶⁰ This is necessary because some of the TSs and intermediates of the investigated molecules exhibit multi-configurational character (See **SI1**). Vibrational force constants were calculated to verify that the stationary state geometries were optimized to the correct structures and to compute vibrational entropies, zero-point energies and thermal corrections at 298 K. Solvent effects were described using the universal solvation model (SMD)⁶⁷ with parameters describing ethyl acetate (EtOAc) because of its structural similarity to (meth)acrylate monomers. Furthermore, the dielectric constant of EtOAc⁵⁹ at ~6 is suitable for describing the dielectric environment produced by common bulk (meth)acrylate monomers with dielectric constants ranging from 2.5 to 11.^{68,69} The monomer used in the computational investigation of monomer addition kinetics was ethyl methacrylate. The orbitals depicted in this study are obtained *via* the Natural Bond Orbital approach (version 3.1) as implemented in Gaussian16.⁷⁰

2.3.2. Experimental Methods

2.3.2.1. Materials

1-methyl pyrrolidine (MePy), DMPT, 1-phenylpyrrole, and PhPy were purchased from Alfa Aesar (Haverhill, MA). NMA, 2,2'-(4-methylphenylimino)diethanol, and PhPi were purchased from TCI (Portland, OR). 1,4-diazabicyclo[2.2.2]octane, DEA, DMA, TeMA, 4-methylmorpholine (MMP) and BPO were purchased from Sigma-Aldrich (Milwaukee, WI). DBU and DMPEA were purchased from Acros Organics (Pittsburgh, PA). *N,N*-diisopropylethylamine and triethylamine were purchased from Chem-Impex International, Inc. (Wood Dale, IL). All amines were purchased at the highest purity of at least 95% and used as received. MDMA was purchased from Combi-Blocks (San Diego, CA). MPP was synthesized according to the synthesis procedure described in **SI7**. BPO was purified by being dissolved in dichloromethane (DCM) and recrystallized in methanol. The monomers used are di(ethylene glycol) ethyl ether acrylate (DEGEEA, Sigma Aldrich, 90% purity, 1000 ppm MEHQ), poly(ethylene glycol) methacrylate (Sigma Aldrich, average $M_n=360$, 500-800 ppm MEHQ), and triethylene glycol dimethacrylate (Tokyo Chemical Industry Co., 95% purity, 60 ppm MEHQ). All other chemicals were of reagent grade and used without further purification

2.3.2.2. Experimental Methods

The conversion of monomer by ambient bulk redox-initiated polymerization was monitored in real time with an FT-IR spectrophotometer (Nicolet Magna-IR Series II, Thermo Scientific, West Palm Beach, FL) by monitoring the C=C stretching absorption band at 1637 cm^{-1} for 20 mins in OMNIC software. We chose DEGEEA monoacrylate to reduce a confounding factor of autoacceleration as opposed to cross-linking multi-functional monomers that exhibit autoacceleration and are commonly used in many polymerization kinetic studies. The spectrophotometer was equipped with an MCT/A detector, and parameters on the FT-IR were set to 2 scans, a resolution of 16, an optical

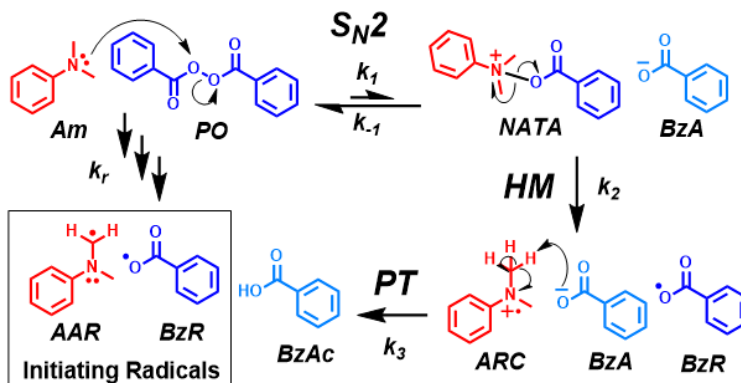
gain of 1, an optical velocity of 1.8988 cm/s, and an optical aperture of 15. We studied the polymerization kinetics initiated with two separate batches of resin with 3 mol% of BPO oxidant and various amine reductants. On a horizontal NaCl salt plate, 15 μ l of BPO resin was first deposited, to which another 15 μ l of amine resin was added. This solution was then mixed with micropipette tips. Another NaCl salt plate was then placed on top of the mixture, after which data acquisition began immediately. A clear baseline of zero conversion during an induction period preceding each polymerization was observed for every sample. The concentrations of the oxidant and reductant were chosen to accommodate approx. 30 seconds of sample preparation through an induction time and to capture the entire polymerization process. For example, efficient amines may have $\sim$ 40 seconds of induction time so that the conditions we chose allowed the capture of $\sim$ 10 seconds of the induction period as well as the subsequent initial polymerization kinetics. On the other hand, some amines may initiate after induction period of several minutes or may not be observed to initiate within 20 mins of mixing the redox pairs. These conditions were used to generate data for **Figures 4, 6, and Table 1**. For the kinetic demonstration of MPP and **Figure 10**, the concentration was changed from 3 mol% to 0.48 mol% for both oxidant and reductant, accompanied by resin change to 50 wt% triethylene glycol dimethacrylate and 50 wt% poly(ethylene glycol) methacrylate in order to accommodate the unprecedented initiating ability of the MPP amine whose full polymerization kinetics were too fast for us to observe under the previous conditions and to replicate more relevant resins for various applications. ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, as indicated in the respective measurement.

2.4 Results and discussions

2.4.1 Proposed Mechanism:

The APRP community has continuously debated the reaction mechanism of amine-peroxide redox initiation since the 1950s, including whether APRP proceeds through outer-sphere ET or inner-sphere ET *via* an S_N2 nucleophilic step.³⁷ However, the latter mechanism has been predominantly supported based on various observations. For instance, Denney and Denney found that all oxygen-18 was contained in the carbonyl groups of the product using an isotope tracer experiment that examined dibenzylamine and benzoyl peroxide (BPO) with oxygen-18-labeled carbonyl groups. This observation supports the S_N2 mechanism (**Scheme 2.1**) between a secondary amine and diacyl peroxide.⁷¹ Sato and Otsu later established that tertiary amines undergo an analogous S_N2 mechanism with diacyl peroxide and verified that the *N*-acyloxytrialkylammonium (NATA) intermediate is responsible for radical generation via homolytic decomposition of its N⁺-O bond.⁷² Pryor and Hendrickson observed a negative kinetic isotope effect ($k_H/k_D = 0.93 \pm 0.03$)⁷³ for the reaction between *N,N*-dimethylaniline (DMA) and BPO that also corroborated the S_N2 mechanism. O'Driscoll and Richezza spectroscopically observed an equilibrium between the DMA and BPO starting materials and an unidentified intermediate.⁷⁴ Sato et al. later used EPR to identify α -aminoalkyl (AAR), benzoyloxy, and phenyl as the initiating radicals generated by the redox reaction between *N,N*-dialkylaniline and BPO.⁷⁵ These studies^{71–75} suggest that the nucleophilic attack by the amine at the peroxy bond generates the metastable NATA species that homolyzes into initiating radicals, leading to a poorly substantiated but broadly accepted conclusion that the S_N2 reaction is the RDS.^{27,29,56,76} However, the kinetic studies of APRP initiation have been hitherto limited to peroxide decomposition that provides essentially no information on the rates of subsequent reactions involving short-lived intermediates.^{53,56–58} The

complex nature of this reactive system has led to a consensus that APRP is non-Arrhenius,²⁵ which effectively dissuaded efforts to further delineate the initiating kinetics and its mechanistic details in APRP. Despite the well-established conclusion that APRP proceeds through an S_N2 nucleophilic attack of the amine on the peroxide, this knowledge alone has not successfully guided researchers in their search for more efficient amines. For instance, various promising redox pairs have been proposed without justification due to the absence of a mechanistic understanding of APRP and these redox pairs often failed to surpass the performance of existing pairs.^{29,51,52,54,77–81} In this report we use quantum chemistry to elucidate the detailed APRP mechanism (**Scheme 2.1**), its associated energetics and RDS, which we then use to design and validate more active APRP amines.



Scheme 2.1. Proposed initiating mechanism for APRP with kinetic constants of the elementary reactions. The model chemistry is the redox pair of benzoyl peroxide (BPO) and N,N -dimethylaniline (DMA). Amine (Am) and peroxide (PO) undergo S_N2 reaction with kinetic constants k_1 and k_{-1} , to produce N -acyloxytrialkylammonium (NATA) and benzoate anion (BzA). The NATA intermediate homolyzes (HM) with kinetic constant k_2 into amine radical cation (ARC) and the benzoyloxy initiating radical (BzR). Finally, ARC and BzA undergo proton transfer (PT) with kinetic constant k_3 to generate benzoic acid (BzAc) and another initiating

radical, α -aminoalkyl radical (AAR). k_r describes the overall rate of initiating radical generation from a redox pair.

2.4.2 Resin Simulation:

The treatment of solvation is crucial to accurately describing the properties of a condensed phase reaction. This is especially important for bulk polymerizations because their chemical environments are considerably different from those of conventional organic reactions. The most notable difference is the viscosity of polymerizable resins relative to solvents that are routinely used for organic reactions. The initial viscosity of common monomers ranges from 50 to at least 1,200,000 mPa·s and increases dramatically during polymerization while that of common solvents only spans a range of 0.3 to 2.3 mPa·s.⁸² The high and increasing resin viscosities affect the behavior of the chemical reactions occurring within them.^{83,84} For instance, in a previous study we found that the high viscosity of the reaction media changed the trend of the ET reactions in thiol-ene polymerization resins by affecting reorganization energies of thiol monomers.⁸⁵ Several other studies have also observed viscosity-dependent effects on chemical reactivity.^{86–90}

The effects of viscosity on chemical reactivity result from the frictional forces imposed by the solvent shell on the solvated reacting molecules that hinder their molecular motion, including their translational, rotational and the internal degrees of freedom to distort the reactants into their TS geometries.^{83,84,91–93} The hindrance of translation and rotation slows the collision and reorientation rates of bimolecular reactions while their entropic effects impact the free energies of activation.^{84,91} Consequently, not only does high viscosity affect bimolecular reaction rates, but it also influences them by lowering translational and rotational entropies *via* reducing the number of thermally accessible translational and rotational states at a given temperature, which directly

affects the activation free energy barriers.^{84,91,92} This is the basis for the successful application of empirical corrections to the free energies calculated from quantum chemical computations where an explicit treatment of viscosity that restricts the movement of solvated reactants is impractical.^{94–99} Not accounting for the effects of high viscosity on bimolecular reaction rates generally leads to an overestimation of reaction and activation entropies and consequently, unrealistic associated free energies and reaction rates.

The empirical corrections that account for solvent viscosity adjust the free energies, for example by reducing or neglecting the entropies of certain hindered modes that should contribute less to the total entropy to remedy the overestimation. Some researchers choose to treat only the translational entropy,^{99,100} while others adjust both the translational and rotational entropies to reproduce experimental results for particular solvent conditions.^{94,95} In the present case, both approaches are utilized to analyze the reaction profiles. G_v denotes Gibbs free energies with only entropic contributions from vibrations, while G_{vr} denotes free energies that include vibrational and rotational entropies but exclude translational entropy. We hypothesize that G_v will accurately reflect the effects of highly viscous environments where translation and rotation are particularly restricted, better describing bulk resins and the increasingly greater mobility constraints imposed as polymerization progresses. In contrast, G_{vr} is intended to represent the less viscous environment of solution polymerization or the resin at the start of polymerization. In this study, both G_v and G_{vr} are reported to provide predictions of the reactions under different conditions, yet we contend that G_v better represents the bulk polymerization conditions and resin during polymerization.

2.4.3. Investigation of a Model Chemistry:

Tertiary aromatic amines and a diacyl peroxide are commonly used to activate radical redox bulk polymerization under ambient conditions.^{20,21} As such, we selected the common redox

pair of *N,N*-dimethylaniline and benzoyl peroxide to serve as a model chemistry to investigate the mechanistic details of radical generation in APRP (**Figure 2.1**). Energies and structures were calculated using density functional theory with the MN15 density functional,⁶⁰ 6-31+G(d,p) basis set,⁶¹ and the SMD solvent model,⁶⁷ which we describe in more detail in **Methods**. The redox reaction begins with the S_N2 nucleophilic attack of the O-O antibonding orbital (σ_{O-O}^*) of the peroxide by the amine lone pair (P_N^{1l}). This step involves a moderately high enthalpic barrier ($\Delta H_{S_N2}^\ddagger = 22.6$ kcal/mol) that arises mostly from the large distortion of BPO required to expose its σ_{O-O}^* orbital to the attacking P_N^{1l} , as shown in **Figure 2.1**.¹⁰¹ This distortion involves rotating the approximately co-planar phenyl rings of BPO to a nearly orthogonal conformation in the S_N2 transition state (**S_N2-TS**)⁸⁶ with a large strain energy ($\Delta H_{Distort}^\ddagger = 38.3$ kcal/mol), where a favorable interaction between the P_N^{1l} and σ_{O-O}^* orbitals lowers the enthalpic penalty by 15.7 kcal/mol.¹⁰¹ The hypothesized cyclic TS^{29,79,80} is confirmed by the predicted **S_N2-TS** geometry, which exhibits a stabilized twist-boat conformation, as shown in **Figure S2.1**.¹⁰²

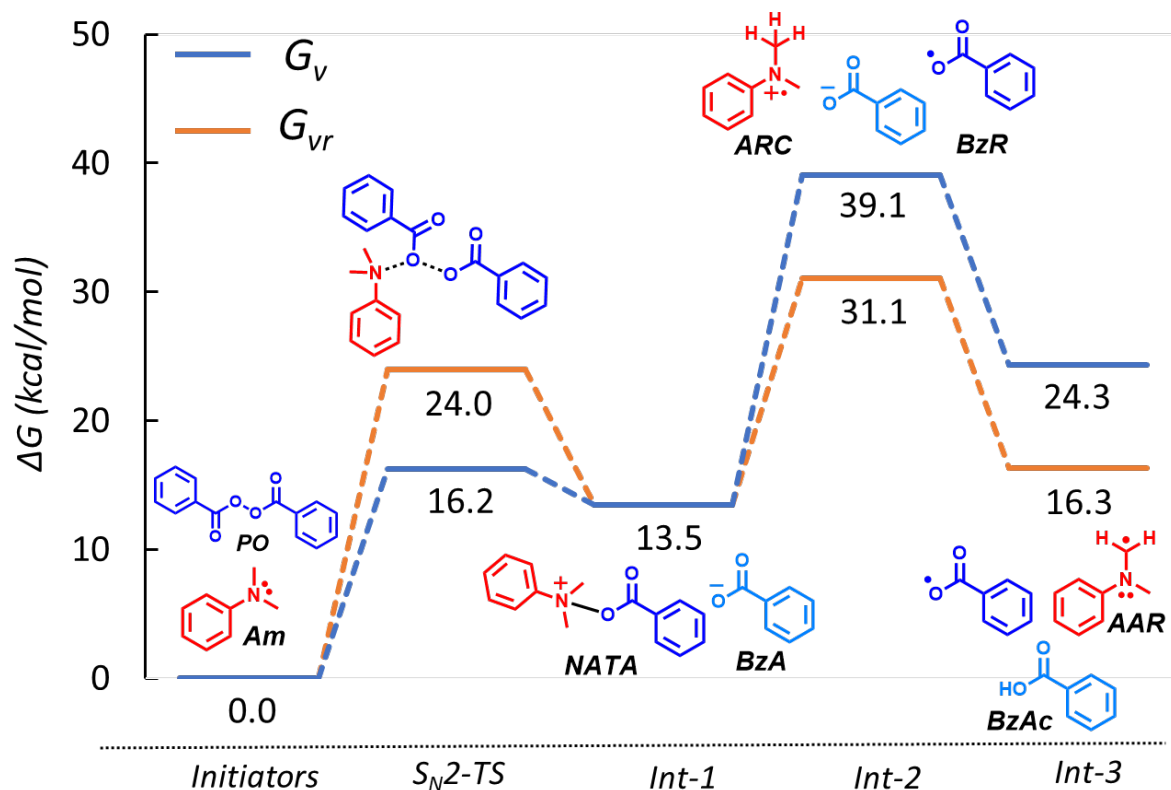


Figure 2.1. Computed schematic reaction profiles for radical generation via the redox reaction between *N,N*-dimethylaniline (DMA) and benzoyl peroxide (BPO). Relative free energies (G_v and G_{vr} at 298.15 K) are given in kcal/mol in ethyl acetate which simulates the (meth)acrylate resin. G_v (shown in blue) represents the reaction energetics in high viscosity resin while G_{vr} (shown in orange) represents the reaction energetics in low viscosity resin. The initiation is overall endergonic, whose unfavorable thermodynamics is compensated for by highly exothermic radical additions of the α -aminoalkyl radical (AAR) and benzoyloxy radical (BzR) to monomer. The trend in S_N2 and homolysis barriers depends on resin conditions, making it more difficult to identify the true rate-determining step. No transition state (TS) for homolysis between Int-1 and Int-2 was found, which we predict has a monotonic potential energy surface. The proton transfer TS between Int-2 and Int-3 lies only 3.4 kcal/mol above Int-2 and is not shown as this step is essentially barrierless.

The predicted activation barrier of S_N2 attack on the peroxide under bulk conditions is lower than under solution conditions because the number of species changes from two reactant molecules to one activated complex (**S_N2-TS**), which results in a lower relative entropic penalty for bulk polymerization ($\Delta G_{v,S_{N2}}^{\ddagger}=16.2$ kcal/mol vs. $\Delta G_{vr,S_{N2}}^{\ddagger}=24.0$ kcal/mol). This S_N2 reaction facilitates an inner-sphere ET, where the amine becomes singly oxidized to form *N*-acyloxytrialkylammonium while the leaving benzoate anion is singly reduced. The comparison of the reaction free energies in high and low viscosity regimes reveals that the entropic effect on the thermodynamics will be insignificant if the number of reactants and products remains the same and the sizes of these molecules are approximately similar ($\Delta G_{v,S_{N2}}^{\circ} \approx \Delta G_{vr,S_{N2}}^{\circ}=13.5$ kcal/mol). The endergonic nature of the S_N2 reaction leads to a reactant-favored equilibrium¹⁰³ between the starting materials and the first intermediates (**Int-1**), which is consistent with the small equilibrium constants measured experimentally using spectrophotometry.⁷⁴

After the S_N2 attack of BPO by the amine, the metastable NATA intermediate undergoes homolysis (HM) into an amine radical cation (ARC) and benzoyloxy radical (BzR), which is the first initiating radical generated from the amine-peroxide reaction. A search for the TS of the HM reaction was conducted, but no saddle point was found because the minimum energy pathway calculation resulted in a monotonic potential energy surface along the N⁺-O HM reaction coordinate from the NATA intermediate to the ARC and BzR products (**Figure 2.3**). In the *N*-acyloxytrialkylammonium equilibrium structure, the nitrogen center assumes a tetrahedral geometry with an N⁺-O bond length of 1.43 Å. As the N⁺-O bond elongates along the HM reaction coordinate, the nitrogen center gradually adopts a trigonal planar geometry concomitant with the formation of the separated ARC and BzR products. In the absence of an accompanying bond

forming event, such as in the initial S_N2 reaction, no significant stabilizing interaction exists during the HM step. As a result, structures along the HM exit channel are not stabilized to create a saddle point characteristic of a TS. Consequently, the reaction energy is the activation barrier for the homolysis step, placing it under thermodynamic control ($\Delta E_{HM}^{\circ} = \Delta E_{HM}^{\ddagger}$). In contrast to the S_N2 reaction, the HM activation free energy is larger in more viscous mediums due to the lower stabilizing entropic contribution from the more restricted translational and rotational motions ($\Delta G_{v, HM}^{\ddagger} = 25.6$ vs. $\Delta G_{vr, HM}^{\ddagger} = 17.6$ kcal/mol), as HM produces two molecules from one. Our computed activation barrier of 25.6 kcal/mol agrees with the spectrophotometrically estimated activation barrier of 25 kcal/mol.⁷⁴

The S_N2 and HM reactions produce reactive intermediates that we predict react with each other. The benzoate anion undergoes an essentially barrierless proton transfer (PT) at the α -carbon of ARC ($\Delta G_{v, PT}^{\ddagger} = 3.4$ kcal/mol) and produces benzoic acid and an α -aminoalkyl radical (AAR), which can react with a monomer.⁷⁵ The competing direct addition of ARC to a monomer is negligible due to its considerably higher barrier ($\Delta \Delta H_v^{\ddagger} \cong 10$ kcal/mol).⁷⁵ The addition of generated radicals to a monomer (AAR and benzoyloxy radical) are barrierless and highly exothermic as these are highly reactive initiating radicals ($\Delta H = -23.5$ and -31.9 kcal/mol, respectively). The rate of continuous radical addition to oligomeric active centers depends on the monomer itself, and is not significantly influenced by the initiating radicals, which we consequently did not study in detail. We observed similar behavior in a more polar environment which used acetonitrile as the solvent (See **SI2.4** for the DMA-BPO reaction coordinate profile in acetonitrile).

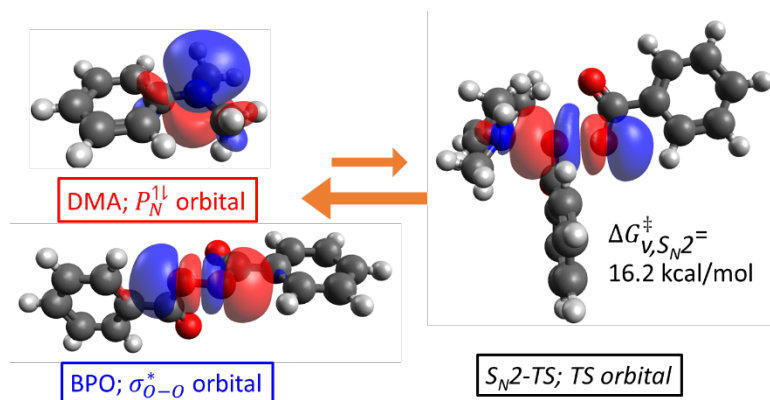


Figure 2.2. Equilibrium structures of DMA (top left) and BPO (bottom left) which react through S_N2 -TS (right). The N lone pair orbital ($P_N^{1\downarrow}$) of DMA, antibonding $O-O$ orbital (σ_{O-O}^*) of BPO, and the orbital representing N^+ -O bond formation and $O-O$ bond breaking in the TS are illustrated. Note the large distortion of BPO from its equilibrium structure to that of S_N2 -TS which results in $H_{Distort}^{\ddagger} = 38.3 \text{ kcal/mol}$.

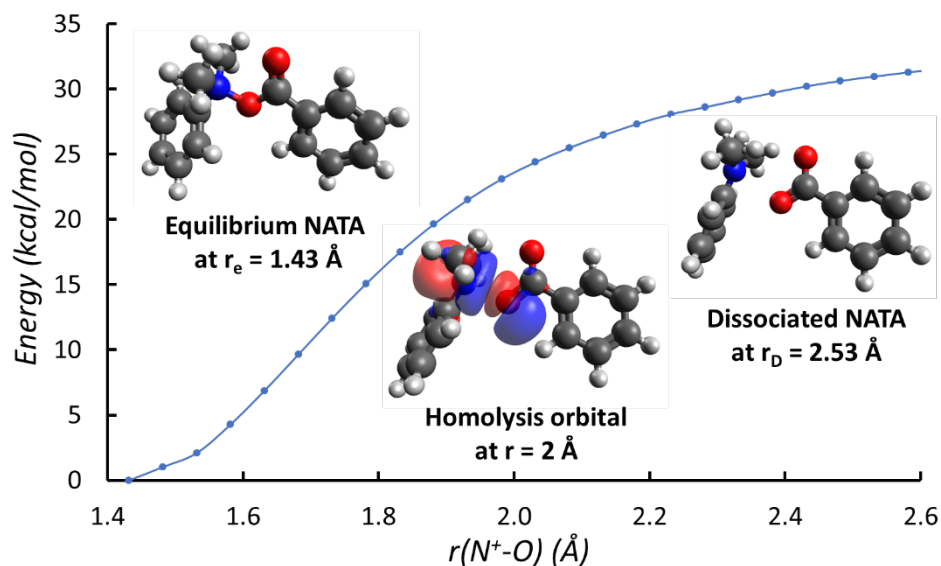


Figure 2.3. Calculated energy profile describing homolysis of N -acyloxytrialkylammonium (NATA) into the amine radical cation (ARC) and benzoyloxy radical (BzR) along the N^+ -O bond

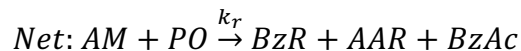
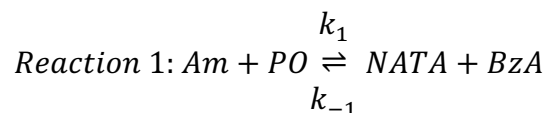
dissociation coordinate. The equilibrium structure of NATA and the homolyzed NATA are shown with the N⁺-O σ* orbital illustrated at the partially dissociated (r = 2 Å) state. Due to the lack of a stabilizing interaction, an activated TS complex cannot be found.

2.4.4 Derivation of the Kinetic Model:

The computed energetics of the redox reaction between *N,N*-dimethylaniline and benzoyl peroxide predict that either the S_N2 or homolysis reactions dictate the rate of radical generation, as the ensuing proton transfer reaction is nearly barrierless. This allowed us to derive the rate equation, k_r , that describes radical generation in APRP under the proposed inner-sphere ET mechanism (See **SI2.3** for the derivation):

$$k_r = k_2 \frac{k_1^{1/2}}{k_{-1}^{1/2}} [Am]^{1/2} [PO]^{1/2} \quad (\text{Eq. 2. 1})$$

Where the rate constants of the elementary reactions are defined by:



The rate equation k_r for radical generation (**Eq. 2. 1**) depends linearly on the homolysis rate constant (k_2), with square root dependence on the S_N2 rate constant (k_1) and with inverse square root dependence on the rate of the reverse S_N2 reaction (k_{-1}). One can obtain a similar but more complex kinetic equation by including various correction terms under the solution polymerization approximation (See **SI2.3** for the derivation). However, this could not be tested in

our bulk polymerization experiments. Because the rate equation predicts that k_r is more sensitive to k_2 than k_1 , and $\Delta G_{v, HM}^\ddagger$ is larger than $\Delta G_{v, SN2}^\ddagger$, we concluded that homolysis, with rate constant k_2 , is the rate-determining step.

We verified our kinetic equation by comparing the quantum-mechanically computed redox rates (k_r) to experimental polymerization rates (R_p) obtained from FTIR spectrometry for various amines (**Table 2.1**). Furthermore, the free radical kinetic equation (**Eq. 2.2**)^{21,56} indicates that R_p should be proportional to the square root of the redox rates ($\sqrt{k_r}$) because all other variables, $[M]$, $[P]$, $[A]$, k_p and k_t , were controlled in our experimental design, where the combined initiator efficiencies (f) of radicals generated from a redox reaction (BzR and various AARs) are assumed to be approximately equal (See **SI2.4** for justification of the initiator efficiency assumption).

$$R_p = k_p \left(\frac{fk_r}{k_t} \right)^{0.5} [M][P]^{0.5}[A]^{0.5} \propto \sqrt{k_r} \quad (\text{Eq 2.2})$$

The results of the comparison between $\sqrt{k_r}$ and R_p are plotted in **Figure 2.4** and demonstrate a clear correlation of $R^2=0.80$, even amongst structurally dissimilar amines. This suggests that computationally guided design and discovery of amine reductants for APRP may be a promising approach for developing superior APRP systems. It should be noted that hitherto reported amine reductants do not differ substantially in their initiating capability, as similar R_p were measured with these amines, excepting the never-reported reductant 4-methoxy-*N,N*-dimethyl-aniline, MDMA (see **Table 2.1** for R_p). This narrow scope of reactivity further suggests that the current level of understanding of the APRP initiation mechanism has not provided sufficient guidance to direct the discovery of amines with a range of initiating kinetics.

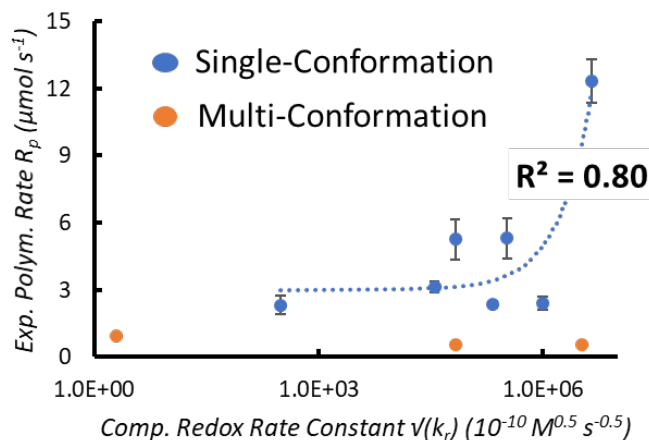


Figure 2.4. Linear correlation between experimental polymerization rates (R_p) and the square root of the computed redox rates ($\sqrt{k_r}$) on a semi-log plot. Blue dots are amines that exhibit single or degenerate conformations, whose k_r are accurately described using our calculations. This ability enables the reliable prediction of amine reactivities with BPO that can be used to guide the discovery of new amine reductants. However, the k_r of amines that exhibit a high level of non-degenerate conformations (orange dots) are not accurately predicted, as shown by the poor correlation between their R_p and $\sqrt{k_r}$. We note that these multi-conformational amines exhibit low APRP reactivities and are thus rejected within our discovery process for efficient amines.

Table 2.1. Experimental and computational kinetics results for APRP

Exp. Polym. Rate R_p ($\mu\text{mol s}^{-1}$) ^a		Comp. Redox Rates $\sqrt{k_r}$ ($M^{0.5} \text{s}^{-0.5}$) ^b
Amines with single active site conformation		
PhPy	2.4 ± 0.3	1.0×10^{-4}
DMPT	5.3 ± 0.9	3.3×10^{-5}
MDMA	12.3 ± 1.0	4.5×10^{-4}
DMPEA	2.3 ± 0.1	2.2×10^{-5}
MePy	2.3 ± 0.4	3.1×10^{-8}
DMA	3.1 ± 0.2	3.6×10^{-6}
TeMA	5.3 ± 0.9	6.8×10^{-6}
Amines with multiple active site conformations		
DEA	0.3 ± 0.1^c	3.4×10^{-4}
PhPi	0.6 ± 0.2	6.9×10^{-6}
MMP	0.9 ± 0.2	2.0×10^{-10}

^aBased on the average time for di(ethylene glycol) ethyl ether acrylate polymerization from 20% to 40% conversion at room temperature with 3 mol% amine and equivalent benzoyl peroxide to monomer, measured by FT-IR spectrophotometer ^bBased on Eyring equation computed with free energy (G_a) from MN15/6-31+G(d,p)/SMD-EtOAc ^cRate calculated from 10-20% conversion due to slow polymerization



PhPy



DMPT



MDMA



DMPEA



MePy



DMA



TeMA



DEA



PhPi



MMP

The correlation of $R^2=0.80$ between R_p and $\sqrt{k_r}$ only includes amines whose predicted rates can be accurately computed, as shown in blue in **Figure 2.4**. We found that in some cases our predicted rates k_r and the measured polymerization rates R_p correlated poorly, and then determined that this disagreement arises from the incorrect assumption of a single low-energy conformation of the reactants in the quantum-chemical computation. For instance, the inclusion of *N,N*-diethylaniline (DEA) substantially lowered the degree of correlation to $R^2=0.26$ because DEA was predicted to be substantially faster than DMA, yet was observed to be ~ 10 times slower. The two ethyl groups of DEA, located near the nitrogen reactive site, have low rotational barriers that lead to an ensemble of conformers at RT. The omission of higher energy conformations in calculating the activation free energy leads to an overestimated k_r because the participation of such conformations in the redox mechanism decreases the apparent experimental k_r and hence,

R_p. Similarly, 1-phenylpiperidine (PhPi) populates several thermally accessible cyclohexane conformations at RT and similarly exhibits an overestimated *k_r*. The inclusion of PhPi does not impact the correlation as significantly as DEA, however, as it exhibits fewer possible conformers (*R*²=0.77). Lastly, 1-phenyl pyrrolidine (PhPy), which has two degenerate conformations due to a constrained ring shows no deviation from the correlation. To account for this effect, amines with a large number of conformers accessible at RT are shown in orange in **Figure 2.4** and are excluded from the linear correlation. Interestingly, the induction times for these amines with multiple conformations are an order-of-magnitude longer than their single conformer counterparts (5-6 mins vs. < 1 min), agreeing with their low predicted APRP reactivities.

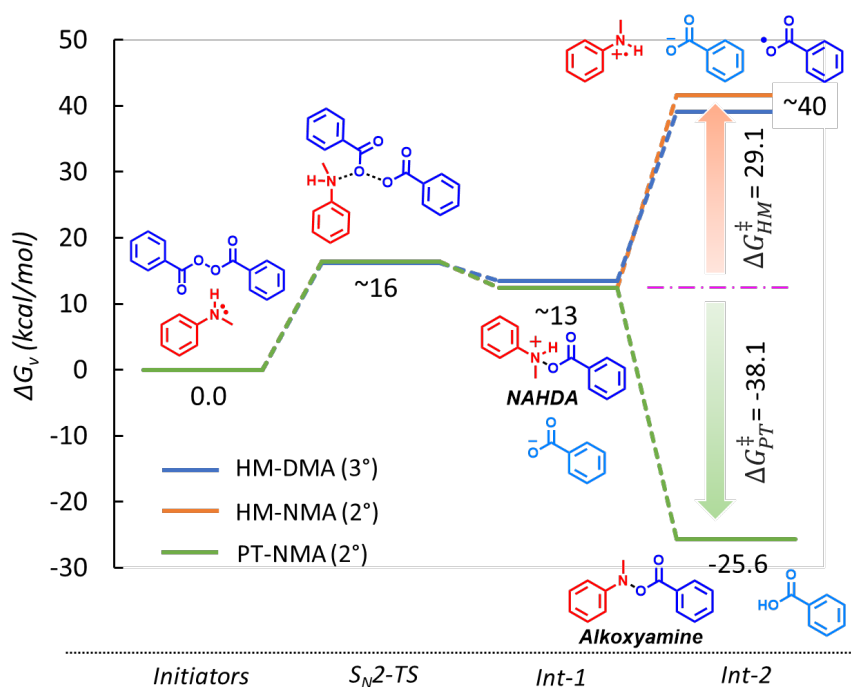


Figure 2.5. Radical generating mechanism of tertiary amine (3°, blue), and the alternate mechanism of secondary amines (2°, green) that generates no radicals. The homolysis (HM) pathways for DMA and *N*-methyl aniline (NMA) share similar energetics, showing a promise of initiating capability from NMA. However, a proton transfer (PT) mechanism in *N*-

acyloxyhydroxydialkylammonium (NAHDA) involving the acidic proton of the $\text{N}^+\text{-H}$ bond is more favorable than HM and yields a neutral alkoxyamine instead of radicals, rendering primary and secondary amines with their acidic protons ineffective amine redox initiators.

2.4.5 Exclusion of Primary and Secondary Amines:

In the search for amines that initiate APRP, researchers have examined both primary (1°) and secondary amines (2°) functionalized with alkyl/aryl groups. Despite the increased rate of BPO decomposition caused by these amines that possess N-H bonds, they were observed to act as polymerization inhibitors.^{54,104} However, researchers continue to utilize such amines to promote redox polymerization. For instance, various protected amine generators were *in situ* deprotected to release amines with N-H bonds for latent APRP.^{105–107} However, insufficient evidence of redox polymerization between the released amine and peroxide was observed, as specifically noted in a recent review.¹¹ Here, we clarify the inability of 1° and 2° amines to act as APRP redox initiators by demonstrating that they proceed through an alternate mechanism which does not lead to radical generation at RT.

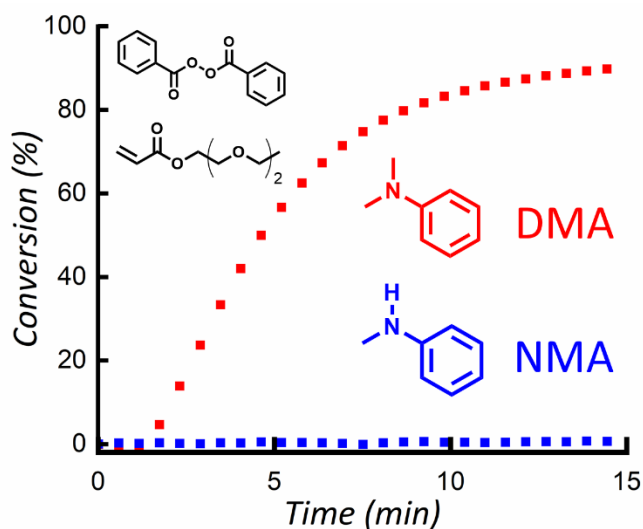


Figure 2.6. Experimental polymerization profiles of the tertiary amine, DMA, and the secondary amine, NMA, in acrylate at 3 mol% concentrations. While DMA leads to full conversion within 15 minutes, NMA produces no measurable conversion of monomer over the same time period.

To compare to our model tertiary amine, we chose the structurally similar *N*-methyl aniline (NMA) species as our model secondary amine (**Figure 2.5**). The S_N2 barriers of DMA and NMA of ~ 16 kcal/mol are nearly identical; apparently, the lack of a methyl group on NMA does not affect the interaction between the O-O antibonding orbital of the peroxide and the amine lone pair, reaffirming our claim above that the energetic requirements of the S_N2 reaction primarily stem from the distortion of BPO to the S_N2 -TS structure. The S_N2 attack on BPO by NMA produces the intermediate compound *N*-acyloxyhydroxydialkylammonium (NAHDA), the analog to NATA of tertiary amines. We predicted that homolysis of NAHDA proceeds through a high activation barrier of 29.1 kcal/mol. Alternatively, we calculated that NAHDA undergoes an alternative mechanism that involves a barrierless proton transfer from the acidic proton of the N^+ -H bond to produce the highly stable alkoxyamine species. The proton transfer in NAHDA from both 1° and 2° amines is significantly more probable than homolysis, which effectively eliminates the radical generation by these amines. Experimental support for our claim of an alternative mechanism exists in synthesis reports that utilized amines with N-H bonds and BPO to synthesize neutral alkoxyamines.^{71,108,109} The HM of the resulting alkoxyamine to generate radicals is highly unfavorable due to a large barrier which we calculate to be 48.6 kcal/mol. Consequently, the experimental polymerization rate of non-tertiary amines is imperceptibly low, as shown in **Figure 2.6**. As a result, we concluded that 1° and 2° amines are not promising candidates for APRP due

to the emergence of an alternative non-productive mechanism *via* proton transfer that leads to stable products that do not undergo homolysis.

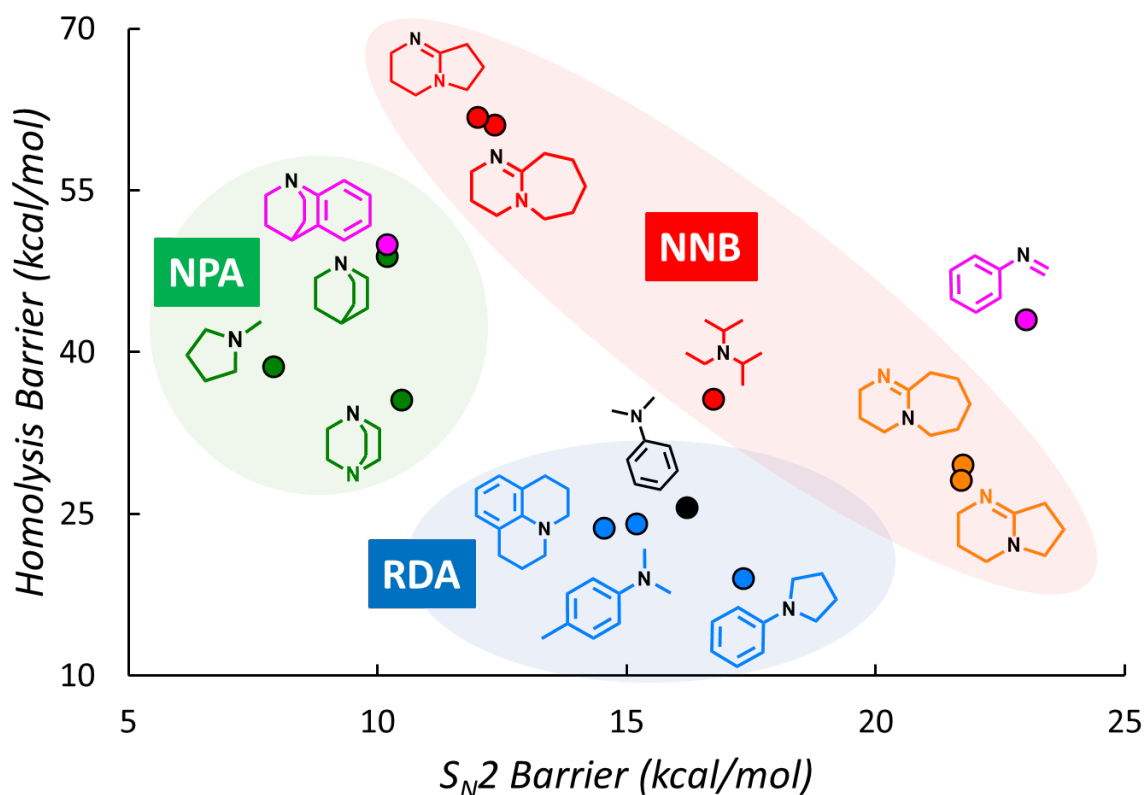


Figure 2.7. Mapping of the HM and S_N2 free energy barriers of the three amine categories (RDA, NNB, and NPA) with DMA shown in black for reference. Each amine category displays a distinct relationship between the two barriers. The reducing aromatic amines (RDA in blue) perform the best in APRP as they have the lowest barriers for the rate-determining HM step, while amines with high basicity (NNB in red) or nucleophilicity (NPA in green) are not promising for APRP due to their high HM barriers. Aromatic amines that do not have optimal orbital orientations (shown in magenta) do not follow the trend of RDA and will not perform well for APRP. Two of the NNBs have two reactive sites that result in different energetics, marked separately by red and orange. The reactive nitrogen of each amine is shown in black.

2.4.6 Tertiary Amine Candidates for APRP:

After eliminating 1° and 2° amines as potential candidates for APRP, we focused our search on tertiary amines that would act as effective redox initiators. We commenced this search by grouping tertiary amines into three categories: non-nucleophilic bases (NNB), nucleophilic amines (NPA), and reducing amines (RDA), and compared them to *N,N*-dimethylaniline as a reference. We then selected multiple amines from each category to examine their redox energetics and polymerization behaviors. For NNB, we selected *N,N*-diisopropylethylamine, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), and 1,5-diazabicyclo(4.3.0)non-5-ene, all of which are considerably stronger bases than DMA. For NPA, we selected 1-methylpyrrolidine, quinuclidine, and 1,4-diazabicyclo[2.2.2]octane, because they are highly nucleophilic nitrogenous compounds with kinetic constants for nucleophilic reactions 6-8 orders of magnitude larger than DMA.^{110,111} For RDA, we selected *N,N*-dimethyl-*p*-toluidine (DMPT), julolidine and 1-phenyl pyrrolidine (PhPy) because of their lower ionization potentials than DMA (6.93, 6.65, 6.8 eV vs. 7.44 eV, respectively).¹¹² We computationally evaluated the S_N2 and HM barriers of these nine amines within the framework of APRP with BPO as the oxidant to elucidate how different categories of amines perform as initiators. These results are summarized in **Figure 2.7**.

Non-Nucleophilic Bases NNBs undergo faster S_N2 reactions with BPO than DMA due to the higher electron densities of their amine lone pairs, while the resultant *N*-acyloxytrialkylammonium intermediate from all parent NNBs are more stable than DMA due to their greater ability to delocalize the positive charge via inductive and resonant electron donation. Furthermore, all NNBs are predicted to have higher homolysis barriers than DMA ($\Delta G_{v,HM}^{\ddagger} = 35.6 - 61.7$ vs. 25.6 kcal/mol). This is because the π -space of the phenyl ring in DMA provides stabilizing electron density to the electron-deficient half-empty p-orbital on nitrogen (P_N^{1+}) in its amine radical cation via orbital

overlap while ARCs from parent NNBS do not possess this same capacity. As a result, the higher barriers of the rate-determining HM step render NNBS poor initiators for APRP and high Brønsted basicity is not necessarily conducive to APRP. As predicted, the experimental kinetics results for NNBS show no or very slow polymerization within the same time scale over which DMA achieved full conversion (See **SI2.5** for experimental kinetics). We note that if an amine possesses non-degenerate nitrogen reactive sites, these centers will exhibit different reactivities (See **SI2.5** for a discussion of the anomalous polymerization behavior of DBU as an initiator for APRP due to two reactive sites).

Nucleophilic Amines NPAs undergo even faster S_N2 reactions than NNBS because they are effective nucleophiles that can attack electrophiles with minimal steric hindrance ($\Delta G_{v,S_N2}^\ddagger = 7.9 - 10.5$ kcal/mol). The NATA intermediate that results from S_N2 reactions of NPAs is also more stable than the NATA from DMA due to similar electron donating effects as discussed above for the NATAs resulting from NNBS ($\Delta G_{v,S_N2}^\circ = -3.0 - 0.5$ kcal/mol). Similarly, the lack of favorable orbital overlaps in amine radical cations of NPAs led to higher homolysis barriers of 35.6 – 48.9 kcal/mol, and consequently resulted in essentially no or slow polymerization (See **SI2.5**). We determined that like NNBS, NPAs with high nucleophilicity are not promising initiators for APRP (**Figure 2.7**). Furthermore, the trends of the barriers for the two rate-influencing steps, S_N2 and homolysis, for NNBS and NPAs tend to be the opposite to that of DMA. NNBS and NPAs generally have lower S_N2 barriers but higher HM barriers than DMA, implying that DMA does not belong to either the NNB or NPA class of amines.

Reducing Amines RDAs behave more similarly to DMA than to NNBS and NPAs in regard to their APRP activity with BPO. For instance, they exhibit similar S_N2 barriers. Additionally, we predicted lower stabilities of the NATA intermediates from RDAs relative to those from NNBS

and NPAs, and lower HM barriers because of RDA's superb ability to stabilize the electron-deficient half-empty p-orbital of the amine radical cation, which is commonly characterized by a low ionization potential. Because the incorporation of phenyl rings provides exceptional stabilization to the ARC to lower the activation energy of homolysis, aromatic amines, namely RDAs, are promising for APRP, especially when they are functionalized by electron donating groups that stabilize their ARCs and make them better nucleophiles.

However, not all aromatic amines are promising candidates for APRP. As mentioned above, it is paramount that the π -space of the phenyl ring overlap with the P_N^{1+} orbital of the ARC for an amine to be efficient in APRP. For instance, although benzoquinuclidine (BQC) and *N*-methylethaniline are aromatic compounds, the P_N^{1+} orbital of their respective ARC products are spatially perpendicular to the π -space of the phenyl rings, and therefore do not resonate with the amine's aromatic rings (See **Figure 2.8** for the orbital comparison of the ARCs of DMA and BQC). This resulted in high predicted homolysis barriers of 49.9 kcal/mol for BQC and 43.0 kcal/mol for *N*-methylethaniline that are nearly twice the HM barrier of DMA (magenta in **Figure 2.7**). The inability of the nitrogen P_N^{1+} orbital and the π -space of the aromatic ring of BQC to resonate is also observed in ^{13}C NMR experiments.¹¹² This new understanding further guides the search for promising amine candidates by directing the focus towards amines that are most likely to be effective in APRP.

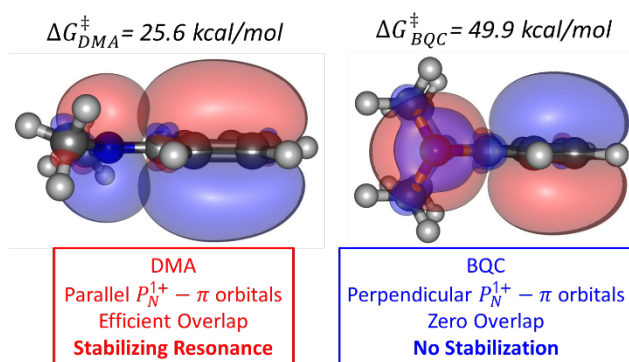


Figure 2.8. Depiction of the natural bond orbitals of the ARC of DMA (left) and benzoquinuclidine (BQC, right). The two orbitals shown for each amine are the P_N^{1+} orbital and the π orbital of the phenyl rings. Note that the P_N^{1+} and π orbitals of DMA spatially overlap to allow resonance that stabilizes the amine radical cation, whereas the P_N^{1+} and π orbitals of BQC are orthogonal and thus do not resonate. This key distinction resulted in considerably different homolysis activation barriers.

2.4.7 Systematic screening of tertiary reducing amines:

Using the insights described above, we explored the chemical space of tertiary reducing amines to identify species with highly favorable energetics and to understand the trends in their associated kinetic parameters by systematically varying their functional groups. We examined RDAs with 21 functional groups all substituted at the phenyl-*para* position while maintaining the *N,N*-dimethyl structure (See **SI2.6**). The *para* position was chosen to maintain consistency between the substitutions and to reduce complexity. A substitution at both *meta* positions was found to be no more advantageous than one substitution at the *para* substitution, for example as shown for *N,N*,3,5-tetramethylaniline (TeMA) vs. *N,N*-dimethyl-*p*-toluidine (DMPT) in **Table 2.1**. As HM influences the redox kinetics most significantly, we primarily investigated the effects of substitutions on the HM barrier. The results of these calculations in comparison to *N,N*-dimethylaniline are highlighted in **Figure 2.9**.

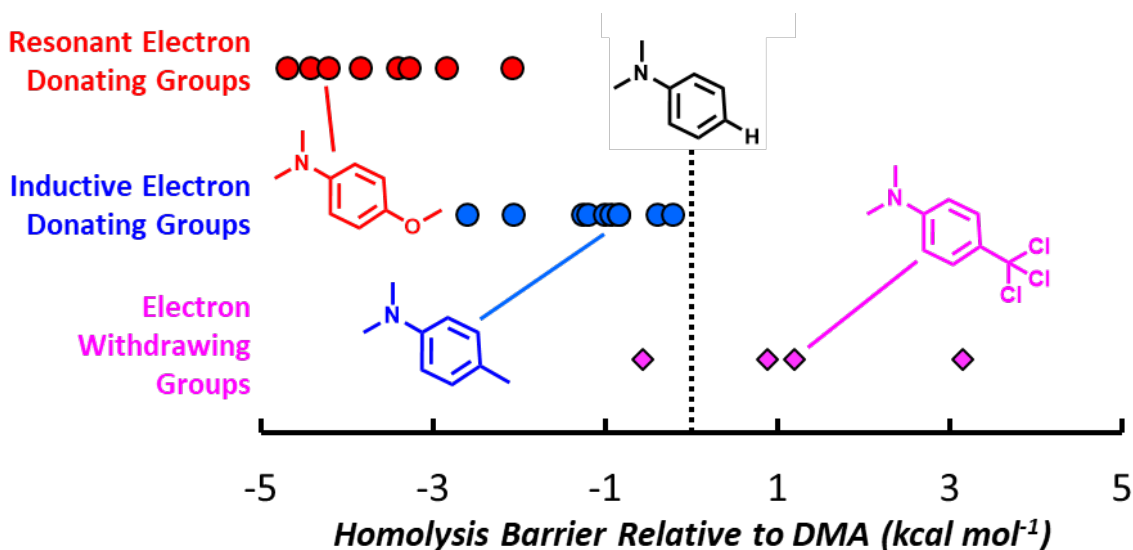


Figure 2.9. Homolysis barriers for *para*-substituted *N,N*-dimethyl aniline derivatives. Substitutions with electron donating groups (EDG) resulted in lower HM barriers while those with electron withdrawing groups (magenta) resulted in higher HM barriers, compared to hydrogen substitution (DMA in black center line). Resonant EDGs (red) lower HM barriers more than inductive EDGs (blue).

The ability to donate electron density to the electron-deficient half-empty p-orbital of the amine radical cation is crucial to lowering the homolysis barrier. As expected, substitutions with electron donating groups (EDG) at the phenyl-*para* position led to lower HM barriers and EDGs that resonate with the π -space of the phenyl rings performed best, i.e. vinyl and methoxy substitutions (red in **Figure 2.9**). Additionally, the barrier-lowering effect from resonating EDGs also extends to the S_N2 barriers by increasing the electron density of the amine lone pair, rendering these amines better nucleophiles ($\Delta G_{v,SN2}^\ddagger = 13.2$ kcal/mol for *p*-methoxy vs. 16.2 kcal/mol for DMA). These barrier differences led to a significant change in the experimental R_P ; the R_P s for 4-methoxy-*N,N*-dimethyl-aniline (MDMA) and DMA were measured via real-time FTIR to be 12.3

± 1.0 and $3.1 \pm 0.2 \mu\text{mol s}^{-1}$, respectively (**Table 2.1**). Inductive EDGs (blue in **Figure 2.9**) such as n-butyl- and methyl- groups performed better than hydrogen (i.e. DMA), although the barrier-lowering effects on either reaction step are not as pronounced as with resonating EDGs. We note that although a hydroxy group was computed to perform similarly to a methoxy group due to the resonance character of the EDG, the former would act as a phenolic inhibitor in radical polymerization and thus should not be used within the context of APRP.^{113,114} Because the *para* substitution does not sterically hinder the $\text{S}_{\text{N}}2\text{-TS}$ and thus *N*-acyloxytrialkylammonium formation, it appears that EDGs substituted at the *para* position generally increase R_{P} . On the other hand, the largest HM barriers were predicted for RDAs with electron withdrawing group (EWG) substitutions such as nitro- and trichloromethyl- groups (magenta in **Figure 2.9**). The trend within EWGs is similar to that of EDGs in that resonating EWGs affect the HM barrier more than inductive EWGs. Furthermore, 40 functional groups with symmetric and asymmetric *N*-substitutions were studied, however they are not discussed in detail here due to the observation that our computational method does not correctly predict the APRP behavior of some *N*-substituted amines due to their possession of multiple conformations (See **SI2.6** for a further discussion of *N*-substituted amines). Nonetheless, some notable exceptions with single or degenerate conformers are worth discussing.

Within our computational study of *N*-substitutions, the pyrrolidine-substitution appears to be optimal, likely due to its higher electron density $P_{\text{N}}^{1\downarrow}$ lone pair and lower steric hindrance than that produced by diethyl-substitution. In contrast, we found that heteroaromatic *N*-substitutions, like pyrrole on the structurally-similar 1-phenylpyrrole, overly stabilize $P_{\text{N}}^{1\downarrow}$ such that the lone pair is insufficiently nucleophilic to readily participate in the $\text{S}_{\text{N}}2$ reaction with an essentially insurmountable $\text{S}_{\text{N}}2$ barrier at RT ($\Delta G_{v,\text{S}_{\text{N}}2}^{\ddagger} = 40.5 \text{ kcal/mol}$). We confirmed this computational

result experimentally (see **SI2.5**), again demonstrating the ability of quantum chemical modeling within our APRP mechanistic framework to predict APRP behavior. Further experimental investigation of other *N*-substituted DMA-derivatives was not conducted. Overall, we concluded that EDGs, especially those exhibiting resonance at the *para*-position increased R_p . Furthermore, as expected and noted in the above discussion, minimal steric hindrance surrounding the reacting nitrogen leads to higher R_p . These insights were the inspiration for our hypothesis that *N*-(4-methoxyphenyl)pyrrolidine (MPP) would act as a competent amine reductant with improved polymerization kinetics. To test this hypothesis we computed the S_N2 and HM barriers for MPP and predict that it should indeed be exceptionally fast for APRP with predicted barriers of $\Delta G_{v,SN2}^\ddagger = 13.1$ kcal/mol and $\Delta G_{v,HM}^\ddagger = 15.1$, resulting in an exceptional redox rate of $\sqrt{k_r} = 1.9 \times 10^{-2}$ in APRP with BPO.

Pursuing our supposition that MPP would exhibit desirable polymerization kinetics as predicted by our quantum chemical calculations, we synthesized and tested its performance against three amines that are currently used by industry for APRP and that are generally believed to be the most efficient amines for APRP. Specifically, we examined 2-[4-(dimethylamino)phenyl]ethanol (DMPEA), DMPT, and 2,2'-(4-methylphenylimino)diethanol. These amines all perform at least as well as our model amine, DMA (**Table 2.1**). Polymerization induced by MPP proceeded too rapidly under the previous reaction conditions (those used in **Figure 2.6** and **Table 2.1**) to make analysis of its performance tractable. Hence, we lowered its concentration from 3 mol% to 0.48 mol% and used a methacrylate monomer which polymerizes more slowly than acrylates. Furthermore, we incorporated a crosslinking dimethacrylate comonomer for a practical demonstration that better mimics resins used in dental applications. The results presented in **Figure 2.10** demonstrate that MPP initiates APRP significantly faster ($\sim 20\times$) than the three currently used

amines under these conditions. After 20 minutes, MPP achieves more than 50% conversion while the other amines only slowly approach 3% conversion. Thus, MPP and potentially other computationally designed amines for APRP promise to allow novel applications that require very rapid polymerization rates under conditions that preclude thermal or photo- polymerization. The striking difference in polymerization rates also suggests that APRP initiated by MPP can be utilized at an order of magnitude lower initiator concentrations, potentially enabling unrealized opportunities that APRP has yet to achieve. Furthermore, because these amines achieve optimal polymerization rates for current applications at reduced initiator concentrations, they may grant aesthetic, mechanical, biocompatibility, and economic advantages over currently employed amines. We contend that these results represent an excellent demonstration of how a detailed understanding of the reaction chemistry, together with computational screening directed by that understanding, can guide and accelerate the discovery of new APRP chemistries.

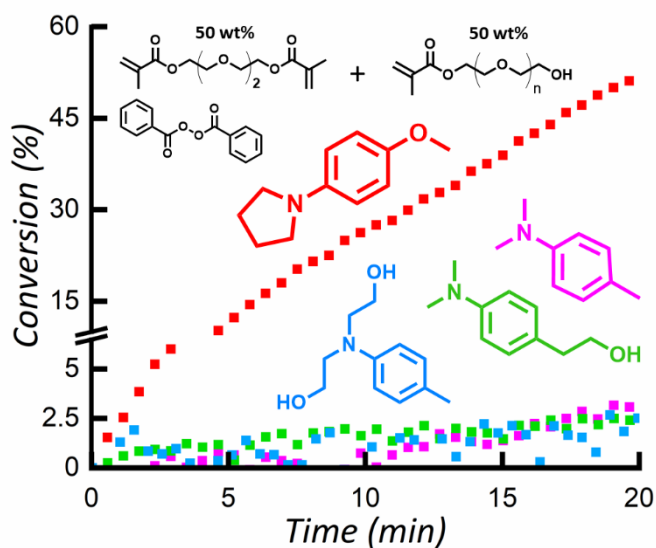


Figure 2.10. Performance of *N*-(4-methoxyphenyl)pyrrolidine (MPP) in red, which was discovered through computational screening of amines for APRP in comparison to amines currently used in industry in magenta, green, and blue. MPP significantly outperforms the others.

Experimental conditions regarding concentration and monomers were changed to accommodate the unprecedented initiating capability of MPP at 0.48 mol% concentrations in methacrylate resin.

2.5 Conclusions

In this work, we have presented the results of an extensive computational and experimental investigation of the mechanism of the widely used amine-peroxide redox polymerization process. We used quantum chemistry to compute the initiation kinetics of a common redox pair, *N,N*-dimethylaniline and benzoyl peroxide, which allowed for the determination that homolysis is the rate-determining step, in disagreement with the prevailing conclusions in this field. Using our new detailed understanding of the mechanism and its associated energetics, including those of the intermediates, we derived a kinetic equation that we then used to correlate computational and experimental kinetic results with $R^2=0.80$ among structurally dissimilar amines. Our results also elucidate that primary and secondary amines do not promote redox polymerization because they proceed through a more favorable alternative proton transfer mechanism that does not generate initiating radicals. To discover more effective amines for redox polymerization, we examined different types of tertiary amines and found that aromatic amines with resonant electron-donation and minimal steric hindrance outperformed other nucleophilic amines and non-nucleophilic basic amines, where conjugation between the electron-deficient half-empty p-orbitals of nitrogen and the π -space of their phenyl rings in their amine radical cation intermediate states effectively lowers the rate-determining HM barrier. Finally, we conducted a small-scale computational and experimental screening effort on various *para*- and *N*-substitutions on such aromatic amines to identify *N*-(4-methoxyphenyl)pyrrolidine (MPP) as an APRP amine that exhibits unprecedented reactivity for redox polymerization relative to other “state-of-the-art” amines.

This demonstration of applying quantum chemical methods for predicting the reactivity of amines in APRP unlocks an array of opportunities to efficiently search the vast chemical space of amines to discover novel amines with desirable properties for redox polymerization. For example, the discovery of amines with high reactivity may allow rapid *in situ* polymerization that can be utilized to promote chemically-induced additive manufacturing or spray-coating of large structures in the automotive and aerospace industries. Additionally, amines that possess fast initiation kinetics, such as MPP, can be used at low concentrations, which enhances important biomaterials applications for developing polymers with low toxicity, better aesthetics, and superior mechanical properties, or simply accelerates current manufacturing applications. This study provides a valuable fundamental framework to practitioners to guide the discovery and optimization of initiating systems for their specific applications, as well as providing a framework for other researchers to investigate similar polymerization processes and inner-sphere electron transfer involving organic compounds.

2.6 Supporting Information

SI2. 1. Benchmarking of Computational Methods

We conducted a benchmarking study to identify density functional theory (DFT) functionals that would reproduce the reaction energetics calculated with the accurate, but highly computationally demanding CBS-QB3 and CCSD levels of theory. The reactions considered within the scope of benchmarking were the S_N2 and homolysis (HM) reactions that have relatively high activation barriers and therefore determine the radical generation rates. *N,N*-dimethylaniline (DMA) and benzoyl peroxide (BPO) serve as the model chemistry in the main text and thus we employed the

same model chemistry for the benchmarking study. The density functionals were considered based on their good performance in predicting the energetics of organic systems.¹¹⁵ We referenced them against the CCSD^{64,65,116} and CBS-QB3^{62,63} methods that produce highly accurate energy profiles. (**Tables 2.1** and **2.2**). In both comparisons, the MN15⁶⁰ density functional performed the best of the considered functionals; it produced the lowest root mean square error (RMSE) of 1.5 kcal/mol against CBS-QB3 and 2.4 kcal/mol against CCSD. The RMSE of other functionals are 2-9 times larger than those of MN15. The superior performance of MN15 may be due to its ability to describe states with both single- and multi-reference character, which is important because the TS1 complex and radical products involved in the reactions considered in the benchmarking study are predicted to have multi-reference character according to the T1 diagnostic, as shown in **Table 2.3**.¹¹⁷ Therefore, it is important to choose a functional that achieves simultaneous accuracy for both single- and multi-reference systems. The MN15 density functional was specifically developed for the purpose of robustly predicting the energy of systems with either single- or multi-reference character accurately by balancing the inclusion of non-local exchange to overcome delocalization error with the adverse effects of treating static correlation using an orbital-dependent hybrid functional. After confirming a small sensitivity of MN15 energies to the basis set, MN15/6-31+g(d,p)⁶¹ was selected and used throughout the study in conjunction with the SMD solvation model⁶⁷ of ethyl acetate, which was chosen for its structural similarity to the acrylate and methacrylate monomers.

Table S2.1. RMSE (kcal/mol) in electronic energies of density functionals against the CCSD reference.

	TS1	Int1	Int2	RMSE
CBS-QB3	6.2	-1.9	-3.2	2.7

APFD	8.0	-3.5	4.9	5.8
B3LYP	10.0	-2.2	9.0	7.9
BMK	-7.1	-3.0	6.0	5.6
LC-wHPBE	-15.4	-5.3	4.5	9.7
M06	2.2	-4.6	5.7	4.4
M062X	-5.0	-2.8	-5.9	4.7
M08HX	-3.7	-1.9	-6.3	4.4
M11	-5.1	1.2	-7.2	5.2
MN15	-1.0(-2.0)	-3.3(-3.7)	-2.4(-2.9)	2.4(3.0)
PBE0	4.3	-3.6	5.5	4.5
SOGGA11X	-8.9	-4.4	6.4	6.8
TPSSH	5.8	-6.2	14.9	9.9
wB97XD	-1.3	-2.3	4.6	3.1

DFT energies were calculated with the 6-311+g(d,p) basis set and CCSD with Energies are reported in kcal/mol. Values in parenthesis are calculated with the 6-

Table S2.2. RMSE (kcal/mol) of enthalpies (H) and Gibbs free energies (G) of density functionals against the CBS-QB3 reference.

	H(Int1)	G(Int1)	H(Int2)	G(Int2)	RMSE
APFD	-1.6	-1.4	8.3	8.3	6.0
B3LYP	-0.3	-0.1	12.4	12.4	8.8
BMK	-1.0	-0.6	10.7	11.1	7.7
LC-wHPBE	-3.3	-3.3	8.7	9.1	6.7
M06	-2.1	-2.0	9.3	9.4	6.8
M062X	-0.7	-0.3	-1.8	-1.6	1.3
M08HX	0.2	0.8	-2.2	-1.7	1.5
M11	3.1	3.5	-1.9	-0.9	2.6
MN15	-1.3 (-1.7)	-0.8 (-1.3)	1.6 (1.0)	2.0 (1.5)	1.5 (1.4)
PBE0	-1.6	-1.4	9.1	9.3	6.6
SOGGA11X	-2.5	-2.2	10.8	11.2	8.0
TPSSH	-4.2	-4.1	18.0	18.1	13.1
wB97XD	-0.5	-0.5	8.3	8.3	5.9

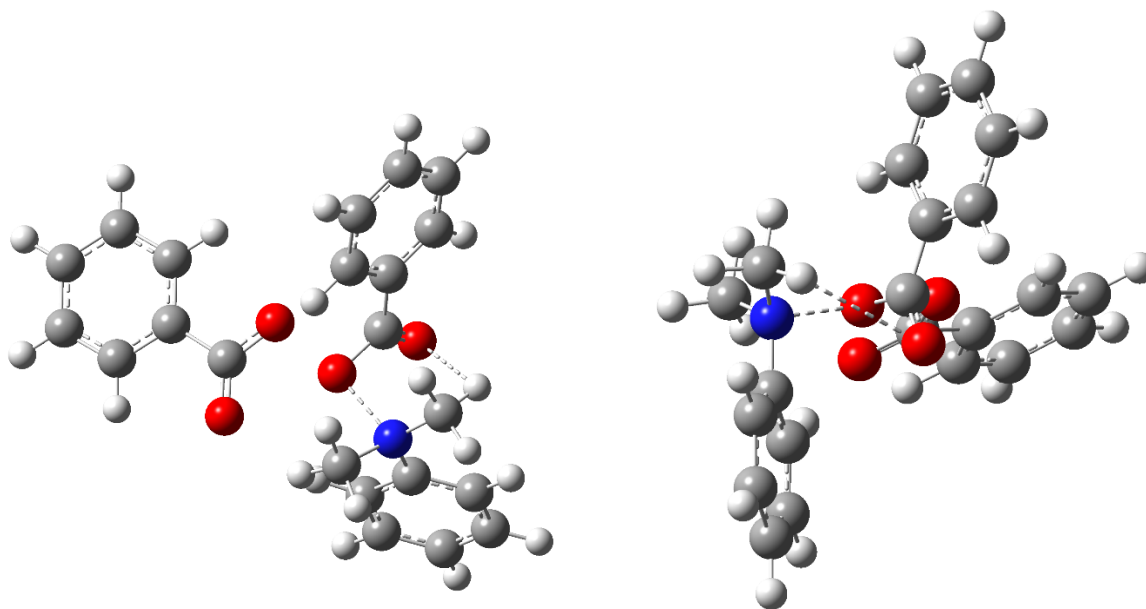
DFT energies are calculated with the 6-311+g(d,p) basis set. Energies are reported in kcal/mol. Values in parenthesis are calculated with the 6-31+g(d,p) basis set.

Table S2.3. T1 Diagnostic values of molecules involved in DMA-BPO reactions

	T1 Value	Diagnostic
DMA	0.012	
BPO	0.016	
TS1	0.023	
NATA	0.014	
Benzoate anion	0.016	
Benzoyloxy Radical	0.020	
Amine Radical		
Cation	0.033	

If the value of T1 is greater than or equal to 0.02, the system is likely to be multi-reference.

SI2.2. Calculated Cyclic Transition State Structure



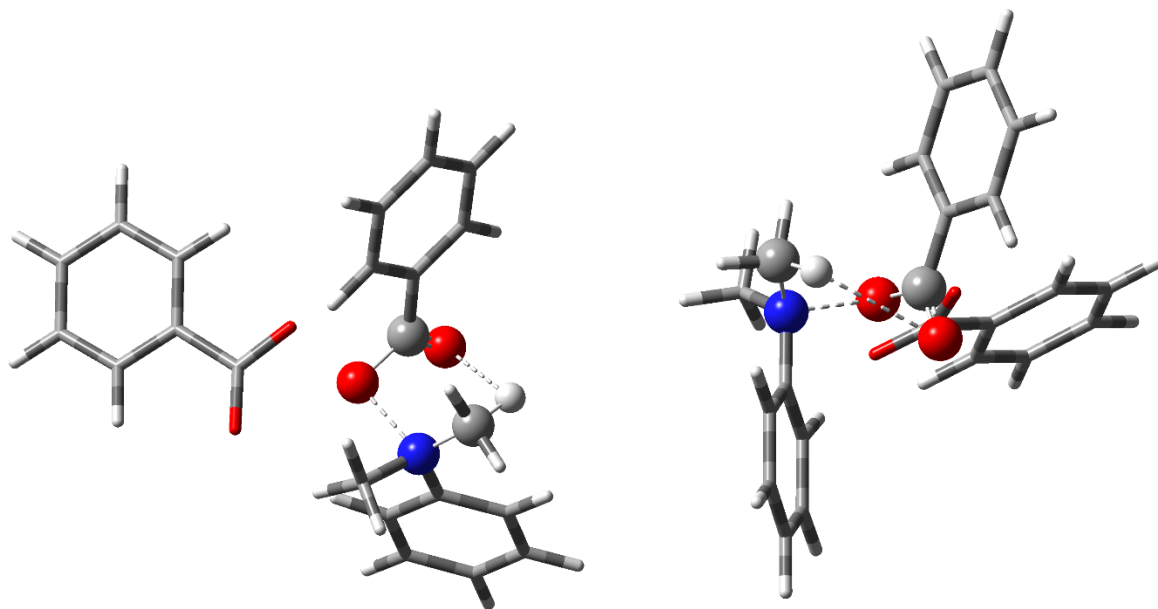
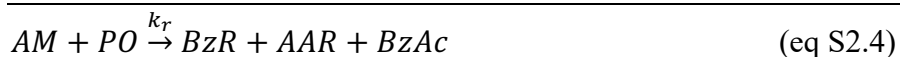


Figure S2.1. Top and side views of the S_N2 transition state (TS) geometries of the reaction between DMA and BPO. The predicted TS involves a twisted boat conformation.

SI2.3. Derivation of the Kinetic Equation

We derive the rate constant for BzAc and AAR production as follows. The elementary reactions are defined by:



Am = Amine, PO = Peroxide, NATA = N-Acyloxytrialkylammonium cation, BzA = Benzoate anion, BzR = Benzoyloxy radical, ARC = Amine radical cation, AAR = α -aminoalkyl radical, BzAc = Benzoic acid

Solution 1. In highly viscous solution

Within the bulk polymerization regime, we assume that Am + PO and NATA + BzA are in equilibrium¹⁰³ due to the high barrier of the HM reaction that prevents **Int-1** (NATA and BzA) from being quickly depleted ($k_2 \ll k_1 \ll k_{-1}$); our assumption of equilibrium formation is confirmed spectrophotometrically.^{74,103} This results in:

$$K_1 = \frac{[NATA][BzA]}{[Am][PO]} = \frac{k_1}{k_{-1}} \quad (\text{eq S2.5})$$

Rearranging equation eq S2.5 yields:

$$k_{-1}[NATA][BzA] = k_1[Am][PO] \quad (\text{eq S2.6})$$

While the material balance between intermediates yields:

$$[NATA] + [ARC] = [BzA] \quad (\text{eq S2.7})$$

The PA reaction is barrierless and much faster than HM ($k_2 \ll k_3$), so that $[ARC] \ll [NATA]$,

$$[NATA] = [BzA] \quad (\text{eq S2.8})$$

Substituting eq S2.8 into eq S2.6 yields:

$$k_{-1}[NATA]^2 = k_1[Am][PO] \quad (\text{eq S2.9})$$

Solving eq S2.9 for $[NATA]$ and substituting eq S2.5 yields:

$$[NATA] = \sqrt{\frac{k_1}{k_{-1}} [Am][PO]} = \sqrt{K_1 [Am][PO]} \quad (\text{eq S2.10})$$

Under the quasi-steady-state approximation (QSSA) of intermediates we have:

$$\frac{d[ARC]}{dt} = k_2[NATA] - k_3[BzA][ARC] = 0 \quad (\text{eq S2.11})$$

Substituting eq S2.10 into eq S2.11 yields:

$$k_2\sqrt{K_1[Am][PO]} = k_3[BzA][ARC] \quad (\text{eq S2.12})$$

The rate equation (k_r) of interest is related to production of BzAc and AAR:

$$k_r = \frac{d[BzAc]}{dt} = \frac{d[AAR]}{dt} = k_3[BzA][ARC] \quad (\text{eq S2.13})$$

Finally, substituting eq S2.13 into eq S2.12 results in:

$$k_r = k_2\sqrt{K_1[Am][PO]} = k_2K_1^{1/2}[Am]^{1/2}[PO]^{1/2} = k_2\frac{k_1^{1/2}}{k_{-1}^{1/2}}[Am]^{1/2}[PO]^{1/2} \quad (\text{eq S2.14})$$

Eq S2.14 indicates that the radical generation rate (k_r) is first-order and proportional to the rate constant of homolysis (k_2) and half-order in the rate constant of the S_N2 reaction (k_1), while it is inversely proportional to the reverse S_N2 reaction (k_{-1}).

Solution 2. In less viscous solution

A material balance between intermediates yields:

$$[NATA] + [ARC] = [BzA] \quad (\text{eq S2.7})$$

The PA reaction is barrierless and much faster than HM ($k_2 \ll k_3$), so that $[ARC] \ll [NATA]$,

$$[NATA] = [BzA] \quad (\text{eq S2.8})$$

In less viscous solution, $k_1 < k_2$ therefore $Am + PO$ and $NATA + BzA$ are not in equilibrium.

Under the QSSA:

$$\frac{d[NATA]}{dt} = k_1[Am][PO] - k_{-1}[NATA][BzA] - k_2[NATA] = 0 \quad (\text{eq S2.15})$$

Substituting in for BzA using eq S2.8 yields:

$$\frac{d[NATA]}{dt} = k_1[Am][PO] - k_{-1}[NATA]^2 - k_2[NATA] = 0 \quad (\text{eq S2.16})$$

And rearranging eq S2.16 into a quadratic form and solving it using the quadratic formula yields:

$$k_{-1}[NATA]^2 + k_2[NATA] - k_1[Am][PO] = 0 \quad (\text{eq S2.17})$$

$$[NATA] = \frac{-k_2 \pm \sqrt{k_2^2 + 4k_{-1}k_1[Am][PO]}}{2k_{-1}} \quad (\text{eq S2.18})$$

Because $[NATA]$ has to be larger than 0, the square root has to be positive. Therefore, eq S2.18 becomes:

$$[NATA] = \frac{-k_2}{2k_{-1}} + \sqrt{\frac{k_2^2 + 4k_{-1}k_1[Am][PO]}{4k_{-1}^2}} \quad (\text{eq S2.19})$$

Rearranging eq S2.19 yields:

$$[NATA] = \frac{-k_2}{2k_{-1}} + \sqrt{\frac{k_2^2}{4k_{-1}^2} + \frac{4k_{-1}k_1[Am][PO]}{4k_{-1}^2}} \quad (\text{eq S2.20})$$

Rearranging eq S2.20 yields an expression for $[NATA]$:

$$[NATA] = \frac{-k_2}{2k_{-1}} + \sqrt{\frac{k_2^2}{4k_{-1}^2} + K_1[Am][PO]} \quad (\text{eq S2.21})$$

Under the QSSA approximation in less viscous solutions ($k_1 < k_2$),

$$k_r = \frac{d[BzAc]}{dt} = \frac{d[AAR]}{dt} = k_3[BzA][ARC] = k_2[NATA] \quad (\text{eq S2.22})$$

Substituting eq S2.21 into eq S2.22 yields:

$$k_r = \frac{-k_2^2}{2k_{-1}} + k_2 \sqrt{\frac{k_2^2}{4k_{-1}^2} + K_1[Am][PO]} \quad (\text{eq S2.23})$$

Eq S2.23 indicates a similar relationship for k_r as given by eq S2.14 that was derived under the highly viscous solution approximation. In eq S2.23, k_r is more sensitive to k_2 than k_1 .

SI2.4. Justification of the Initiator Efficiency Assumption

Each amine-peroxide redox reaction can produce an α -aminoalkyl radical (AAR) and a benzoyloxy radical (BzR) that initiate radical polymerization and are observed at the chain ends of polymers.⁷⁵ When deriving our kinetic equation, we assumed that the initiator efficiencies, namely the combined efficiency of AAR (f_{AAR}) and of BzR (f_{BzR}), are a constant between various redox pairs. As BzR is produced in every redox reaction with benzoyl peroxide, a potential violation of our initiator efficiency assumption revolves around whether the efficiency of AARs generated from different amines are the same. In short, if various AARs have a similar initiation efficiency, then our kinetic equation is applicable to a wide range of redox pairs. The following data suggest that this assumption is valid.

Although initiator efficiency is determined by a multitude of factors that depend on the specifics of the polymerization environment, we only focus on two components that are highly dependent on the identity of the primary radicals, while the remaining factors are essentially constant in the same polymerization environment. The cage recombination efficiency (F_c) is a result of the radical cage effect where a pair of radical product molecules remain in near contact for a short period of time due to the surrounding solvent molecules before they either recombine or diffuse away from each other.⁸⁹ F_c indicates how many radicals escape the solvent cage to add to monomer before geminate termination occurs. Additionally, the energetics of AAR radical addition to monomer differentiates the likelihood of each AAR adding to monomers after escaping the solvent cage.

According to Tyler and coworkers, F_c is proportional to the square root of mass over the radius squared ($F_c \propto \sqrt{\text{mass}/\text{radius}^2}$).^{89,118} We computed radii of AARs via the Monte-Carlo method based on their electronic density calculated at the MN15/6-31+g(d,p)/SMD-EtOAc level

of theory. As expected from the similar mass and size of amines studied, we found that a proportionality of ~ 0.6 was found for every AAR studied (**Table S2.4**). However, we also found that the dipole moments of these molecules differ substantially, which affects the degree of the potential electrostatic interaction between AARs and the surrounding solvent.⁸⁹ Despite this, we determined that such dipole interactions will be minimal in relatively non-polar monomer resins. As a result, we concluded that the main requirement of cage recombination efficiencies was sufficiently supported.

Table S2.4. Masses and radii of various α -aminoalkyl radical (AAR) with their dipole moments.

The cage recombination efficiency is proportional to $\sqrt{mass}/radius^2$ and found to be similar in the AARs we studied. The effect of dipole interactions between AARs and monomers should be marginal due to the non-polar nature of monomers.

AAR	Mass (g/mol)	Radius (Å) ^d	$\frac{\sqrt{mass}}{radius^2}$ ^e	Dipole Moment (Debye) ^f
PhPy ^a	147.2	4.4	0.6	2.5
DMPT	135.2	4.5	0.6	1.7
MDMA	151.2	4.6	0.6	3.1
DMPEA	165.2	4.7	0.6	3.0
MePy_Me ^b	85.2	3.9	0.6	2.4
MePy_Pyr ^c	85.2	4.0	0.6	1.0
DMA	121.2	4.3	0.6	1.9
TeMA	149.2	4.7	0.5	1.6
MPP	177.2	4.8	0.6	1.3

^aRadical at the alpha position, as it is 14 kcal/mol more stable than radical at the beta position. ^bRadical at the methyl position. ^cRadical at the alpha-pyrrolidine position. ^dComputed via Monte-Carlo sampling at MN15/6-31+g(d,p)/SMD-EtOAc. ^eProportionality constant for the cage recombination efficiency. ^fCalculated at MN15/6-31+g(d,p)/SMD-EtOAc.

For the second requirement of our initiator efficiency assumption, we studied reaction and activation free energies of various AARs adding to monomer (**Table S2.5**). The reaction free energies range from -28.1 to -31.0 kcal/mol and reaction enthalpies from -22.7 to -23.7 kcal/mol. Considering standard enthalpy of polymerization of a methacrylate is -13.1 kcal/mol, addition of AARs to monomers should be even faster.²⁹ Because we are studying reactions of the same family, we can apply Bell-Evans-Polanyi principle and draw a qualitative conclusion that AARs we

studied would add to monomers with similar activation barriers.¹¹⁹ Without fail, activation barriers were found to be nearly identical among a select few AARs. The similarity in the energetics are attributed to comparable spin densities on the alpha carbon of the AARs in the singly occupied molecular orbital (SOMO) of similar energies. The minimal effect of substituent effects on radical reactivity is starkly contrasted with a wide range of substituent effects on initiation reactivity, as described in the manuscript. With the second requirement fulfilled, we implemented the initiator efficiency assumption with confidence.

Table S2.5. Monomer addition energetics of various α -aminoalkyl radical (AAR) with ethyl methacrylate with spin densities and SOMOs of AARs. The energetics between AARs are very similar, indicating that they will react with monomers at a similar rate. The similarity of such reactivities can be ascribed to the similar spin density and their singly occupied molecule orbital (SOMO) energies.

AAR	G _v (kcal/mol)	H (kcal/mol)	Spin Density ^d	SOMO (eV)
PhPy ^a	-29.8	-23.7	0.76	-4.4
DMPT	-29.7 (-8.2)	-23.3 (-2.6)	0.78	-4.5
MDMA	-29.7 (-8.4)	-23.1 (-2.7)	0.77	-4.4
DMPEA	-31.0 (-8.7)	-23.4 (-2.6)	0.78	-4.6
MePy_Me ^b	-28.8	-22.7	0.76	-4.3
MePy_Pyr ^c	-28.1	-23.2	0.80	-4.3
DMA	-29.8 (-8.1)	-23.4 (2.5)	0.78	-4.6
TeMA	-29.0	-23.3	0.78	-4.5

All energies were calculated at MN15/6-31+g(d,p)/SMD-EtOAc. G_v and H are reaction energies while Parenthetical values are activation energies ^aRadical at the alpha position, as it is 14 kcal/mol more stable than radical at the beta position. ^bRadical at the methyl position. ^cRadical at the alpha-pyrrolidine position, only 1.5 kcal/mol more stable than MePy_Me. ^d Natural population analysis (version 3.1) as implemented in Gaussian 16.

SI2.5. DMA-BPO Reaction Coordinate Profile in Acetonitrile

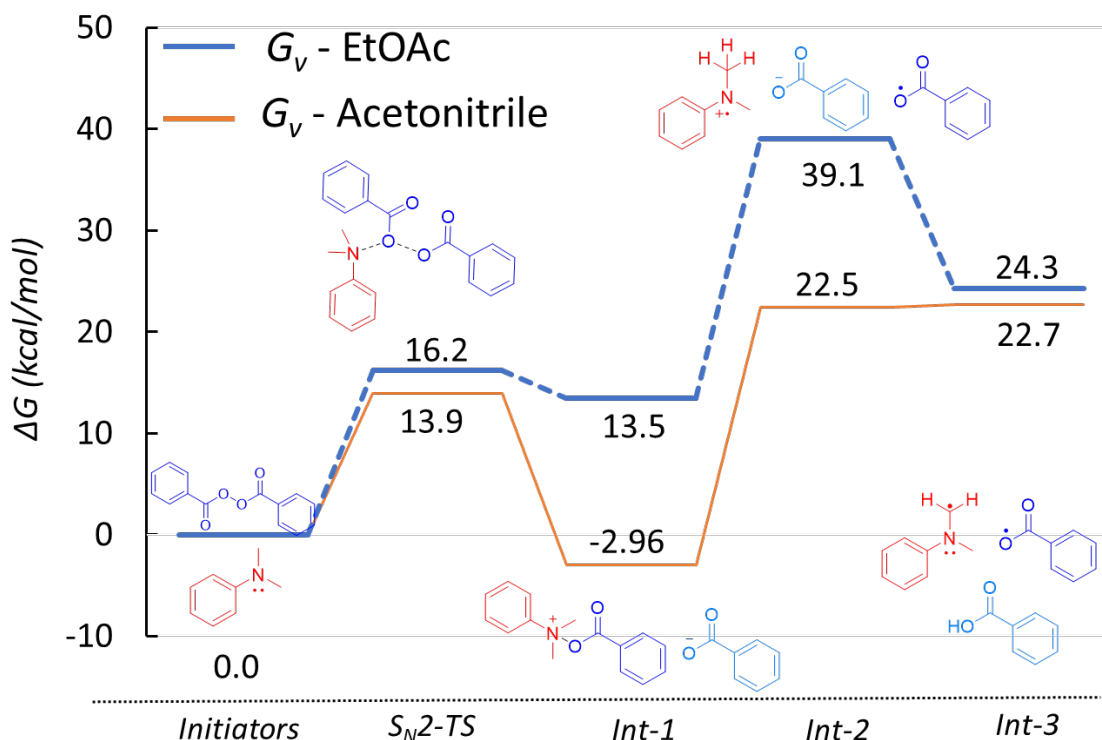


Figure S2.2. DMA-BPO reaction coordinate profile in acetonitrile. S_N2 and homolysis barriers in acetonitrile are similar to those in EtOAc. However, the aminoalkyl radical generation is not as favorable as in EtOAc because charged species are more stable in acetonitrile. Therefore, in a more polar medium, amine-peroxide redox polymerization may not be as efficient.

SI2.6. FT-IR Experimental Kinetic Profiles

Each figure in this section contains redox polymerization profile triplicates of different amines with BPO at 3 mol% concentrations in di(ethylene glycol) ethyl ether acrylate, unless otherwise noted. Although induction times were removed in the figures to concisely demonstrate polymerization rates, average induction times are provided in the figure captions. We defined the induction time as the time taken for a conversion to reach 5% to account for the noise in the FT-

IR measurements. Due to the likelihood of human inconsistency in sample preparation, we did not use induction times as quantitative values.

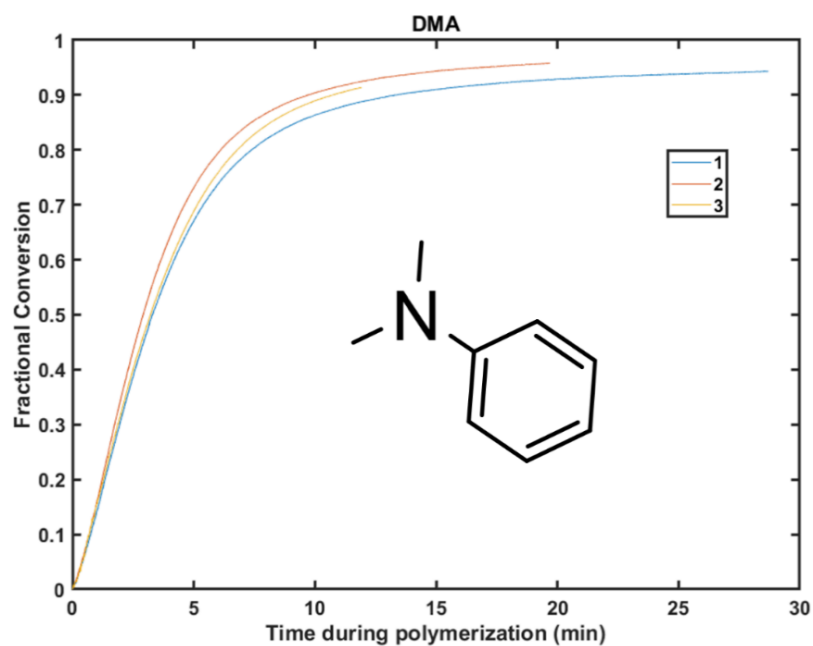


Figure S2.3. Polymerization profiles of *N,N*-dimethylaniline (DMA) with an average induction time of 1.23 min. This amine results in full conversion within 15 mins, and we used DMA as a reference throughout the manuscript.

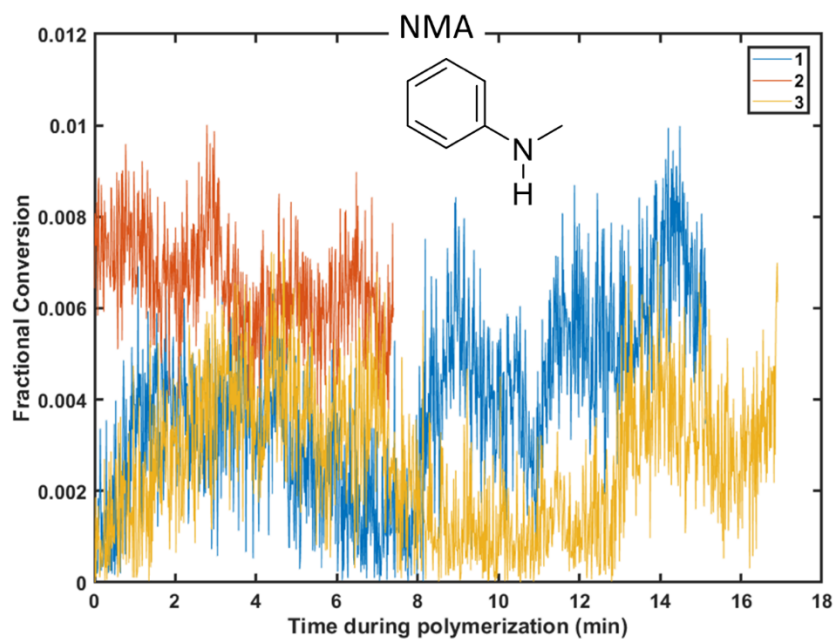


Figure S2.4 Polymerization profiles of N-Methylaniline (NMA), a DMA analog. There is no polymerization in these experiments. Note the small scale of the vertical axis.

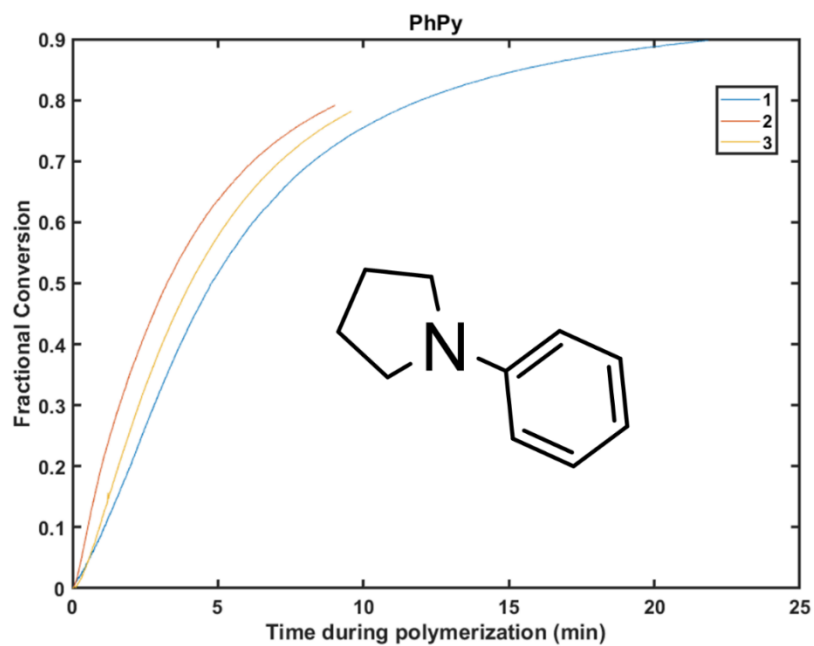


Figure S2.5 Polymerization profiles of 1-phenylpyrrolidine (PhPy) with an average induction time of 0.76 min.

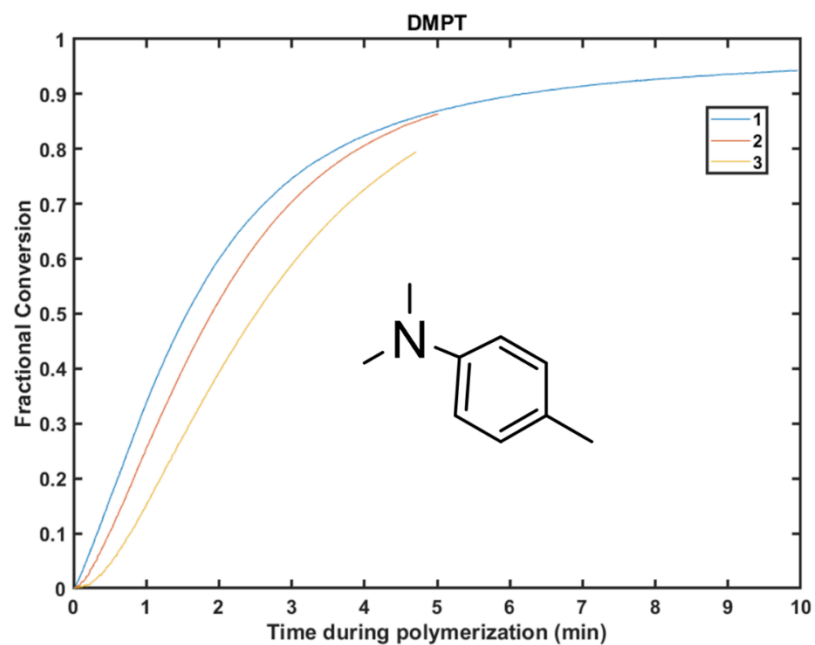


Figure S2.6 Polymerization profiles of *N,N*-dimethyl-*p*-toluidine (DMPT) with an average induction time of 0.53 min.

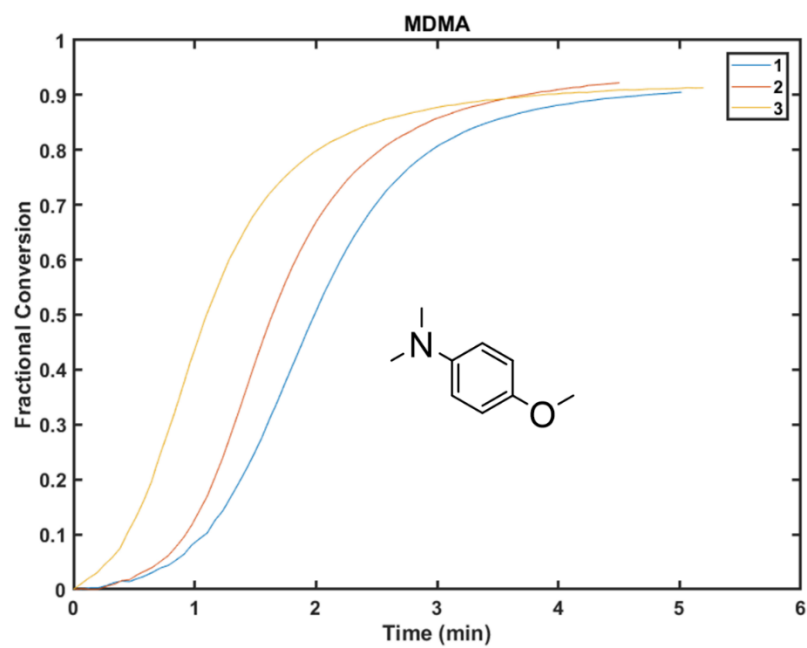


Figure S2.7 Polymerization profiles 4-Methoxy-*N,N*-dimethylaniline (MDMA) with an average induction time of 0.85 min.

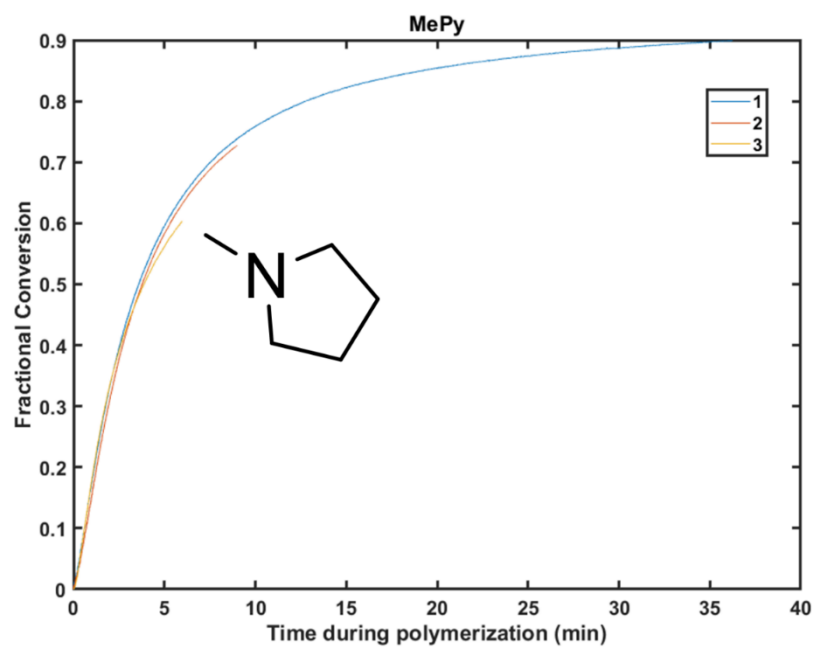


Figure S2.8 Polymerization profiles of 1-methyl pyrrolidine (MePy) with an average induction time of 1.02 min.

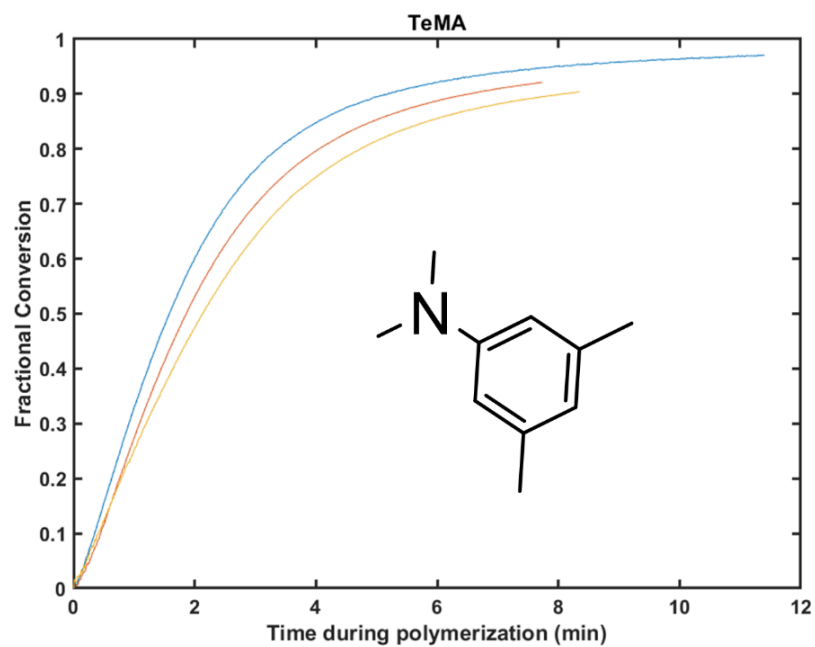


Figure S2.9 Polymerization profiles of 1 *N,N*-3,5-tetramethylaniline (TeMA) with an average induction time of 0.51 min.

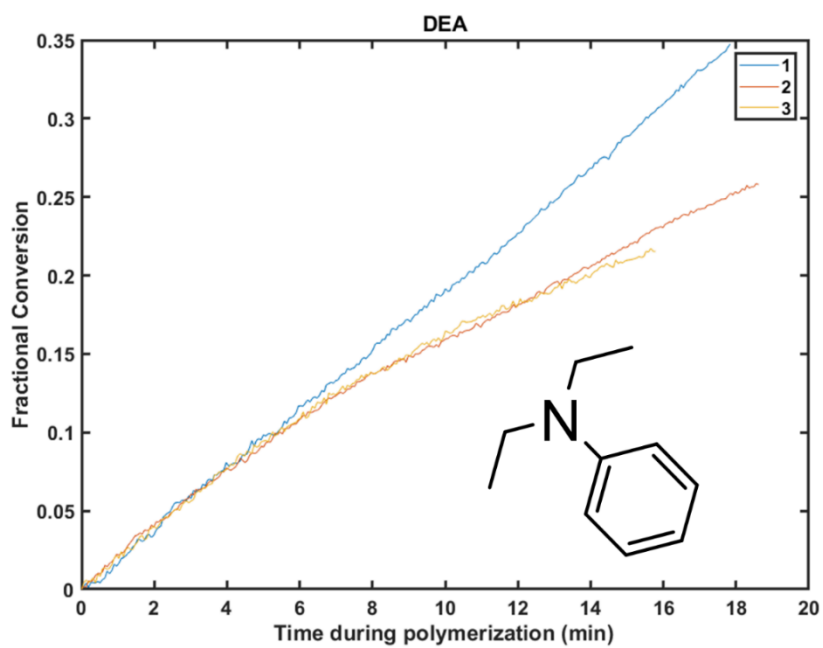


Figure S2.10 Polymerization profiles of *N,N*-diethylaniline (DEA) with an average induction time of 6.37 min.

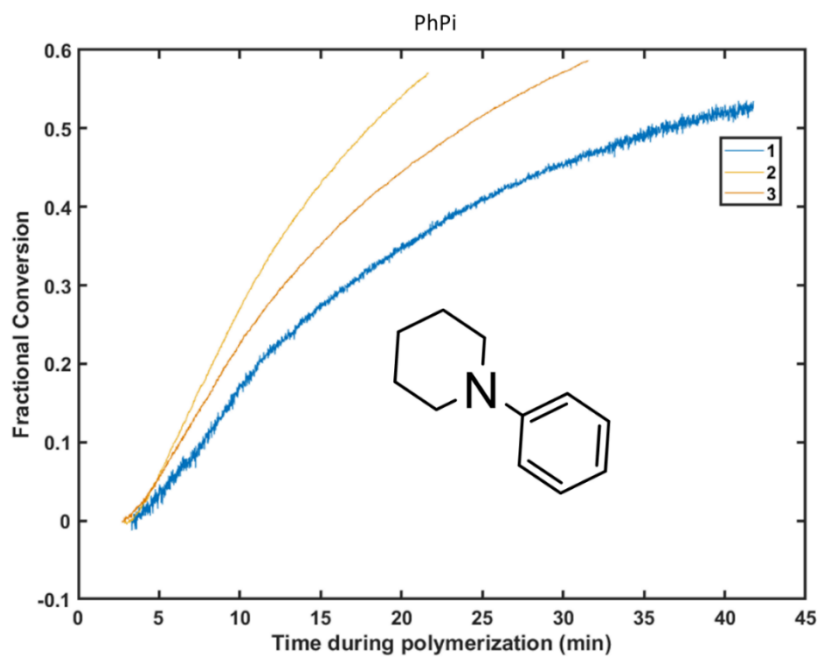


Figure S2.11 Polymerization profiles of 1-phenylpiperidine (PhPi) with an average induction time of 4.58 min.

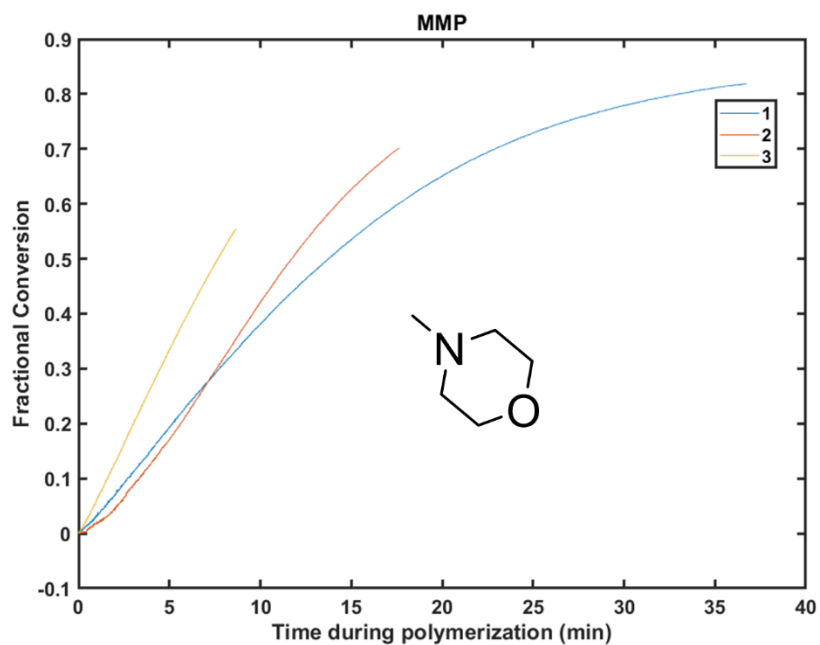


Figure S2.12 Polymerization profiles of 4-Methylmorpholine (MMP) with an average induction time of 4.94 min.

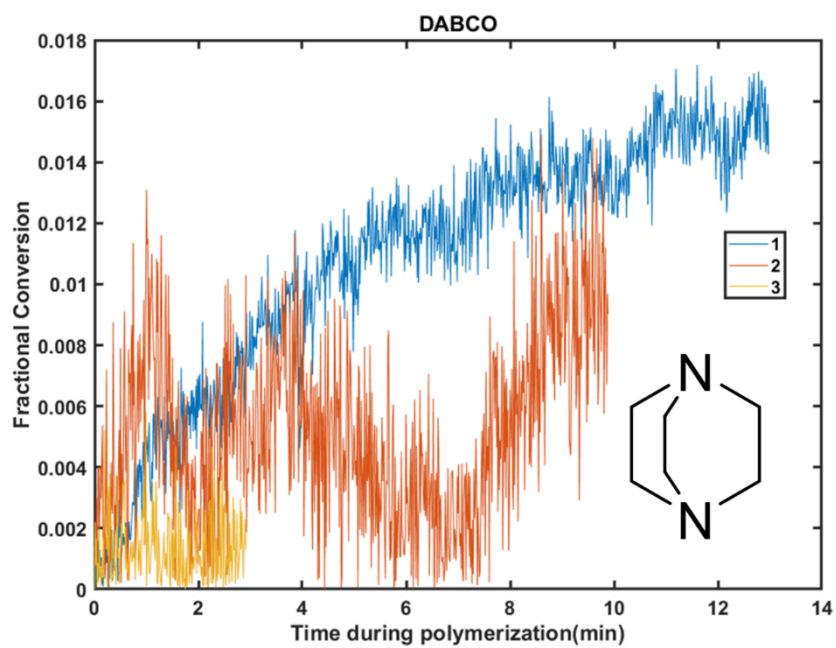


Figure S2.13 Polymerization profiles of 1,4-diazabicyclo[2.2.2]octane (DABCO) with an average induction time of 0.76 min. Note the small scale of the vertical axis.

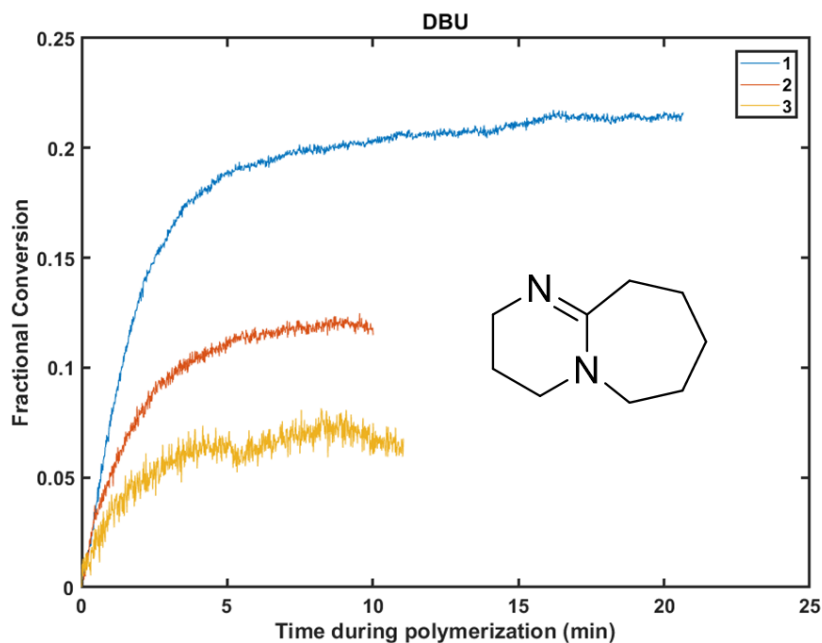


Figure S2.14. Polymerization profiles of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The polymerization behavior of DBU is unique in that DBU achieved 5 - 20% conversion and then plateaued while DMA continuously polymerized to >90% conversion in identical conditions (See S5). This conflicted with our initial prediction that DBU should not result in any polymerization at 298 K due to its very high HM barrier of 61.7 kcal/mol. However, after calculating the barrier for reaction at the alternative sp^3 nitrogen site in DBU, we found that the HM barrier was only 29.5 kcal/mol, enabling relatively slow radical generation. This explains the early plateauing polymerization profile of DBU with the partial conversion. The majority of the DBU population becomes NATA at the sp^2 nitrogen reactive site due to a lower S_N2 barrier than at the sp^3 nitrogen. Only a relatively small fraction of DBU undergoes the S_N2 reaction at the sp^3

nitrogen site that leads to radical generation. We concluded that NNBs, because the amines investigated here are structurally similar to other NNBs such as trialkylamine and amidine, are not suited for redox polymerization, and high basicity does not lead to fast redox activity (**Figure 2.7**). Furthermore, multiple nitrogen reactive sites in a molecule can influence radical generation rates.

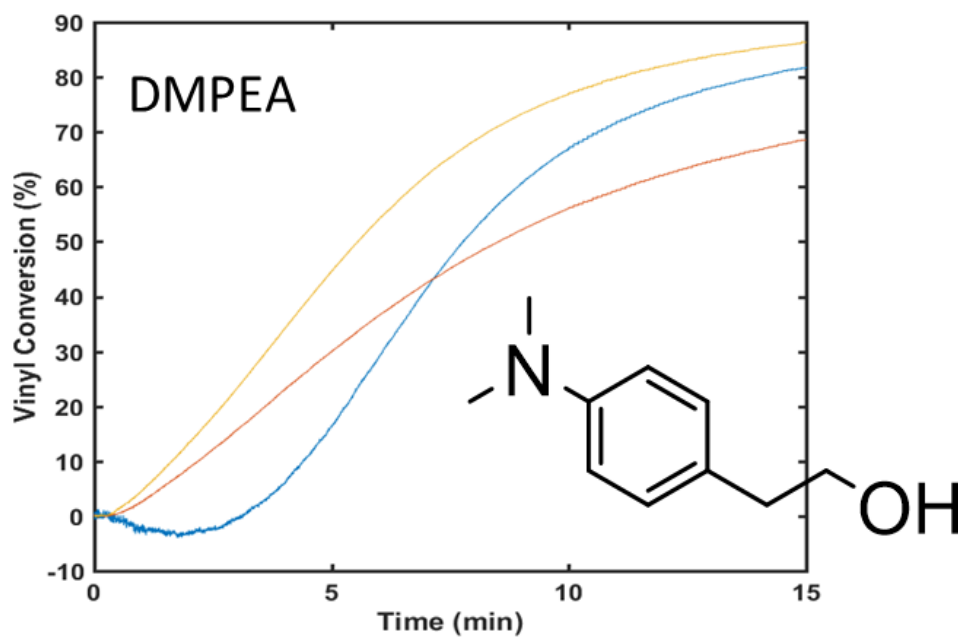


Figure S2.15 Polymerization profiles of 2-[4-(Dimethylamino)phenyl]ethanol (DMPEA).

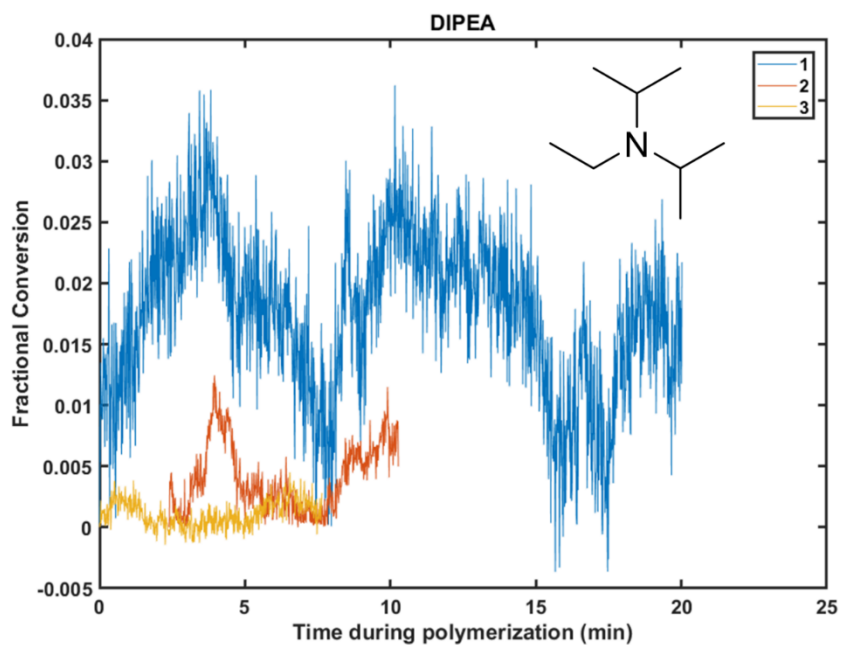


Figure S2.16 Polymerization profiles of *N,N*-Diisopropylethylamine (DIPEA). Note the small scale of the vertical axis.

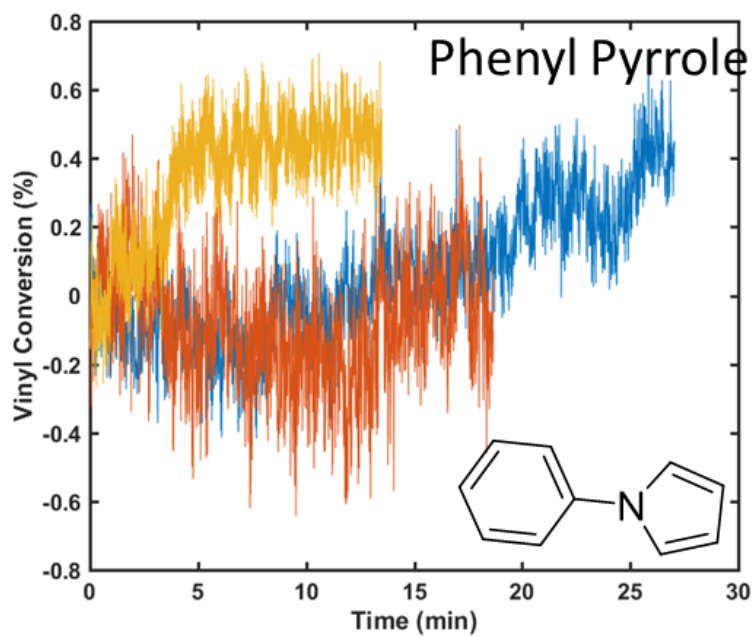


Figure S2.17 Polymerization profiles of 1-Phenylpyrrole. Note the small scale of the vertical axis.

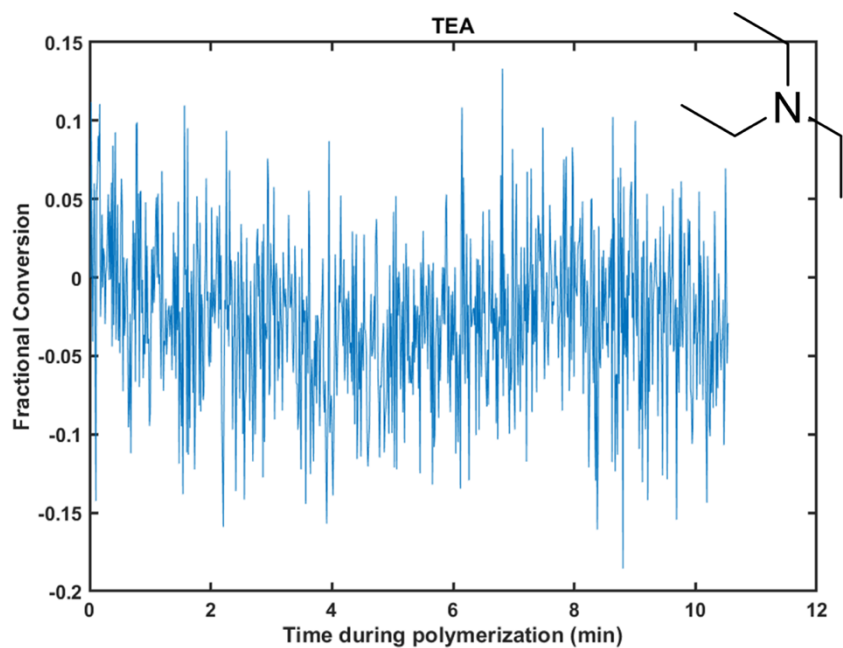
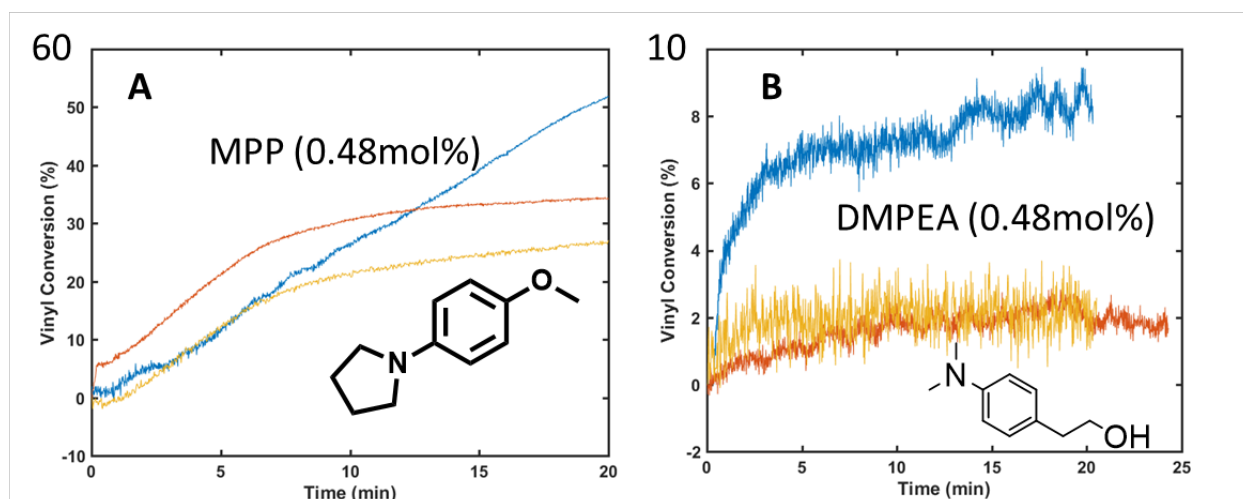


Figure S2.18 Polymerization profile of triethylamine (TEA). Note the small scale of the vertical axis.



Reduce Concentration in methacrylate for Figure 10.

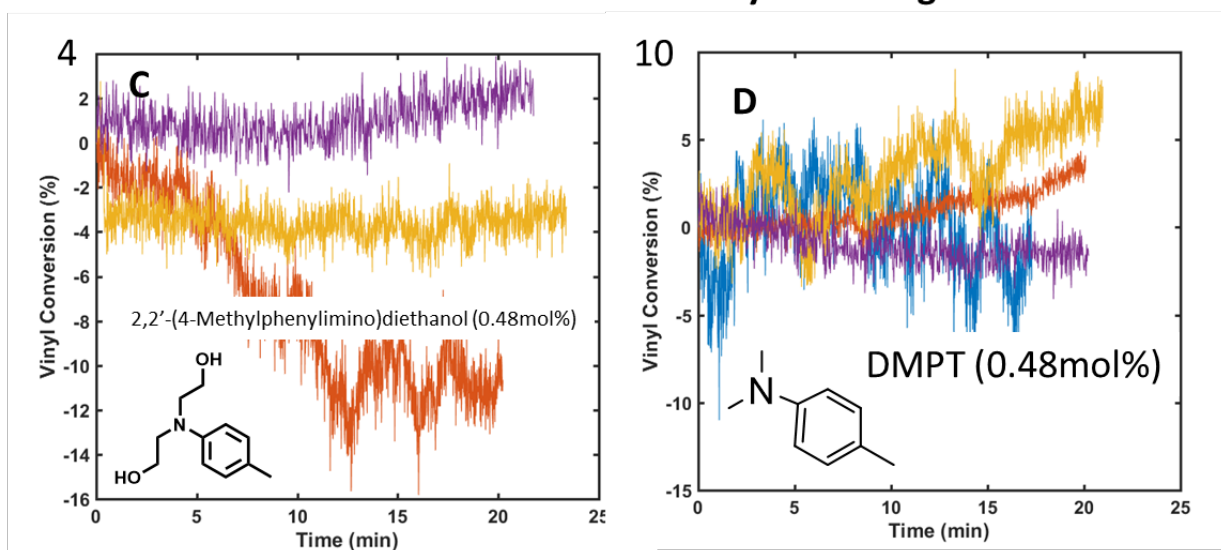


Figure S2.19. Polymerization profiles of **A**: N-(4-Methoxyphenyl)pyrrolidine (MPP), **B**: 2-[4-(Dimethylamino)phenyl]ethanol (DMPEA), **C**: 2,2'-(4-Methylphenylimino)diethanol, and **D**: *N,N*-dimethyl-*p*-toluidine (DMPT) in 50 wt% poly(ethylene glycol) methacrylate and 50 wt% Triethylene glycol dimethacrylate resin at 0.48 mol% concentration. Note the small scale of the vertical axes.

SI2.7. Discussion of Symmetric and Asymmetric N-substitutions along with para-substitution Data

The computational investigation of *N*-substitutions further supports our previous conclusion that the addition of electron donating groups results in a decreased homolysis barrier. However, unlike substitution at the para-position of DMA, substitution at the *N*-positions resulted in two concomitant negative effects. First, adding functional groups to the reacting nitrogen, especially larger groups, increased the steric hindrance, leading to larger reaction barriers for the S_N2 step. Second, the substitution of functional groups at the *N*-positions, particularly resonant electron donating groups, lowers the driving force for S_N2 reactions due to delocalization of electron density of the lone pair. This was most notable in the pyrrole- substitution which had an S_N2 barrier of 40.5 kcal/mol, which was confirmed by the lack of observation of polymerization in the experimental kinetic study. As mentioned in the main text, the substitutions at the *N*-positions were further complicated by the large disparity between the predicted and experimental polymerization rate, as shown in the example of *N,N*-diethylaniline (DEA). This disparity casts doubt on the accuracy of our DFT calculations when modeling the *N*-substitutions. As a result of these complications, no definitive insights beyond what is mentioned in the manuscript were stated in regard to the effects of *N*-substitutions on the overall polymerization. Experimentally, however, PhPy had a significantly faster polymerization rate than DEA, despite having approximately equivalent inductive electron donating effects. This is likely due to the different steric demands of these two molecules, where PhPy was least sterically hindered for the S_N2 reaction. It is therefore

hypothesized that reducing the steric hindrance around the N atom results in a decreased S_N2 barrier, increasing the polymerization rate.

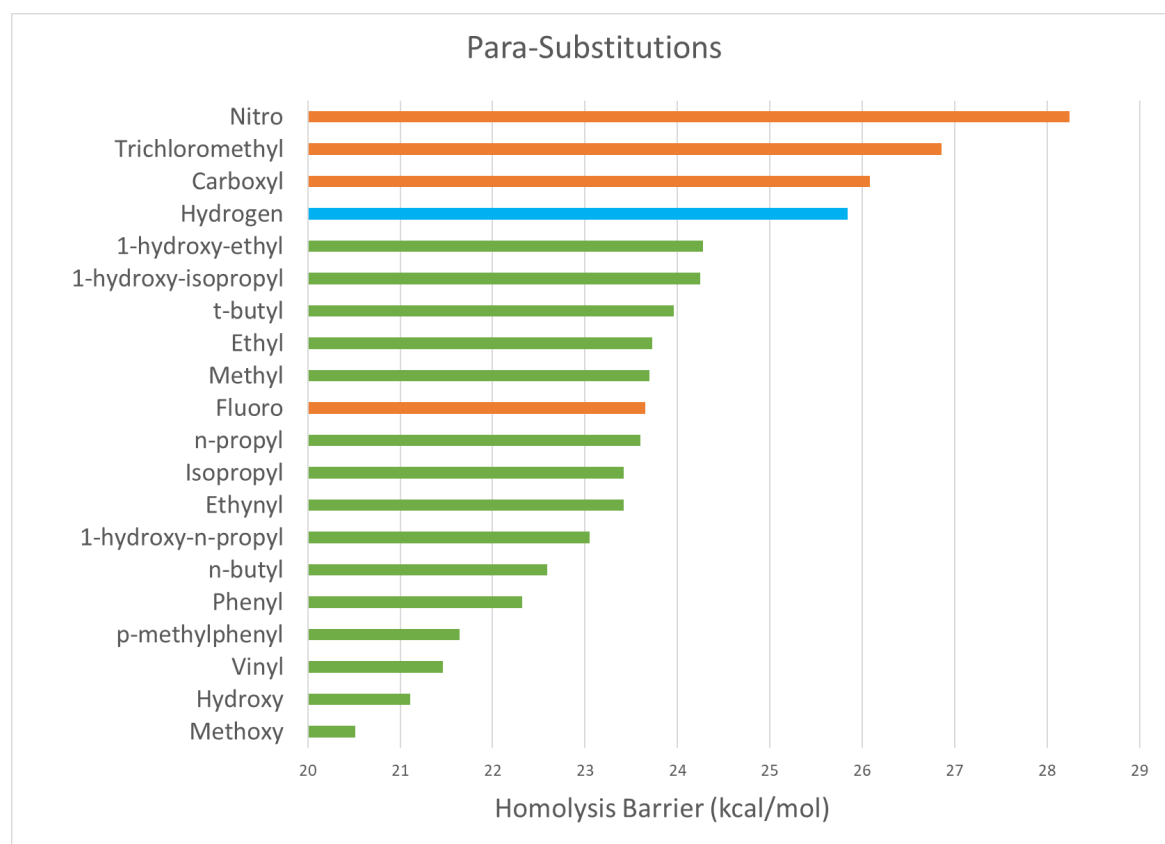


Figure S2.20. Homolysis barriers of dimethylaniline derivatives with *para*-substitutions. As mentioned in the manuscript, the electron donating groups, especially resonating groups, lower the homolysis barrier.

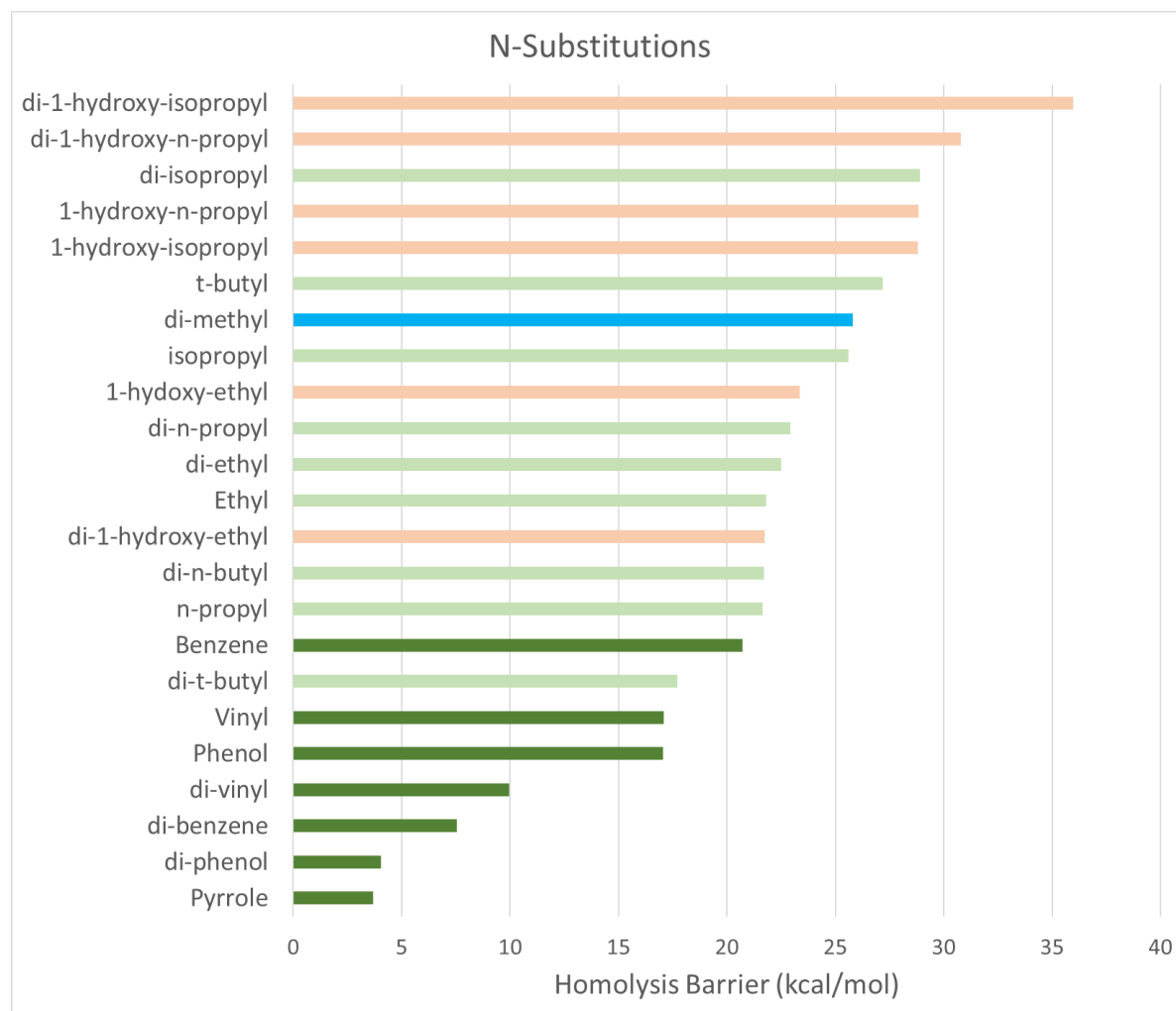


Figure S2.21. Homolysis barriers of aniline derivatives with *N*-substitutions and *N,N*-substitutions. In the case of single substitutions, the other substitution is methyl in order to maintain the tertiary aromatic amine structure. A similar conclusion that electron donating groups are beneficial can be drawn here.

SI2.8. *N*-(4-methoxyphenyl)pyrrolidine Synthesis and Characterization

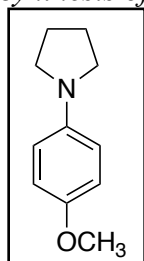
Materials

1,4-dibromobutane, anhydrous Acetonitrile, *p*-anisidine were purchased from Sigma Aldrich. Potassium carbonate and potassium iodide were purchased from Fisher Scientific. All other chemicals were of reagent grade and used without further purification.

NMR Spectroscopy

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, as indicated in the respective measurement.

Synthesis of *N*-(4-Methoxyphenyl)pyrrolidine



To the solution of 5g (0.04mol) *p*-anisidine in 60 mL of anhydrous acetonitrile was added 8.9g (0.06 mol) of K_2CO_3 and 0.03 g (0.15 mmol) of KI followed by the addition of 7 g (0.032 mol) of 1,4-dibromobutane. The reaction mixture was refluxed for 8 hrs. Acetonitrile was then removed, and the crude product was re-dissolved in ethyl acetate. The organic layer was then washed with water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to obtain a yellow solid. The crude residue was purified by column chromatography (silica gel, hexane) to obtain a pale yellow solid. Yield: 59%, ^1H NMR (CDCl_3 , $\square$ ppm): 6.87 (d, $J = 9$

Hz, 2H), 6.56 (d, $J = 8.9$ Hz, 2H), 3.79 (s, 3H), 3.30 – 3.23 (m, 4H), 2.05 – 1.99 (m, 4H); ^{13}C NMR (CDCl_3): 150.73, 143.24, 115.01, 112.59, 56.03, 48.25, 25.42.

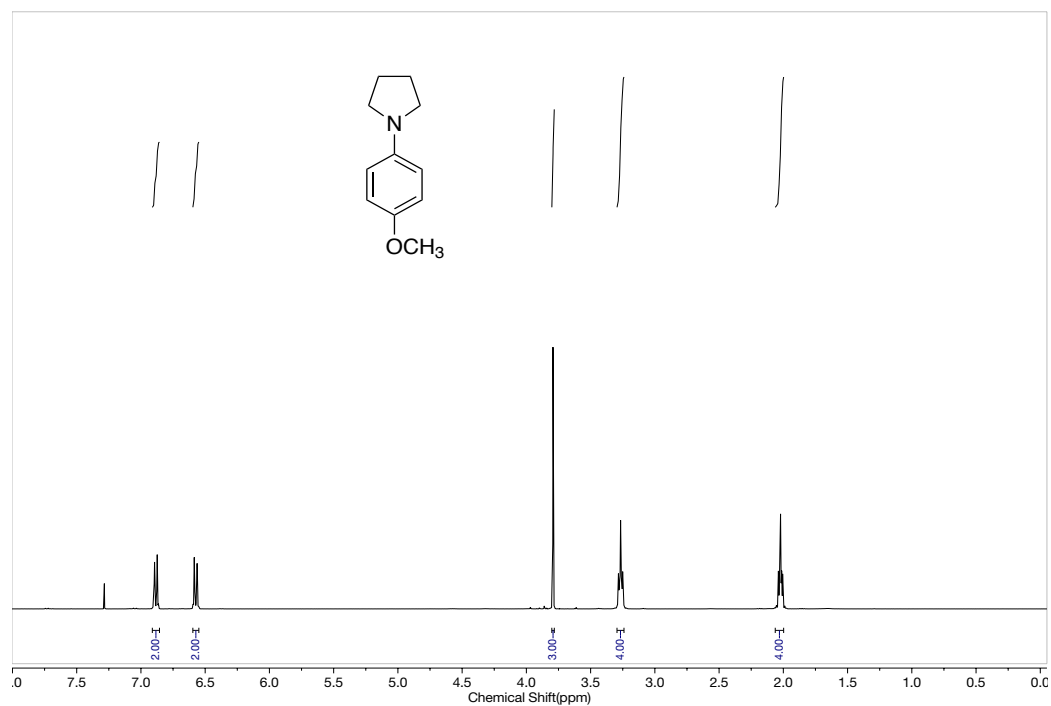


Figure S2.22. ^1H -NMR of *N*-(4-Methoxyphenyl)pyrrolidine.

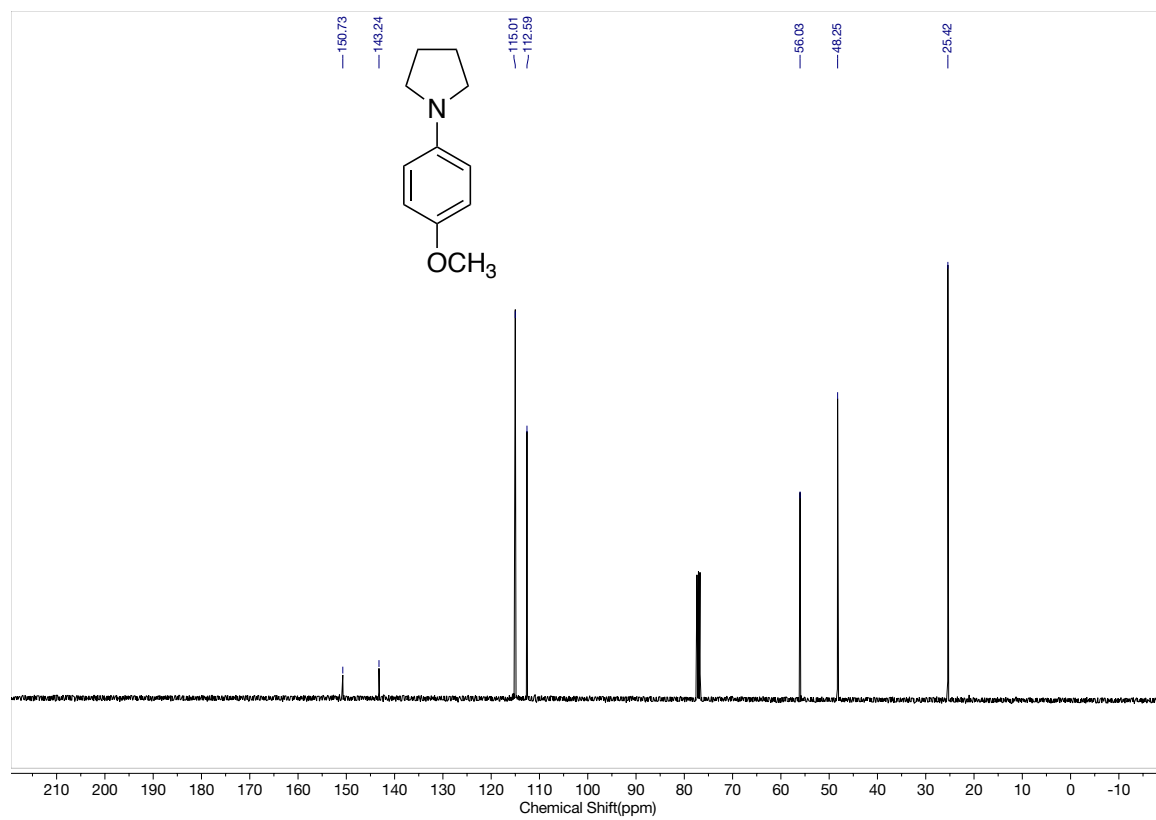


Fig.

Figure S2.23. ^{13}C -NMR of *N*-(4-Methoxyphenyl)pyrrolidine.

Chapter 3: Computational and Experimental Evaluation of Peroxide Oxidants for Amine-Peroxide Redox Polymerization

The work described in this chapter is adapted from a manuscript in preparation: Charles B. Musgrave III, **Kangmin Kim**, Nicholas R. Singstock, Austyn M. Salazar, Jeffrey W. Stansbury, Charles B. Musgrave, where Charles B. Musgrave III and I contributed equally to this work

3.1 Abstract

Amine-peroxide redox polymerization (APRP) is the prevalent method for producing radical-based polymers in the many industrial and medical applications where light or heat activation is impractical. We recently developed a detailed description of the APRP initiation process through a combined computational and experimental effort to show that APRP proceeds through S_N2 attack by the amine on the peroxide, followed by the rate-determining homolysis of the resulting intermediate. Using this new mechanistic understanding, a variety of peroxides were computationally predicted to be peroxide oxidant initiators with fast initiating kinetics. Furthermore, the rate of APRP initiation can be improved by radical and anion stabilization through increased π -electron conjugation or by increasing the electrophilicity of the peroxy bond through the addition of electron-withdrawing groups. On the other hand, the addition of electron-donating groups lowered the initiation rate. These design principles enabled the computational prediction of several new peroxides that exhibited improved initiation rates over the commonly used benzoyl peroxide. For example, the addition of nitro groups (NO_2) to the para positions of benzoyl peroxide resulted in a theoretical radical generation rate (1.9×10^{-9}) $\sim$ 150 times faster than the radical generation rate with non-functionalized benzoyl peroxide (1.3×10^{-11}). These accelerated kinetics enabled the development of a redox-based direct writing process that exploited

the extremely rapid reactivity of an optimized redox pair with a custom inkjet printer, capable of printing custom shapes from polymerizing resins without heat or light. The application of more rapid APRP kinetics could enable the acceleration of existing industrial processes, make new industrial manufacturing methods possible, and improve APRP compatibility with biomedical applications through reduced initiator concentrations that still produce rapid polymerization rates

3.2 Introduction

Approximately 45% of all polymer products are manufactured using radical polymerization (RP), of which a significant portion is initiated by redox initiators.¹⁻⁴ Redox RP uses the chemical energy stored in a reductant-oxidant pair to produce initiating radicals. This provides several important advantages including energy-efficient room temperature (RT) activation, unrestricted product shape and size,^{5,6} the ability to activate without light, and the capacity to reach higher filler concentrations during photocuring. Amine-peroxide redox polymerization (APRP) uses metal-free amine reductant-peroxide oxidant pairs as initiators to achieve additional benefits over metal-containing initiators,⁷⁻¹⁷ including biocompatibility⁷ and facile implementation in solvent-free bulk polymerization.⁸ Additionally, the cost of amine and peroxide initiators is significantly less than other photo initiators, making APRP preferable from an economic standpoint. This has led to the wide application of APRP and its extremely active development since its discovery in the 1950s, as evidenced by the over 45,000 APRP-related patents filed since 1975.⁹ Biomaterial synthesis processes used in dental and orthopedic applications, where restricted conditions render thermal and photo-activation processes impractical, have exploited APRP's unique advantages. These advantages have also motivated APRP's investigation for emerging applications in photo-activated APRP initiator development,

frontal polymerization,¹⁹ self-healing materials,^{20,21} interfacial polymerization,²² and adhesives.²³ Despite the significant impact of APRP, no fundamental study examining the molecular features that determine initiation rates had been reported until 2019. This gap presents an opportunity to investigate how the choice of the amine-peroxide pair might be leveraged to optimize the rate of polymerization.

We previously conducted an extensive study of APRP via a combined computational and experimental investigation (*J. Am. Chem. Soc.* **2019**, *141*, 6279-6291). In this study, we proposed and validated an APRP initiation mechanism that allowed us to accurately predict new amines for accelerated APRP. Using this approach, we identified, synthesized, and tested *N*-(4-methoxyphenyl)pyrrolidine (MPP), which generated radicals ~20 times faster than the previous state-of-the-art tertiary aromatic amines, making it the fastest amine for APRP to date. While this previous study delved into the reactivity of structurally varied amine reductants with benzoyl peroxide (BPO), it did not examine the potential of pairing amines with various peroxides with different reactivities.

Previous studies regarding the reactivity of peroxide oxidants within the APRP framework have been limited and primarily observational. Moore and co-workers evaluated five peroxides (BPO, lauroyl peroxide, methyl-ethyl-ketone peroxide, *tert*-butyl peroxide, and *tert*-butyl peroxybenzoate)²² within the APRP framework for use in self-healing composites, discovering that when added to the amine, three out of the five peroxides had either no effect or adverse effects on the polymerization rate and activation temperature, the exceptions being BPO and methyl-ethyl-ketone peroxide. Chen *et al.* investigated four peroxides (BPO, *tert*-butyl peroxybenzoate, dicumyl peroxide, *tert*-butyl peroxide) and found that polymerization efficiency was inversely correlated with thermal stability during photopolymerization. However, the amines used in this study were

the tertiary, non-aromatic diazabicyclo[5.4.0]undec-7-ene (DBU) amine and secondary amines, which were found to be either poor initiators or even inhibitors of APRP. Moore's study was less focused on the peroxides' reactivity and instead aimed at investigating self-healing properties of polymers that incorporated separately encapsulated amine-peroxide pairs. Chen's study utilized APRP-inhibiting amines, making their conclusions regarding peroxide performance less relevant to identifying superior amine-peroxide pairs for APRP. Additionally, these two studies combined only studied five distinct peroxides, which is insufficient for characterizing the peroxide chemical space. Ultimately, the assessment of peroxide performance for APRP has been limited. The lack of a fundamental understanding regarding the effects that govern peroxide reactivity within APRP motivates a structure-activity relationship study of the peroxide chemical space. Understanding the molecular features that dictate initiation kinetics may enable the design of superior peroxide initiators for accelerated APRP.

In this contribution, we utilize the fundamental understanding elucidated by our previous study to investigate peroxides that could further improve kinetic rates to expand the scope of APRP. Our computational analysis of 15 peroxide oxidants elucidates how structural variations dictate radical generation kinetics and peroxide stability, which is supported by real-time Fourier-transform infrared spectroscopy (FTIR). While most peroxides performed in polymerization experiments according to our computational predictions, we found one peroxide whose polymerization behavior significantly deviated from our computational prediction. This anomalous peroxide was predicted to generate radicals faster than all other peroxides, but we observed only a negligible amount of polymerization along with significant coloration of the resin. This inconsistency between our predicted and measured results for this one peroxide was investigated and explained with a new mechanism involving an outer-sphere electron transfer (ET)

step as opposed to our previous finding that the operative mechanism proceeded through inner-sphere ET for other amine-peroxide pairs within APRP. Our results demonstrate a unique instance where the identities of the reductants and oxidants determine which of these two branches in the mechanistic path of an inner- or outer-sphere ET step are taken, while also providing researchers valuable guidance towards the development of novel APRP chemistries. Lastly, the results of our two studies of APRP guided the development of a redox-based direct writing process that leveraged the extremely rapid reactivity of an optimized APRP pair with a custom inkjet printer.

3.3 Methods

3.3.1 Computational Methods

All DFT calculations were performed in Gaussian 16.03.A using the MN15 density functional with the 6-31+G(d,p) basis set. In our previous study, this level of theory performed the best among combinations of 13 commonly used functionals when benchmarked against the highly-accurate but computationally expensive CCSD(T) and CBS-QB3 methods, resulting in a RMSE of 1.4 kcal/mol for activation energies. Gas-phase frequencies were computed at the experimental temperature (298 K) and used to predict zero-point energies, enthalpies, and entropies. These predicted frequencies were also used to confirm local minima for reactant, intermediate, and product states, as well as saddle points for transition states. To include solvation effects, we applied the SMD implicit solvent model with solvent parameters describing ethyl acetate, which mimic the dielectric properties of (meth)acrylate bulk resin. In order to more accurately capture the bulk resin environment in which librational modes are hindered by neighboring molecules, we removed translational and rotational entropies from the free energy expression and reported free energies $G_v(T)$ that only include entropic contributions from the vibrational states. This correction was previously shown to produce more accurate reaction and activation free energies for reactions in

solvent in comparison to experimental results while computed changes in free energies without this correction overestimated entropic contributions. More comprehensive computational details are provided in the **Methods** section of the SI.

3.3.2 Experimental Methods

Materials: *N,N*-dimethylaniline and BPO were purchased from Sigma-Aldrich (Milwaukee, WI). All amines were acquired with the highest purity available of at least 95% and used as received. We purified BPO by dissolving it in dichloromethane (DCM) and recrystallized in methanol. The monomers used are di(ethylene glycol) ethyl ether acrylate (DEGEEA, Sigma Aldrich, 90% purity, 1000 ppm MEHQ) and bisphenol A ethoxylate diacrylate (Mn 512, EO = 2). All other chemicals were of reagent grade and used without further purification. Phthaloyl peroxide and MPP were synthesized according to the respective references.

FT-IR: The conversion of monomer by ambient bulk redox-initiated polymerization was monitored in real time with an FT-IR spectrophotometer (Nicolet Magna-IR Series II, Thermo Scientific, West Palm Beach, FL) by monitoring the C=C stretching absorption band at 1637 cm^{-1} for 20 mins in OMNIC software. We chose DEGEEA monoacrylate to reduce a confounding factor of autoacceleration as opposed to cross-linking multi-functional monomers that exhibit autoacceleration. The spectrophotometer was equipped with an MCT/A detector, and parameters on the FT-IR were set to 2 scans, a resolution of 16, an optical gain of 1, an optical velocity of 1.8988 cm/s , and an optical aperture of 15. We studied the polymerization kinetics initiated with two separate batches of resin with 3 mol% each of peroxide oxidant and *N,N*-dimethylaniline (DMA) reductants. On a horizontal NaCl salt plate, 15 μl of peroxide resin was first deposited, to which another 15 μl of DMA resin was added. This solution was then mixed with a micropipette tip. Another NaCl salt plate was then placed on top of the mixture, after which data acquisition

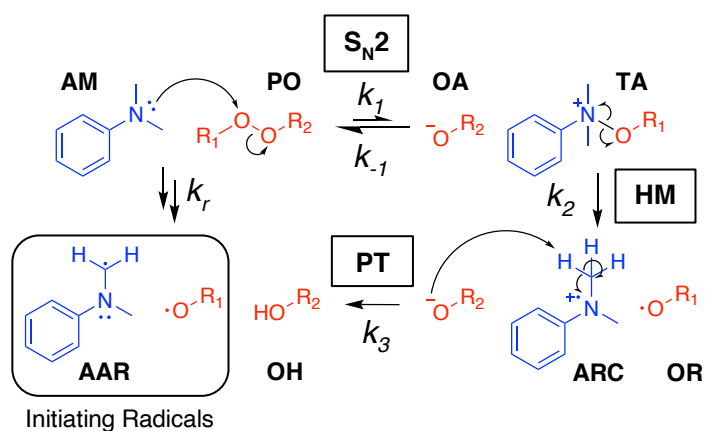
began immediately. A clear baseline of zero conversion during an induction period preceding each polymerization was observed for every sample.

NMR: ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, as indicated in the respective measurement.

UV-Vis Spectroscopy: The UV-Vis spectra of redox pairs in dimethylformamide were recorded in PMMA cuvettes with 1 cm optical path lengths in a UV-Vis spectrophotometer (Thermo-Fischer Scientific) after baseline correction with a blank run.

Direct Writing System: Our custom direct writing system was built with a Raspberry Pi 3+ which controlled two 12V DC peristaltic pumps (AE1207) to pump the resins, and two stepper motors (SM15L) to enable X and Y axis directional control of the writing nozzle. 3 mm inner diameter x 5 mm outer diameter silicone tubing was used to transport the resins to the mixing nozzle. Custom python software was developed to enable APRP direct writing with the Raspberry Pi.

3.4 Results and discussions



Scheme 3.1. The APRP mechanism when using *N,N*-dimethylaniline (DMA) as the amine begins with S_N2 nucleophilic attack of the peroxide (PO) by the amine (AM). The resultant trialkyl-ammonium (TA) and oxy anion (OA) intermediates mediate an inner-sphere ET where

AM becomes singly oxidized and the leaving **OA** becomes singly reduced. After the S_N2 attack of **PO** by **AM**, the metastable **TA** intermediate undergoes homolysis (HM) into an amine radical cation (**ARC**) and oxy radical (**OR**), which is the first initiating radical generated from the amine-peroxide reaction. We will show below that these two reactions (S_N2 and HM) govern the overall initiation kinetics in the APRP mechanism, where HM is the rate-determining step. Meanwhile, reactive intermediates resulting from the S_N2 and HM reactions react with each other; **OA** and **ARC** may undergo a barrierless proton transfer (PT) at the α -carbon of **ARC** to produce a weak acid (**OH**) and an initiating α -aminoalkyl radical (**AAR**).⁴⁶

3.4.1 Amine-Peroxide Redox Mechanism

The APRP initiation mechanism is detailed in **Scheme 3.1**. Our previously derived kinetic model for the APRP mechanism correlated the computationally calculated radical generation rate (k_r) and the experimentally determined polymerization rate (R_p) with good agreement ($R^2 = 0.80$). The governing rate equation: $k_r = k_2(k_1^{1/2}/k_{-1}^{1/2})[Am]^{1/2}[PO]^{1/2}$ is first order in the HM rate (k_2) and half-order in the overall S_N2 rate (defined as k_1/k_{-1}), thus supporting the claim that HM is the rate-determining step. For this model, S_N2 is assumed to be reversible due to its endergonic nature, and HM is assumed to have no distinct transition state (TS) based on its monotonic potential energy surface (*vide infra*). Because these assumptions resulted in a good correlation of $R^2 = 0.80$ for various amines, the kinetic model was predicted to be sufficient for peroxides reacting within the APRP mechanism. Herein, the reactivities of various peroxides are evaluated by applying our kinetic model and comparing computational predictions to experimental data. Kinetic constants are calculated from computed free energy activation barriers of each elementary step using Eyring's kinetic equation.

Benzoyl peroxide (BPO) was chosen as the reference peroxide for this study, as nearly all preexisting APRP applications incorporate BPO as an oxidant. *N,N*-dimethylaniline (DMA) was selected as the reference amine reductant as it was determined to be a relatively efficient redox initiator and its small molecular size permits efficient computation. While this study examines APRP kinetics for different peroxides, the identity of the amine (DMA) remains constant in every reaction studied unless otherwise noted.

3.4.2 Acyl peroxide

The reaction between the BPO and DMA reference redox pair (**Figure 3.1**) was computed to have a forward S_N2 free energy barrier ($\Delta G_{S_N2}^\ddagger$) of 16.2 kcal/mol and a free energy of reaction ($\Delta G_{S_N2}^\circ$) of 13.5 kcal/mol, and thus a small reverse barrier of 2.7 kcal/mol (**Table 3.1**). The HM reaction exhibits a monotonic potential energy surface so that the HM free energy of reaction and activation are equal ($\Delta G_{HM}^\circ = \Delta G_{HM}^\ddagger$) and calculated to be 25.6 kcal/mol. These activation free energies lead to a $k_r = 1.3 \times 10^{-11} \text{ s}^{-1}$ for BPO. The major contribution to the S_N2 barrier arises from torsion about the O-O bond to enable backside attack of the O-O antibonding orbital ($O-O^*$).

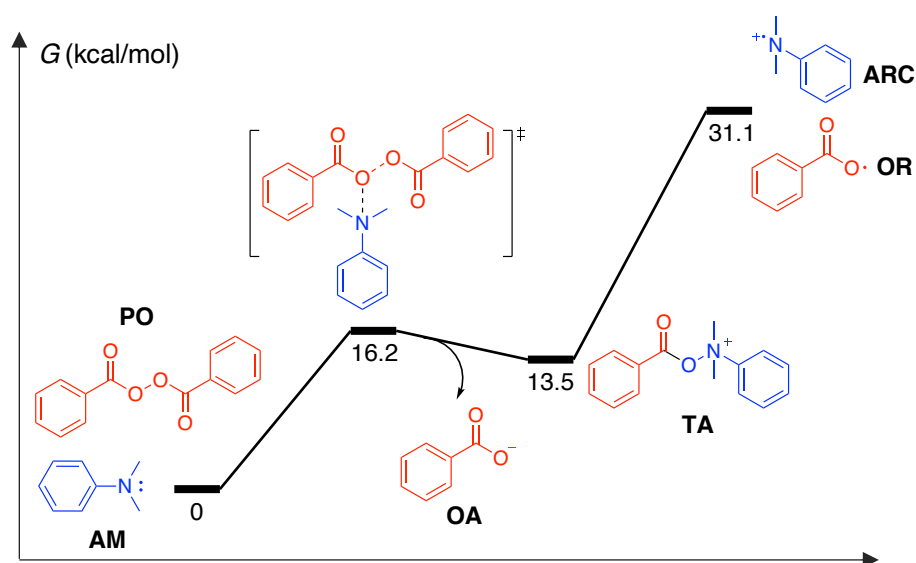


Figure 3.1: Free energy profile of the APRP initiation between DMA and BPO leading to the generation of the first initiating radical. Free energies are in units of kcal/mol and calculated at the MN15/6-31+G(d,p)/SMD-ethyl acetate level of theory.

First, peroxides resulting from functionalization of BPO were examined. We exclusively modified the *para* groups of the phenyl rings of BPO, as these positions would affect the peroxide reactivity more significantly (para vs. meta) and without inducing steric clashing through Pauli repulsion (para vs. ortho). To maintain the symmetry of the peroxides, para substitutions were applied to both phenyl rings. We selected methyl and methoxy groups (MeBPO and MeOBPO) as electron donating groups (EDG) and chloro and nitro groups (ClBPO and NiBPO) as electron withdrawing groups (EWG). These four distinct substitutions provide a range of variation that allow the evaluation of EWG/EDG contributions to peroxide reactivity (**Figure 3.2**). We expect that methyl and chloro groups primarily affect the electronic structures of the peroxides via an inductive effect while methoxy and nitro groups do so via a resonance effect.

Our computations showed that EDG substitutions increase the S_N2 barrier by 1-2 kcal/mol and decreased stability of the intermediates by ~ 1 kcal/mol, resulting in a lower k_1 with a similar k_{-1} . Specifically, MeBPO had forward and reverse S_N2 barriers of 17.3 and 3.0 kcal/mol, while MeOBPO had forward and reverse barriers of 18.3 and 3.6 kcal/mol (**Table 1**). This results because electron donation from the EDG reduces the electrophilicity of the oxygens of the peroxy bond, making S_N2 attack on the electron-rich oxygens by the amine more difficult. The atomic charges calculated via atomic polar tensor (APT) population analysis were -0.64 e, -0.66 e, and -0.66 e for the oxygens of the O-O bond of BPO, MeBPO, and MeOBPO, respectively. This confirms the hypothesis that addition of an EDG to the peroxide increases the electron density on the O-O bond

to inhibit attack by the amine lone pair. Electron donation destabilized S_N2 products (by 0.83 kcal/mol for MeBPO and 1.2 for MeOBPO) by increasing localized cationic charge on the nitrogen of the **TA** (0.16 e, 0.17 e, and 0.19 e for BPO, MeBPO, and MeOBPO) and by increasing localized anionic charge on the oxygen of the **OA** (-1.23 e, -1.24 e, and -1.25 e for BPO, MeBPO, and MeOBPO). As a result, EDG substitutions disfavor S_N2 reactions to a small but non-negligible extent. The effect of an EDG on HM is less straightforward. Relative to BPO, the HM barrier *decreased* for MeBPO and *increased* for MeOBPO, the difference being even smaller than the changes to the S_N2 reaction barriers. Additionally, this trend was not captured by the APT population analysis; in all relevant intermediates (**OA**, **OR**, **NATA**), both MeBPO and MeOBPO exhibited greater electron density on the oxygens from the broken O-O bond when compared to BPO. Because MeBPO and MeOBPO exhibit the same charge density trend (more anionic oxygens), we would expect both to have larger HM barriers, contrary to what was calculated; this indicates that charge density is not the primary descriptor for HM. Ultimately, these calculations are within the error of DFT (MN15 achieves a 1.4 kcal/mol RMSE relative to CBS-QB3), making a chemical explanation ambiguous. Regardless, radical generation rates were similar for MeBPO ($k_r = 1.5 \times 10^{-11} \text{ s}^{-1}$) and lower for MeOBPO ($k_r = 9.8 \times 10^{-13} \text{ s}^{-1}$) relative to unsubstituted BPO. Hence, these results suggest that EDG substitutions are not effective for achieving greater radical generation rates.

In contrast to EDG substitutions, EWG substitutions lowered both S_N2 and HM barriers while stabilizing the intermediates between these two reaction steps, which invariably increased k_r . Chloro and nitro groups lowered the computed S_N2 barriers by 1.3 and 3.6 kcal/mol and stabilized the **TA** and **OA** intermediates by 1.5 and 4.3 kcal/mol relative to BPO, respectively. EWG substitutions render the peroxy bond more electron-deficient, which elicits a greater

electrophilic reaction response while substantially stabilizing the leaving **OA**. The APT oxygen charges on **OA** were computed to be -1.23 e, -1.23 e, and -1.22 e, for BPO, ClBPO, and NiBPO, respectively. Interestingly, EWG functionalization resulted in increased electron density on the oxygen in the **TA** intermediate, yielding a polar N-O bond. The oxygens' APT charges are -1.06 e, -1.07 e, and -1.08 e in BPO, NiBPO, and ClBPO, respectively while the nitrogens' APT charges are 0.165 e, 0.158 e, and 0.192 e for BPO, NiBPO, and ClBPO in **TA**. For both ClBPO and NiBPO, increased negative charge on the oxygen resulted in a more polar N-O bond, which in turn leads to more facile HM by which the N-O bond dissociates. The increased bond polarity might be expected to provide greater Coulomb attraction and thus a shorter, stronger N-O bond. However, the N-O bond lengths of ClBPO and NiBPO are not shorter, meaning that Coulomb attraction does not lead to any significant stabilization. Further examination shows that the increased bond polarity creates a charge gradient, which leads to greater wavefunction curvature at the bond midpoint, ultimately increasing the electronic kinetic energy that destabilizes the N-O bond. The calculated HM barriers of NiBPO and ClBPO are 24.7 and 24.8 kcal/mol, both of which are smaller than BPO's 25.6 kcal/mol HM barrier. As a result, both ClBPO with a k_r of $1.8 \times 10^{-10} \text{ s}^{-1}$ and NiBPO with a k_r of $1.9 \times 10^{-9} \text{ s}^{-1}$ are predicted to perform more efficiently relative to unsubstituted BPO.

In addition to phenyl ring functionalization at the para positions of BPO, we expanded our evaluation to include other diacyl peroxides such as dinaphthyl, diacetyl, and the cyclic analogue of BPO, phthaloyl peroxide (**Figure 3.2**). Dinaphthyl peroxide (NathPO) is predicted to perform similarly to BPO with nearly identical energetics of $\Delta G_{S_N2}^\ddagger = 16.3 \text{ kcal/mol}$ and $\Delta G_{HM}^\ddagger = 24.6 \text{ kcal/mol}$ while the S_N2 barrier is 0.1 kcal/mol higher and the HM barrier is 1.0 kcal/mol lower than that of BPO. The naphthyl groups slightly lower the electron density of the peroxide oxygens relative to the phenyl group (-0.63 with naphthyl vs. -0.64 with phenyl), while their

increased steric bulk imposes a larger distortion energy penalty to expose the O-O antibonding orbital for S_N2 attack. The effects of the increased distortion energy and decreased O-O electron density mostly cancel each other, leading to minimal change of the S_N2 barrier. However, the extended aromatic system produces a more polar N-O bond in the **TA** intermediate; the oxygen charge in **TA** is -1.08 e with the naphthyl substitution, relative to -1.06 e with the phenyl substitution, leading to a destabilized N-O bond and a lower HM barrier by 1.0 kcal/mol. Regardless of the slightly lower predicted HM barrier, NathPO exhibits no significant improvement over BPO. In the case of diacetyl peroxide (AcPO), replacing the phenyl groups with methyl groups resulted in slower predicted kinetics for AcPO relative to BPO, indicating that aromatic systems facilitate redox reactions through resonance stabilization of radicals within the APRP mechanism. The inductive electron donation from alkyl groups leads to an increase in AcPO's S_N2 barrier of 5.2 kcal/mol while its HM barrier decreases by 1.7 kcal/mol. This result again emphasizes the need and challenge of simultaneously optimizing the kinetics of both the S_N2 and HM reactions for efficient redox initiation, despite the APRP rate being more sensitive to HM than S_N2. Although the barrier for the rate-determining HM step was lowered, the larger increase in the S_N2 barrier leads to an overall lower rate of radical generation of $k_r = 4.3 \times 10^{-12} \text{ s}^{-1}$. Finally, BPO's cyclic analogue – phthaloyl peroxide (PhthPO) – was predicted to possess a low S_N2 barrier of 8.8 kcal/mol and a high HM barrier of 33.8 kcal/mol. The low S_N2 barrier results from unrestricted access of the σ_{O-O}^* antibonding orbital and thus the absence of the O-O bond torsion penalty required of other peroxides to expose their σ_{O-O}^* antibonding orbitals (**SI**. TS1 structures of PhthPO and BPO). In addition, PhthPO is the only peroxide that was predicted to produce intermediates with an exergonic S_N2 free energy ($\Delta G_{S_{N2}}^\circ = -19.1 \text{ kcal/mol}$) despite the greater entropic penalty resulting from the anion group not leaving. The unique energetics

predicted for PhthPO result in $k_r = 9.4 \times 10^{-6} \text{ s}^{-1}$, which is orders of magnitude faster than all other peroxides examined according to our kinetic model based on an inner-sphere electron transfer APRP mechanism.

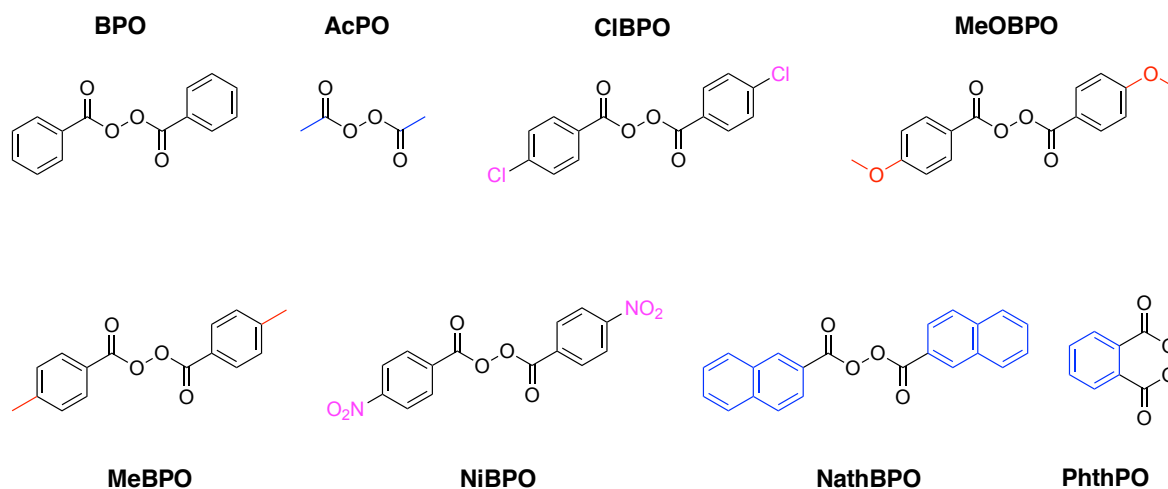


Figure 3.2: Diacyl peroxides investigated in this study. Groups shown in magenta denote electron-withdrawing groups, those in red, electron-donating groups, and those in blue indicate aromatic groups.

Table 3.1: MN15 free energy barriers, radical generation rate constants (k_r), and bond dissociation energies (BDE) with corresponding decomposition temperature (Td) for peroxides investigated in this study. Free energy barriers and bond dissociation energies are provided in kcal/mol, rate constants in s^{-1} , and Td in degrees C.

Category	Peroxide	$\Delta G_{S_N2}^\ddagger$	$\Delta G_{HM}^\ddagger$	k_r	$BDE (T_d)^a$
Acyl	BPO	16.2	25.6	1.3×10^{-11}	40.0 (80-85)
	MeBPO	17.3	25.0	1.4×10^{-11}	39.3 (85)

	MeOBPO	18.3	26.5	9.8×10^{-13}	40.5
	CIBPO	14.9	24.8	1.8×10^{-10}	39.8 (75) ^B
	NiBPO	12.6	24.7	1.9×10^{-10}	41.7
	NathPO	16.3	24.6	4.5×10^{-11}	38.8
	AcPO	21.4	23.9	4.3×10^{-12}	38.1
	PhthPO	8.8	33.8	9.4×10^{-6}	30.2 ^a (90-110)
Alkyl	DCPO	45.8	26.2	1.9×10^{-22}	38.8 (75-130)
	CIDCPO	44.5	25.5	2.8×10^{-15}	39.2
Carbonate	BEPC	14.3	24.4	1.7×10^{-9}	37.5 (35-40) ^C
	BPPC	9.2	22.2	1.8×10^{-6}	36.7
Inorganic	PDSF	32.6	40.0	5.0×10^{-21}	21.3 ^b
	HOOH	28.6	36.5	9.5×10^{-30}	51.0

^aT_d of BEPC is estimated from SADT of diacetyl peroxydicarbonate and dimyristyl peroxydicarbonate

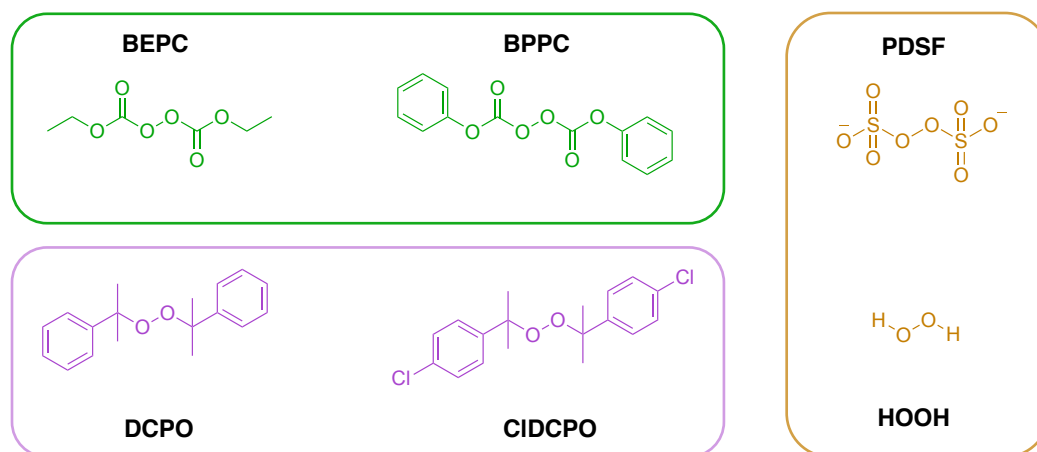


Figure 3.3: Non-acyl peroxides investigated in this study, including dicarbonate peroxides (green), dialkyl peroxides (purple), and the inorganic disulfate and dihydrogen peroxides (gold).

3.4.3 Alkyl, Carbonate, inorganic peroxides

In addition to diacyl peroxides, other common peroxide classes (**Figure 3.3**) were computationally evaluated to further explore potential candidates for accelerated APRP. Dicumyl peroxide (DCPO) is a non-acyl peroxide with two phenyl rings, used primarily as a thermal initiator that enables chain branching and cross-linking within polymer production. DCPO is similar to BPO but has tertiary carbons in place of carbonyl groups adjacent to the peroxide O-O bond. Because DCPO is an alkyl peroxide, the orbitals of its peroxy bond do not overlap with the π space of its phenyl rings, unlike BPO. This precludes aromatic stabilization of its peroxy radicals (**Figure 3.4**). DCPO and its para-chloro-substituted counterpart (CIDCPO) were both computed to have S_N2 barriers of ~ 45 kcal/mol for APRP polymerization, which is inaccessible at room temperature. In contrast, we compute modest HM barriers of 26.2 and 25.5 kcal/mol for DCPO and CIDCPO. However, the large S_N2 barriers render APRP initiation with dicumyl peroxides infeasible at practical temperatures. We validated these predictions using FT-IR (**Figure 3.6**), which showed that 3 mol% DCPO does not initiate polymerization for 20 min when added to 3

mol% DMA in DEGEEA monomer. This indicates that both DCPO and likely ClDCPO are insufficiently electrophilic due to the lack of acyl groups. Even AcPO, which possesses no phenyl rings, has lower S_N2 barriers than DCPO and Cl-DCPO; this indicates that the carbonyl groups neighboring the peroxide bond are more essential for accelerating APRP than decoupled phenyl rings that do not overlap with O-O orbitals. In contrast to BPO-derivatives in which EWG's significantly increase reactivity, Cl substitution of the phenyl groups did not lower the S_N2 barrier of ClDCPO because similarly, the tertiary-carbon disrupts the π conjugation between the O-O bond and the aromatic rings, thus preventing favorable orbital interactions.

Peroxyarbonates (dicarbonate peroxides) were also examined (**Figure 3.3**). Peroxyarbonates possess ester groups that contain additional oxygens that bridge the carbonyls to the alkyl groups of BEPC and phenyl groups of BPPC. We previously determined that acyl peroxides are superior to alkyl peroxides due to the π conjugation between the peroxy group and the carbonyls, regardless of the presence of phenyl groups. This π conjugation delocalizes the electron density of the peroxy oxygen lone pairs, thus enhancing the electrophilicity of the O-O bond. The carbonates of dicarbonate peroxides were predicted to provide both increased π conjugation and electron-withdrawing character, rendering the O-O bond more electrophilic. This increased O-O electrophilicity should lead to lower S_N2 barriers while retaining sufficient radical and anion stability through improved electron delocalization. Peroxyarbonates should therefore exhibit improved kinetics over acyl peroxides. To examine this hypothesis, we investigated bis(ethyl) peroxyarbonate (BEPC, **Figure 3.3**) and bis(phenyl) peroxyarbonate (BPPC, **Figure 3.3**) within our APRP model. Our results predict that BEPC has comparable kinetics and BPPC has improved kinetics relative to Ni-BPO, which is predicted to be the most efficient non-cyclic BPO derivative for APRP operating through the APRP inner-sphere ET mechanism (vide supra).

DFT predicted S_N2 and HM barriers of 14.3 and 24.6 kcal/mol for BEPC and 9.2 and 22.2 kcal/mol for BPPC. The low S_N2 and HM barriers for both peroxy carbonate species suggest that they indeed possess improved kinetics over BPO, agreeing with our previous conclusion that aromatic systems and EWG groups facilitate APRP reactions. However, despite these promising predictions for APRP initiated by peroxy carbonates, we excluded them as viable candidates to accelerate APRP due to their low decomposition temperatures ($T_d = 35-40$ C for BEPC; **Table 3.1**).

Lastly, we evaluated two inorganic peroxides (**Figure 3.3**): peroxydisulfate (PDSF) and hydrogen peroxide (HOOH). In PDSF, each oxygen of the peroxy bond is bound to a tetrahedral sulfur which contains two sulfinyl bonds ($S=O$) and a thiolate bond ($S-O^-$). The abundance of electronegative oxygens bound to the sulfurs is expected to increase peroxy electrophilicity through the inductive effect and correspondingly decrease the S_N2 barriers of PDSF such that it may perform as an efficient peroxide within the APRP framework. On the other hand, steric hindrance from the tetrahedral geometry and substantial Pauli repulsion from the oxygen lone pairs may increase the S_N2 barrier. These two competing effects resulted in an intermediate S_N2 barrier of 32.6 kcal/mol, which falls between the predicted barriers of acyl and alkyl peroxides and too high for PDSF to efficiently initiate room-temperature APRP. Additionally, PDSF's HM barrier of 40.0 kcal/mol indicates that the tetrahedral geometry led to the lack of orbital overlap between the radical oxygen and the three sulfate oxygens and resulted in the absence of radical stabilization. Consequently, our results predict that PDSF would perform poorly for APRP initiation, which was confirmed by FT-IR experiments (Figure xx). For the case of hydrogen peroxide (HOOH), the lack of functional groups excluded the potential for electrophilicity or radical/anion stabilization. Yet, HOOH has a lower S_N2 barrier (28.6 kcal/mol) than DCPO, primarily due to reduced steric hinderance as opposed to increased electrophilicity. Conversely, HOOH's HM free energy barrier

is higher than DCPO's because HOOH lacks the ability to stabilize radicals while DCPO's tertiary carbons stabilize radicals. Ultimately, with a predicted $k_r = 9.5 \times 10^{-30} \text{ s}^{-1}$ HOOH was predicted to perform the worst of the peroxides considered in this study for APRP initiation.

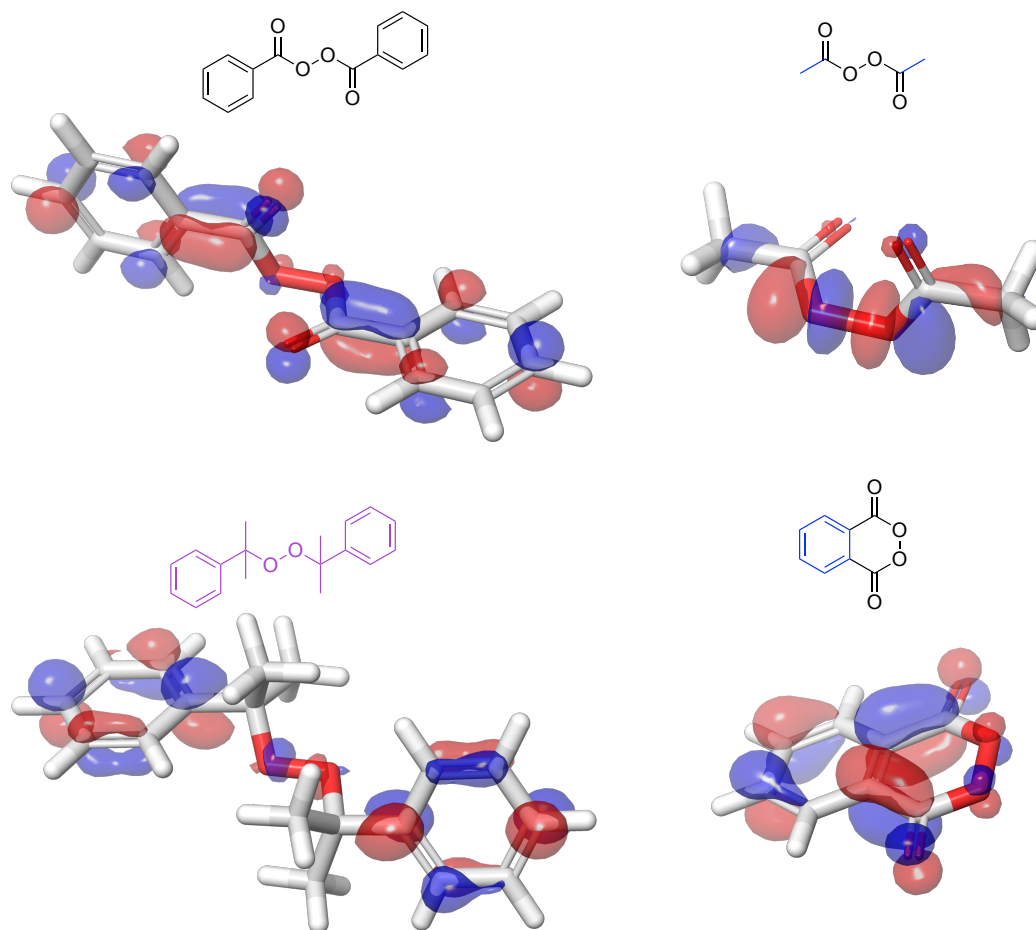


Figure 3.4 MN15 Lowest unoccupied molecular orbitals (LUMOs) of a) benzoyl peroxide (BPO), b) acetyl peroxide (AcPO), c) dicumyl peroxide (DCPO), and d) phthaloyl peroxide (PhthPO). The LUMO is illustrated because upon S_N2 attack, the leaving oxy anion becomes singly reduced with the additional electron occupying what was previously the LUMO. The LUMO for BPO is large and delocalized over the entire molecule. In contrast, AcPO's LUMO is smaller, but still delocalized over the molecule. The LUMO of DCPO is large but with no orbital amplitude

localized on the tertiary carbons, indicating no conjugation between the O-O bond and the phenyl rings. The LUMO of PhthPO is large and delocalized over the entire molecule.

3.4.4 In-depth investigation of phthaloyl peroxide (PhthPO)

DFT predicted that PhthPO will outperform all 15 peroxides studied here, including various BPO derivatives and new peroxycarbonate structures. PhthPO has superior thermostability ($T_d > 90$ C) and is employed primarily in synthetic chemistry. With the promise of unprecedented APRP efficiency and relatively high thermal stability, we synthesized PhthPO and monitored its initiation behavior by FTIR (**Figure 3.6**). Contrary to our prediction, negligible polymerization was observed. Instead, upon addition of the PhthPO resin to DMA the resin changed from colorless to brown, a behavior distinct from the other peroxides that exhibited no noticeable color change (**Figure 3.5**). The UV-Vis spectrum of the reacted mixture of phthaloyl peroxide added to *N,N*,4-trimethyl-aniline absorbed in the visible range with peaks at ~ 400 and ~ 550 nm. This color change suggests that PhthPO undergoes a reaction that involves a disparate mechanism from the inner-sphere ET APRP mechanism we've heretofore assumed for APRP.

To explore alternative reaction mechanisms for PhthPO with *N,N*-dimethylaniline we calculated the activation barrier for outer-sphere ET to directly produce the amine radical cation of DMA and PhthPO radical anion products. Such an ET would result in dissociation of the peroxy bond, which can be theoretically understood as dissociative ET by Saveant's model. For the outer-sphere ET from amine to peroxide, Saveant's model (eqs. 1 and 2) requires three parameters; the peroxide bond-dissociation energy (*BDE*), the total reorganization energy (λ_{tot}) comprised of solvent reorganization and molecular reorganization, and the net free energy of reaction (ΔG^0).

$$\Delta G^\ddagger = \Delta G_0^\ddagger (1 + \Delta G^0 / 4\Delta G_0^\ddagger)^2 \quad (eq. 1)$$

$$\Delta G_0^\ddagger = (BDE + \lambda_{tot})/4 \quad (eq. 2)$$

For outer-sphere ET from DMA to PhthPO, DFT predicted a BDE of 30.2 kcal/mol, $\lambda_{tot} = 0.25$ kcal/mol, and a $G^0 = 14.7$ kcal/mol. Hence, the predicted dissociative ET barrier is 16.7 kcal/mol, which produced an outer-sphere rate constant (k_{OS}) of 3.4 s^{-1} , as opposed to PhthPO's predicted inner-sphere ET rate constant of $9.4 \times 10^{-6} \text{ s}^{-1}$. Consequently, although the kinetic constant of inner-sphere ET with phthaloyl peroxide was predicted to be the largest of all peroxides investigated, the kinetic constant of outer-sphere ET with the same molecule was found to be six orders of magnitude larger, indicating that the DMA-PhthPO redox pair will invariably undergo outer-sphere ET. A similar analysis was conducted for a more nucleophilic amine that may permit facile S_N2 attack and initiate the desirable APRP reaction cascade through inner-sphere ET, but we concluded that regardless of the identity of amine reductant partner, PhthPO remained incompetent as an oxidant for APRP (SI. Discussion of PhthPO reaction with a nucleophilic amine).

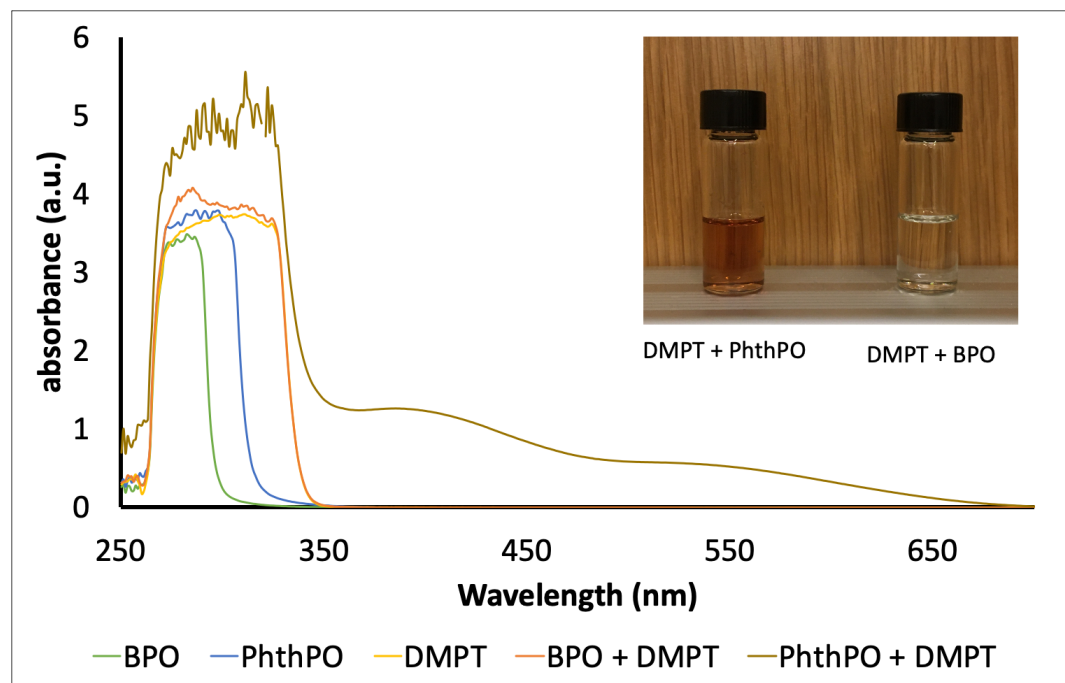


Figure 3.5. UV-Vis spectra of redox initiators. PhthPO was compared to BPO by adding to N,N-dimethyl p toluidine (DMPT), a proxy for DMA. When BPO is combined with DMPT, no significant change occurred while the addition of DMPT to PhthPO resulted in an obvious change in the spectrum. Analytes were dissolved in dimethylformamide at the concentration of 6.1 mM.

3.4.5 Summary of peroxides studied

The compiled redox kinetic constants of all peroxides considered to react with DMA are reported in **Table 1**. When these peroxides were examined in our FT-IR polymerization study (**Figure 3.6**), those that were predicted to have lower rate constants than BPO were observed to exhibit no significant polymerization including HOOH, SPO, etc. Conversely, BPO rapidly progressed to full conversion within xx min (**Figure 3.6**). We expect that peroxides with rate constants larger than BPO's exhibit rapid polymerization behavior based on the APRP mechanism unless like PhthPO they undergo outer-sphere ET or are thermally unstable. Yet, these likely involve synthetic challenges and potential hazards, precluding them from being considered in our current experimental study. Therefore, BPO is reaffirmed as a good compromise of rapid redox kinetics and sufficient thermal stability.

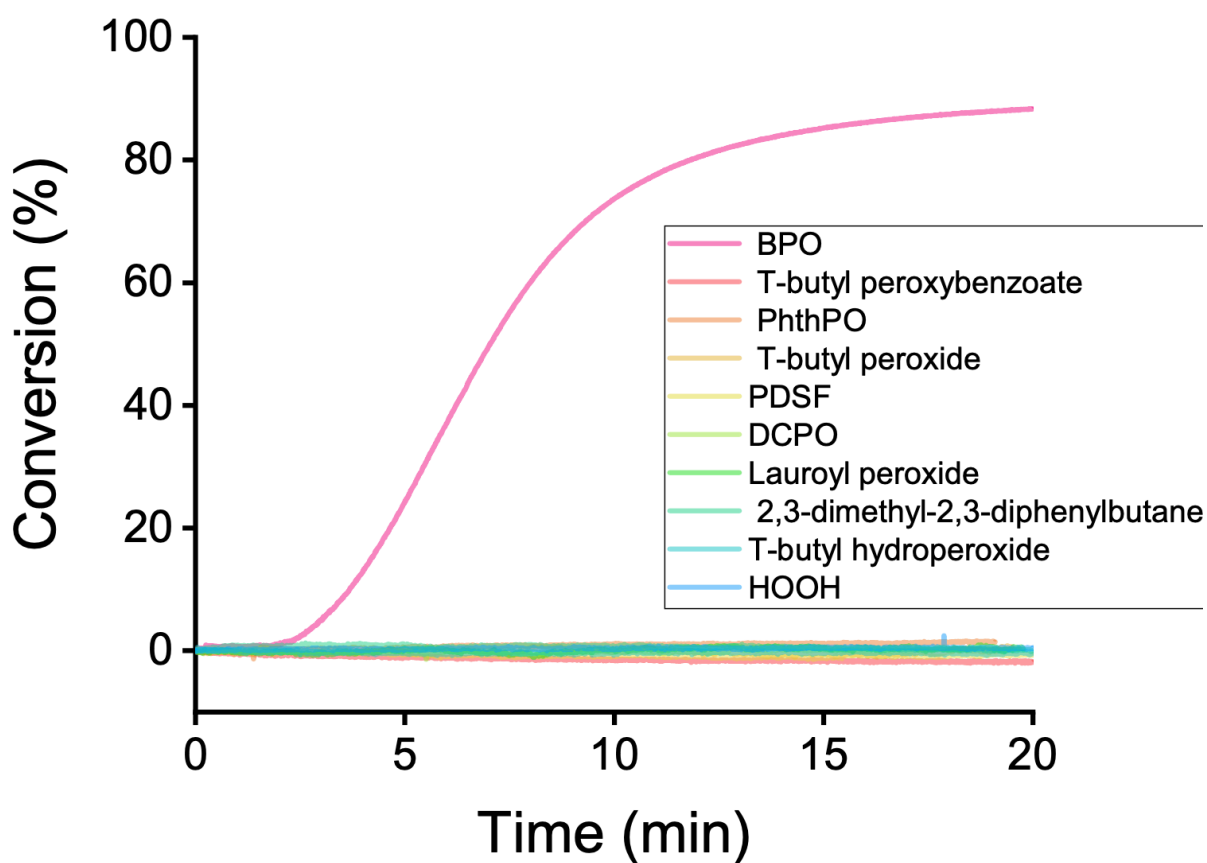


Figure 3.6. experimental kinetic profiles of various peroxides. 3 mol% of amine and peroxides were used in DEGEEA resin.

3.4.6 Direct writing application of APRP based on an efficient APRP pair.

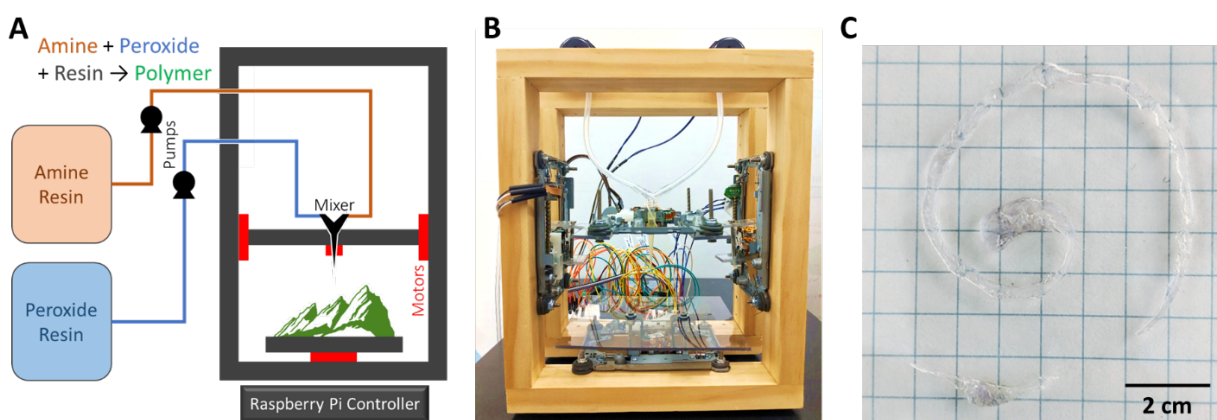


Figure 3.7 a) Schematic of our custom direct writing system depicting the two separate pump lines from the amine and peroxide resin tanks that flow into a mixing nozzle, enabling the in situ combined amine-peroxide resin to be printed through the nozzle onto a support platform. b) A picture of the direct writing system. c) a polymer spiral written via amine-peroxide redox polymerization. Bisphenol A ethoxylate diacrylate (M_n 512, EO = 2) with 1.5 wt% BPO and MPP was used.

From the present peroxide study and our previous investigation of amine initiators (REF), we've determined that the N-(4-methoxyphenyl)pyrrolidine (MPP) and BPO redox pair may accelerate the rate of APRP to an extent that enables the direct writing of resins. The potential benefits of an APRP-enabled direct writing system include low cost of the initiator system relative to photoinitiators, high filler concentrations for structural or electronic applications, proven low toxicity for use in medical applications, and high inter-layer strength due to curing across layer boundaries. We designed our direct writing system based on an inkjet printer using a redox chemistry of MPP and BPO (**Figure 3.7**). This system has two pumps which flow a moderate viscosity amine resin and peroxide resin into a mixing nozzle which is connected to motors that move along the horizontal X and Y axes (**Figure 3.7 a**). Polymerization begins in the mixing nozzle where the two resins combine, and the resulting amine-peroxide resin is then pumped onto a support platform that is positioned along the X and Y axes by two motors to provide 2-dimensional control. The addition of other resin reservoirs would enable multi-material printing to fabricate printed objects with variable material properties and the addition of a Z-axis motor could enable 3D printing. We used this writing system (**Figure 3.7 b**) to print a spiral design with an average width of approximately 5 mm with some segments near 1 mm resolution (**Figure 3.7 c**).

The large variability in printing width could be improved by incorporating more consistent pumps and a method to better control the pump rate; furthermore, a narrower nozzle may enable a resolution <1 mm. Gelation was achieved in under 10 seconds with some oxygen-inhibited layer with xx resin at a concentration of xx. Although substantial work remains to more fully realize the APRP direct writing technology, this proof-of-concept demonstration indicates that APRP can be successfully implemented as the initiation method in a direct writing system and suggests that if the potential benefits of this technology are achieved, it could become the preeminent 3D printing system for a range of applications including structural, electronic, and medical devices where high filler concentrations and low toxicity could enable state-of-the-art printed objects.

3.5 Conclusion

In this work, we have presented an extensive computational investigation of 15 peroxide oxidants to initiate amine-peroxide redox polymerization through a mechanism we previously reported to accurately predict experimental APRP rates. We found that acyl groups not only increase the electrophilicity of peroxides to enhance the S_N2 reaction but also stabilize anion and radical intermediates generated from the parent peroxides. As such, functionalization of acyl groups either through addition of *para*-EWG's (to increase peroxy electrophilicity) or through addition of phenyl rings (to improve resonance stabilization) is imperative for high redox efficiency. Alkyl peroxides have low homolysis barriers due to their tertiary carbons that stabilize radical intermediates, yet their reduced electrophilicity at the peroxy bond increases the S_N2 barrier and lowers alkyl peroxides' overall reactivity. While peroxycarbonate structures appeared promising in terms of their predicted initiation kinetics resulting from their higher electrophilicity and stronger resonance, their low thermal stability currently hinders their practical use for

accelerated APRP. Inorganic peroxides such as peroxydisulfate and hydrogen peroxide are predicted to perform poorly in APRP initiation. Phthaloyl peroxide, which appeared to be the most promising candidate from our analysis, does not proceed through the inner-sphere electron transfer APRP mechanism but instead proceeds through an outer-sphere ET to produce non-initiating radicals, rendering phthaloyl peroxide ineffective for APRP. However, the ability to switch between different ET mechanisms based on the amine-peroxide pair is nonetheless novel and provides additional chemical and mechanistic insight into amine-peroxide redox chemistry; this discovery could enable an entirely new class of redox pairs that generate initiating radicals through outer-sphere ET. Ultimately, we find that benzoyl peroxide remains the gold standard peroxide for APRP due to its rapid APRP kinetics and high thermal stability. Furthermore, we demonstrate an APRP direct-writing system that leverages an optimized redox pair, where automated mixing of two resins on a movable platform enabled printing of a spiral polymer. This amine-peroxide direct-writing technology has the potential to be the preeminent form of 3D printing where high filler concentrations and low toxicity are imperative.

3.6 Supporting Information

S3.1. Methods

S3.1.1. Computational Methods.

All calculations were performed within the GAUSSIAN 16 Revision A.03 software package⁸⁷ using density functional theory based on the MN15 density functional⁸⁸ and 6-31+G(d,p) basis set⁸⁹ with solvent effects described by the universal solvation model (SMD).⁹⁰ The MN15

functional was chosen because it performed the best of 13 functionals evaluated compared to the highly accurate, but computationally demanding, CBS-QB3^{91,92} and CCSD(T)^{93–95} methods with an RMS error of 1.4 kcal/mol for reaction and TS energies relative to the CBS-QB3^{91,92} method (see **SI1**). The accuracy of this functional likely results from its ability to simultaneously describe both single- and multi-reference systems.⁸⁸ This is necessary because some of the TSs and intermediates of the investigated molecules exhibit multi-configurational character (See **SI1**). Vibrational force constants were calculated to verify that the stationary state geometries were optimized to the correct structures and to compute vibrational entropies, zero-point energies and thermal corrections at 298 K. Solvent effects were described using the SMD solvent model with parameters describing ethyl acetate (EtOAc) because of its structural similarity to (meth)acrylate monomers. Furthermore, the dielectric constant of EtOAc⁸⁷ at ~ 6 is suitable for describing the dielectric environment produced by common bulk (meth)acrylate monomers with dielectric constants ranging from 2.5 to 11.^{96,97} The monomer used in the computational investigation of monomer addition kinetics was ethyl methacrylate. The orbitals depicted in this study are obtained *via* the Natural Bond Orbital approach (version 3.1) as implemented in Gaussian16.⁹⁸

S3.1.2. Experimental Methods

The conversion of monomer by ambient bulk redox-initiated polymerization was monitored in real time with an FT-IR spectrophotometer (Nicolet Magna-IR Series II, Thermo Scientific, West Palm Beach, FL) by monitoring the C=C stretching absorption band at 1637 cm⁻¹ for 20 mins in OMNIC software. We chose DEGEEA monoacrylate to reduce a confounding factor of autoacceleration as opposed to cross-linking multi-functional monomers that exhibit autoacceleration and are commonly used in many polymerization kinetic studies. The

spectrophotometer was equipped with an MCT/A detector, and parameters on the FT-IR were set to 2 scans, a resolution of 16, an optical gain of 1, an optical velocity of 1.8988, and an optical aperture of 15. We studied the polymerization kinetics initiated with two separate batches of resin with 3 mol% of BPO oxidant and various amine reductants. On a horizontal NaCl salt plate, 15 μ l of BPO resin was first deposited, to which another 15 μ l of amine resin was added. This solution was then mixed with micropipette tips. Another NaCl salt plate was then placed on top of the mixture, after which data acquisition began immediately. A clear baseline of zero conversion during an induction period preceding each polymerization was observed for every sample. The concentrations of the oxidant and reductant were chosen to accommodate approx. 30 seconds of sample preparation through an induction time and to capture the entire polymerization process. For example, efficient amines may have $\sim$ 40 seconds of induction time so that the conditions we chose allowed the capture of $\sim$ 10 seconds of the induction period as well as the subsequent initial polymerization kinetics. On the other hand, some amines may initiate after induction period of several minutes or may not be observed to initiate within 20 mins of mixing the redox pairs. These conditions were used to generate data for **Figures 4, 6, and Table 1**. For the kinetic demonstration of MPP and **Figure 10**, the concentration was changed from 3 mol% to 0.48 mol% for both oxidant and reductant, accompanied by resin change to 50 wt% triethylene glycol dimethacrylate and 50 wt% poly(ethylene glycol) methacrylate in order to accommodate the unprecedented initiating ability of the MPP amine whose full polymerization kinetics was too fast for us to observe under the previous conditions and to replicate more relevant resins for various applications. ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, as indicated in the respective measurement.

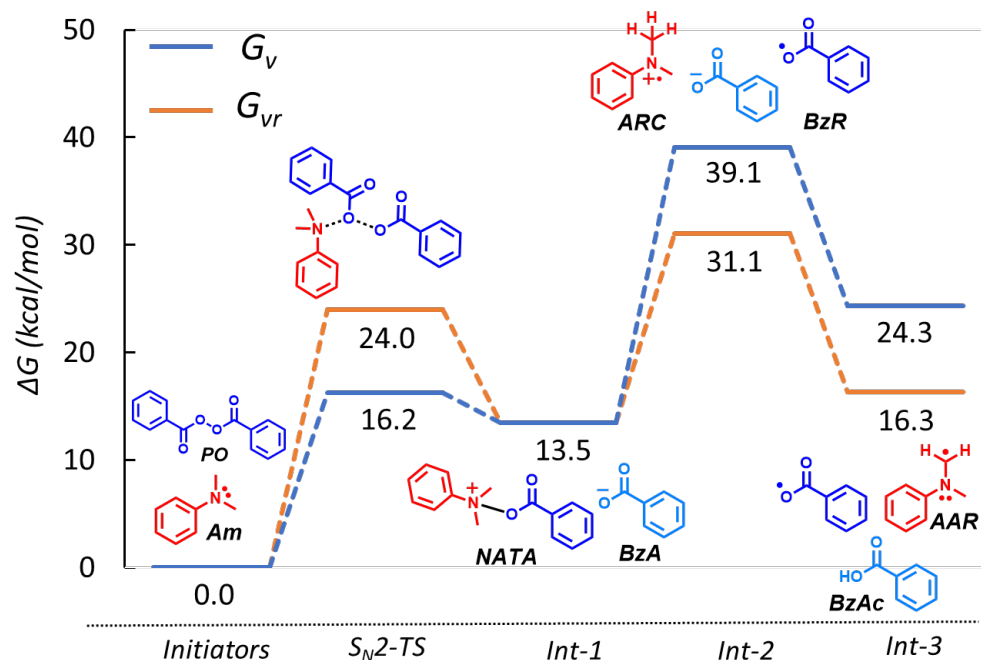


Figure S1. Computed schematic reaction profiles for radical generation via the redox reaction between *N,N*-dimethylaniline (DMA) and benzoyl peroxide (BPO). Relative free energies (G_v and G_{vr} at 298.15 K) are given in kcal/mol in ethyl acetate which simulates the (meth)acrylate resin. G_v (shown in blue) represents the reaction energetics in high viscosity resin while G_{vr} (shown in orange) represents the reaction energetics in low viscosity resin. The initiation is overall endergonic, whose unfavorable thermodynamics is compensated for by highly exothermic radical additions of the α -aminoalkyl radical (AAR) and benzoyloxy radical (BzR). The trend in S_N2 and homolysis barriers changes based on resin conditions, making it more difficult to identify the true rate-determining step. A transition state does not exist between **Int-1** and **Int-2** due to no formation of an activated complex.

Asymmetric Peroxides: two asymmetric peroxides from Sigma, did not result in interesting results.

Not many commercialized asymmetric peroxides (<https://pubs.acs.org/doi/abs/10.1021/jo100793j>). synthesis needed.

Thus far we have only considered symmetric peroxides. As stated above, EWG substitutions lower the S_N2 forward barrier, while EDG substitutions lower the homolysis barrier. These competing electronic effects prompted us to investigate asymmetric peroxides. In the case of asymmetric peroxides regioselectivity must be taken into account. Each oxygen of the O-O bond of asymmetric peroxides will exhibit different reactivity, such that S_N2 attack yields two distinct transition states, S_N2 rate constants and oxyammonium products with two different homolysis rates. The Curtin-Hammett principle states that the selectivity of the competing reactions can be calculated from the difference in activation barriers. Using this and the pseudo-steady state approximation we derived the selectivity of competing reactions as a function of $\Delta G(T)_v^\ddagger$ (Eq. 3):

$$\frac{[P_1]}{[P_2]} = \exp \left[\frac{-\Delta G_{v,1}^\ddagger - \Delta G_{v,-2}^\ddagger + \Delta G_{v,-1}^\ddagger + \Delta G_{v,2}^\ddagger}{RT} \right] \quad (3)$$

Figure S2: Sample reaction coordinate for an asymmetrical peroxide. Reactant position begins in the middle, and orange and blue lines indicate reaction progression through either side of the asymmetrical peroxide. The derived selectivity equation (3) is shown above the plot, with each free energy variable being denoted along the reaction coordinate.

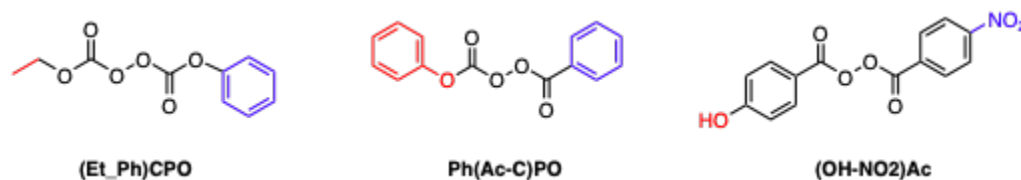


Figure S3: Asymmetrical peroxides investigated. Colors used to distinguish different peroxide functional groups.

The asymmetric peroxides we examined were composed of halves of the symmetric peroxides we considered above. For example, we formed (Et-Ph)CPO (see Figure XX) by combining halves of the two carbonate peroxides EtCPO and PhCPO. Our goal is to produce asymmetric peroxides that perform better than its two symmetric parents. We investigated (Et-Ph)CPO because we hypothesized that it would perform radical generation faster than its symmetric progenitors, EtCPO and PhCPO. Our reasoning was based on including the ethyl side of the peroxide to provide low steric hindrance to S_N2 attack by the amine reductant and the phenyl side to provide radical and anionic stabilization *via* its extended π system. We also investigated the kinetics of two other asymmetric peroxides: Ph(Ac-C)PO and (OH-NO₂)Ac. Ph(Ac-C)PO is the hybrid of BPO and PhCPO where one side is an analog of BPO and contains an acyl group attached to a phenyl ring, while the other is an analog of PhCPO and contains a carbonate group attached to a phenyl ring. We also examined (OH-NO₂)Ac as a simple asymmetric peroxide functionalized by different groups at the para positions of the phenyl rings; an -OH group on one phenyl and an -NO₂ on the other. Despite its higher electronegativity, the oxygen of the -OH contains two lone pairs and therefore acts as a π electron-donating group. In contrast, the -NO₂ group is electron-withdrawing due to N and O's higher electronegativity and the group's inability to act as a π electron donor.

Table S1: Free energy barriers and selectivities of asymmetrical peroxides. All energies were computed with MN15 6-31G+(d,p) in ethyl ethanoate modeled by SMD.

Peroxide	S _N 2 attack	$\Delta G_{v,forward}^\ddagger$	$\Delta G_{v,reverse}^\ddagger$	Selectivity	
(Et-Ph)CPO	phenyl	12.9	0.9	3.2E-06	=[phenyl]/[ethyl]
	ethyl	12.1	7.6		*prefers ethyl attack

Ph(Ac-C)PO	acyl	12.8	8.5	7.1E07	= $\frac{[\text{acyl}]}{[\text{carbonate}]}$
	carbonate	13.1	-1.9		*prefers acyl attack
(OH-NO ₂)Ac	NO ₂	17.8	10.3	4.4E-08	= $\frac{[\text{OH}]}{[\text{NO}_2]}$
	OH	15.0	-2.6		*prefers NO ₂ attack



Figure S4: K_r values for asymmetric peroxides and their symmetric analogs. Asymmetric peroxides are denoted by green data points, whereas symmetric analogs are denoted by the orange and red data points.

With asymmetric peroxide selectivities determined (see table XX), we again compute free energy barriers and subsequent K_r values (figure XX). We see that in all three cases, the asymmetric peroxides were able to outperform one of their symmetric analogs, while also falling slightly short of the other symmetric analog. This phenomena is likely due to INSERT REASONING HERE. We therefore conclude that this methodology of hybridized asymmetric peroxides provides no kinetic benefit over symmetric peroxides for APRP.

S3.2. Phthaloyl peroxide

This motivated us to investigate the peroxides illustrated in Figure XX which all undergo a unimolecular APRP mechanism, and contain an EWG or EDG on the phenyl ring. These peroxides are asymmetric and each oxygen in the O-O bond will exhibit different S_N2 and homolysis reactivity due to the relative positions of the phenyl-functional groups. In the context of electrophilic aromatic substitution, halogens are ortho/para deactivating groups. In the meta configuration, EWGs render the ortho and para positions of the phenyl ring partially negatively charged *via* the inductive effect, and therefore increase the peroxide's ability to stabilize the anion and radicals they produce. The resulting increased stability is expected to lead to lower S_N2 and homolysis barriers, and therefore faster initiation kinetics. In contrast, para and ortho configurations should have the opposite effect; their positions relative to the carbonyl groups should inhibit extended π conjugation and thus destabilize the anion and radical successors resulting in increased S_N2 and homolysis barriers. Nitro is predicted to act as a meta-directing EWG, and should therefore undergo a S_N2 attack that places the Nitro group in the meta position (relative to the anionic carbonyl). Our DFT results confirm this prediction. Using our previously derived selectivity equation (eqn. 3), the S_N2 product ratio at 298 K is predicted to be $9.7E-38$ favoring a meta-configured Nitro group, which is the S_N2 attack that renders the ortho and para positions partially negative. In contrast, halides are predicted to act as ortho/para-directing EWGs. PthAc_F and PthAc_Cl should therefore undergo attack in which the functional groups are ortho/para relative to the anionic carbonyl groups. The product ratios for PthAc_F, and PthAc_Cl, were calculated to be $8.2E-36$, **X**, and $6.0E-36$ (respectively) in favor of para/ortho configurations,

thus confirming our prediction. We ignore the non-selective reaction paths and report the kinetic constants of the favorable APRP mechanisms below.

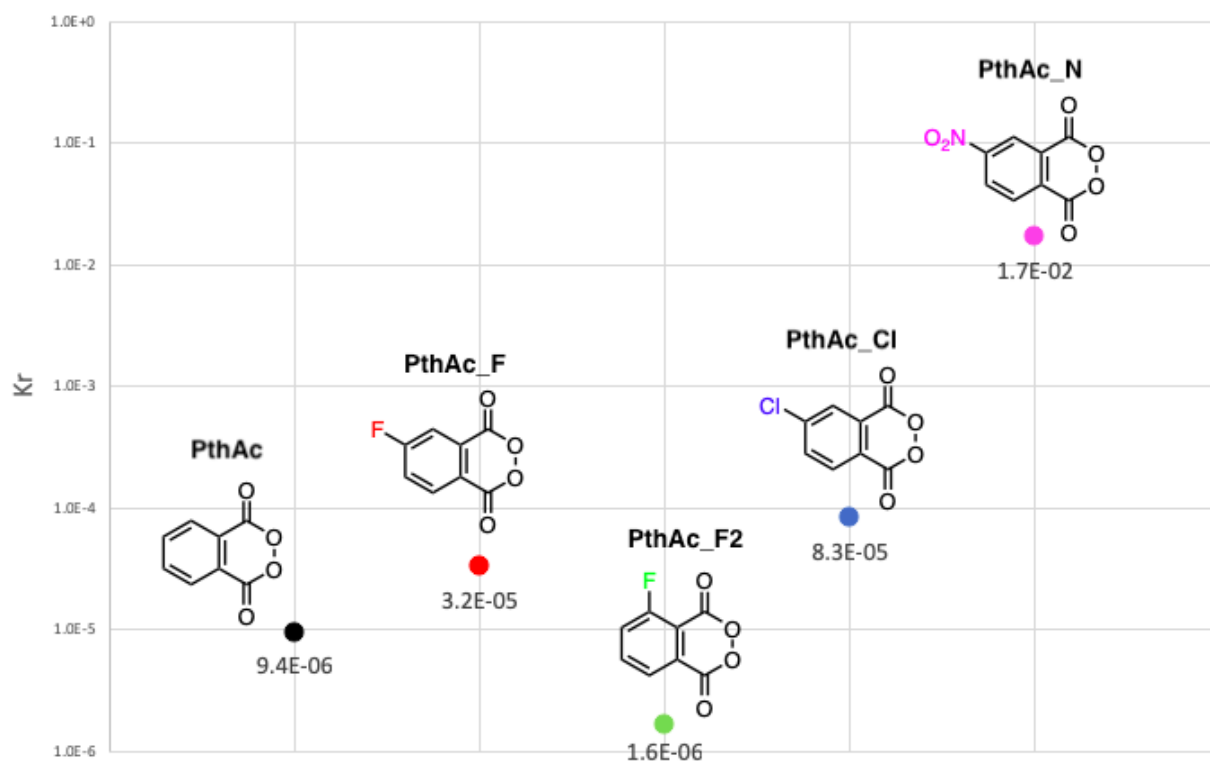


Figure S3.5: Further phthaloyl peroxides investigated, as well as the original PthAc for reference. Colors used to distinguish different functional groups.

Our results predict that the addition of functional groups to the phenyl rings of phthaloyl peroxides further improved the kinetics of their redox initiation, with the exception of PthAc_F2. As predicted, PthAc_F and PthAc_Cl undergo S_N2 attack at the bottom oxygens (rendering the halides to a para configuration) followed by homolysis to produce kinetic constants greater than their phthaloyl progenitor.

We next investigated whether PhthPO might be viable as the peroxide for APRP when paired with a nucleophilic amine that may drive it to undergo the desired inner-sphere ET. A more nucleophilic amine has a greater driving force for attack on an electrophilic site, meaning S_N2

attack on an electrophilic oxygen should be more facile. We chose to examine 1-methylpyrrolidine (MePy) as the nucleophilic amine that might facilitate inner-sphere ET with PhthPO. We calculated rate constants for inner and outer sphere ET to afford the amine radical cation and peroxide radical anion products. We found the S_N2 and HM barriers to be 3.8 and 24.2 kcal/mol, corresponding to a respectable k_r of 0.2 s^{-1} for the MePy-PhthPO pair. While this k_r is considerably higher than that for the standard DMA amine we predict that the k_r for outer-sphere ET also improves; We predict the MePy-PhthPO k_{OS} to be 35.0 s^{-1} , over two orders of magnitude higher than k_r . This prediction is confirmed by experiment. We again synthesized PhthPO, mixed it with MePy, and monitored the initiation behavior using FT-IR. Again, we observed negligible amount of polymerization, and the solution changed color to blue. We conclude that PhthPO favors outer-sphere ET regardless of the amine's nucleophilicity, rendering it incompetent as a peroxide to initiate APRP.

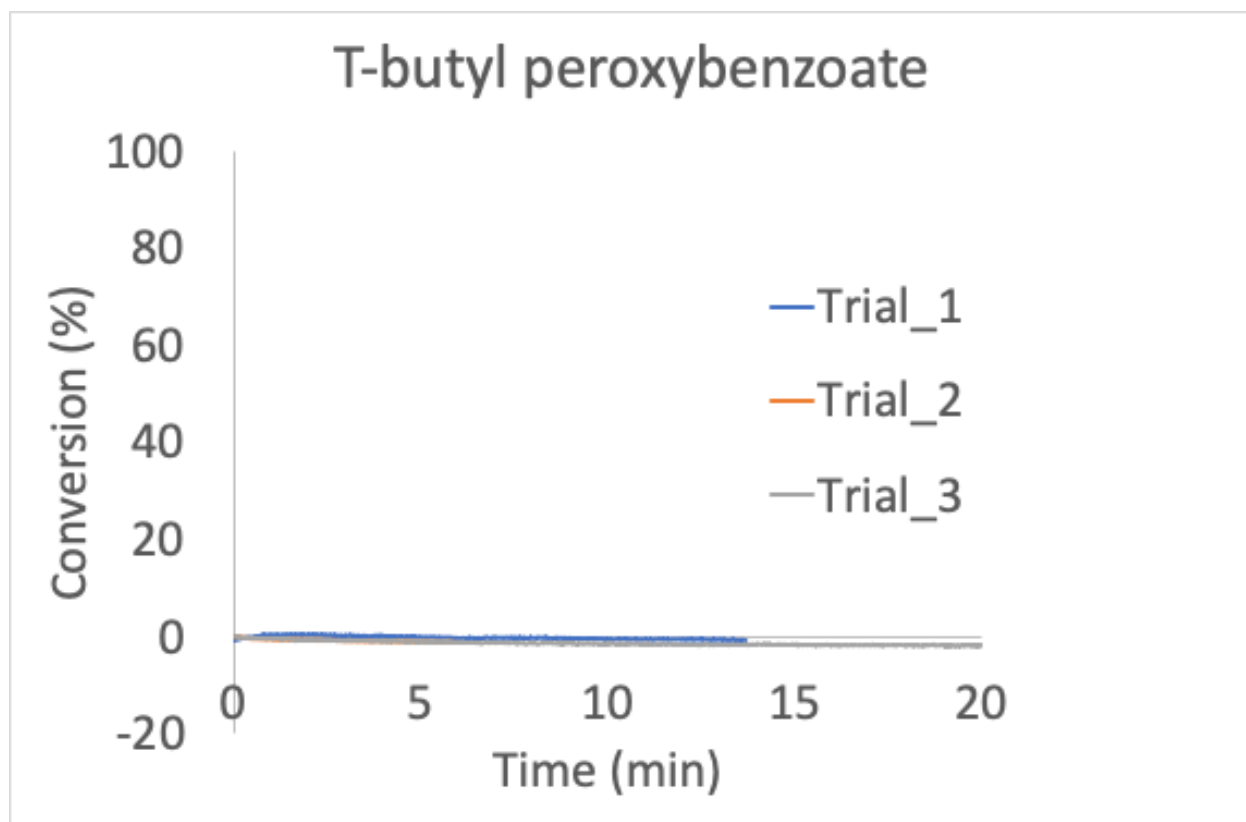


Figure S3.6. Polymerization profiles of t-butyl peroxybenzoate

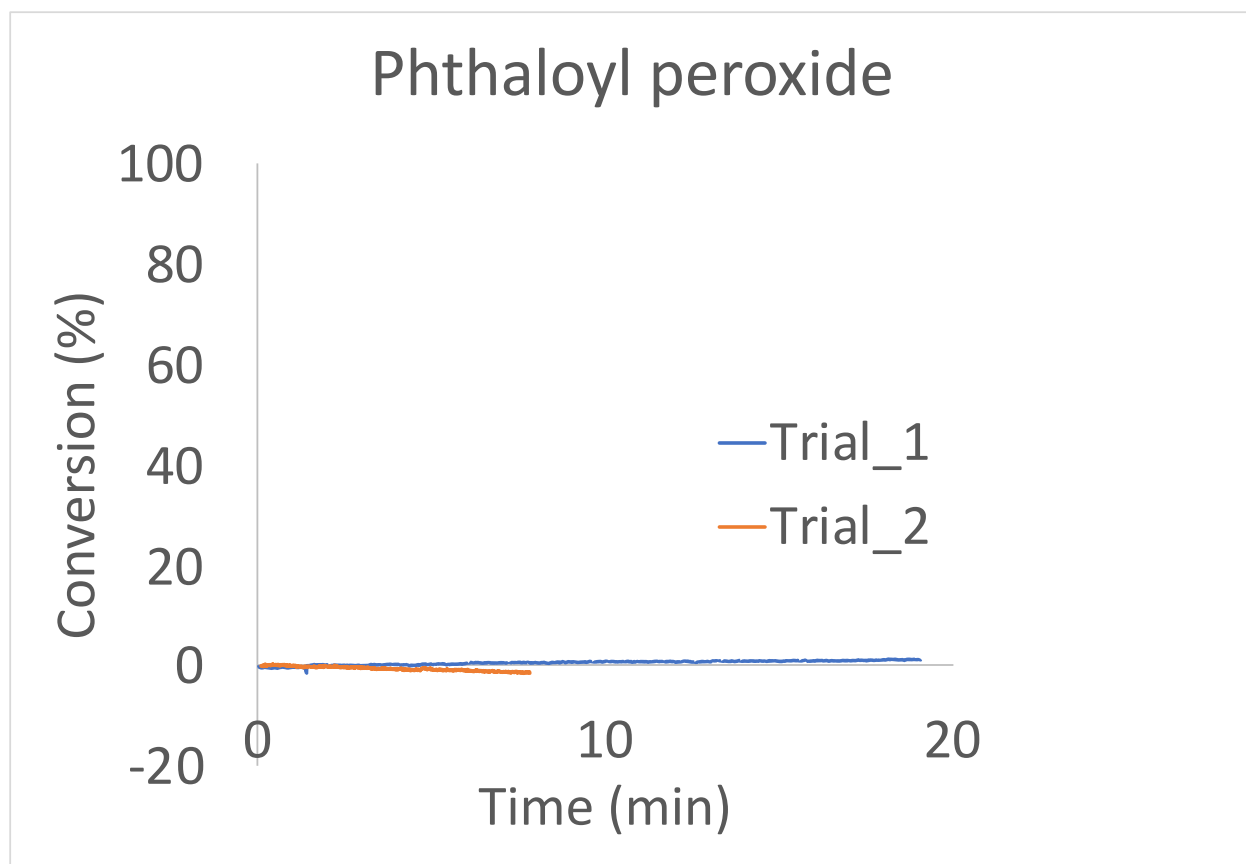


Figure S3.7. Polymerization profiles of Phthaloyl Peroxide

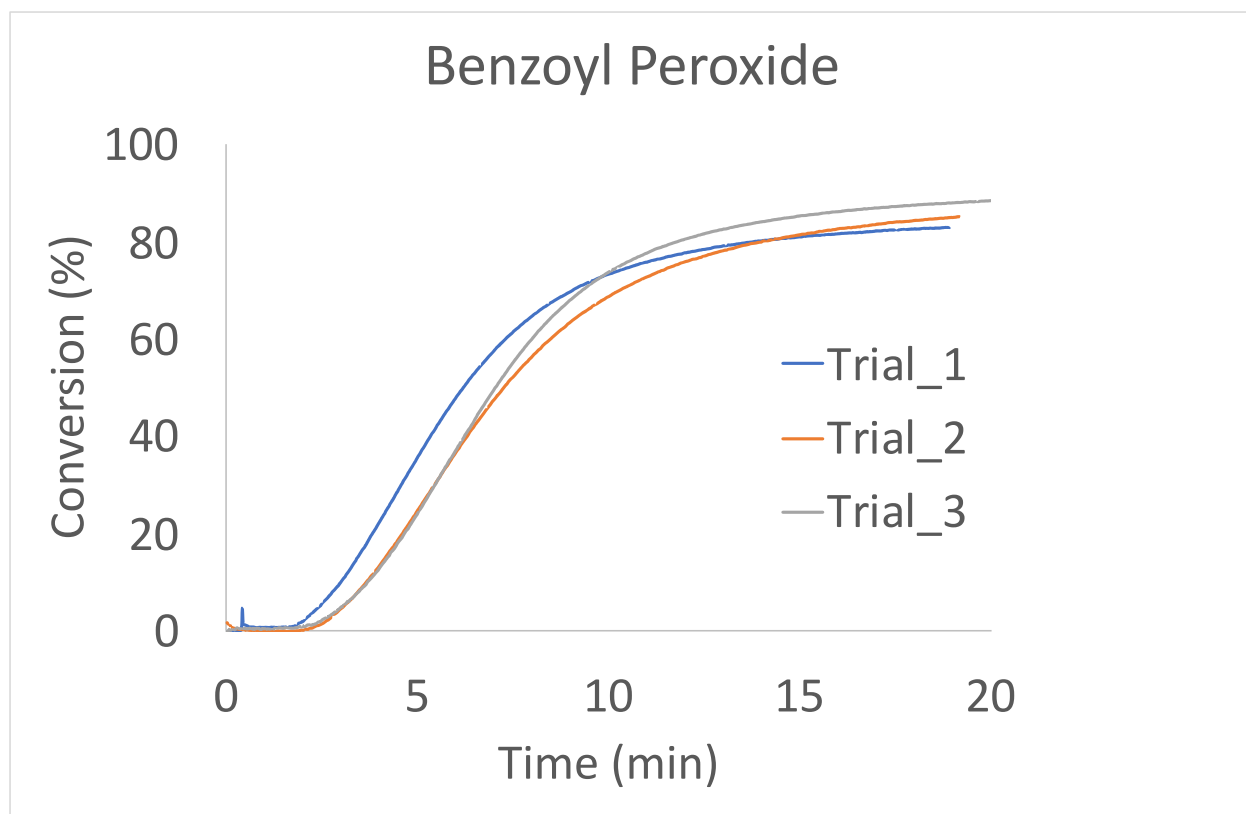


Figure S3.8. Polymerization profiles of Benzoyl Peroxide

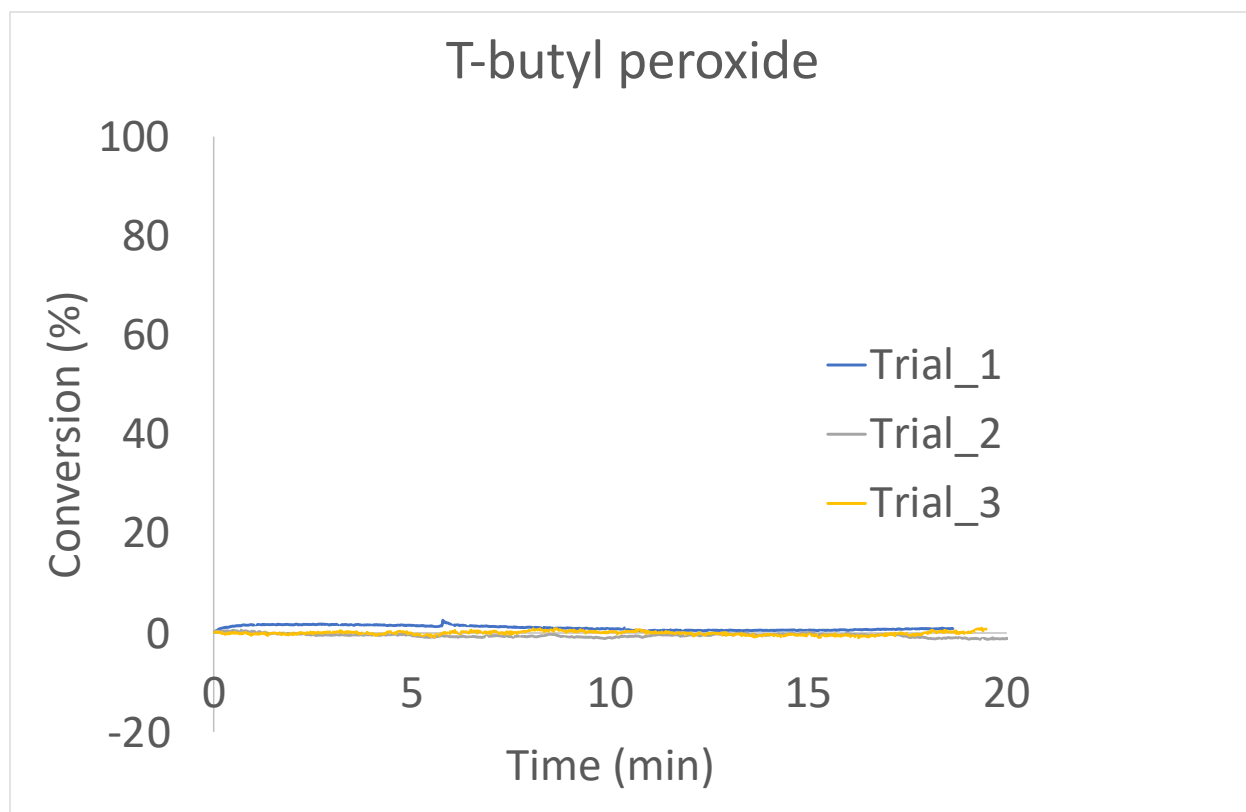


Figure S3.9. Polymerization profiles of t-butyl peroxide

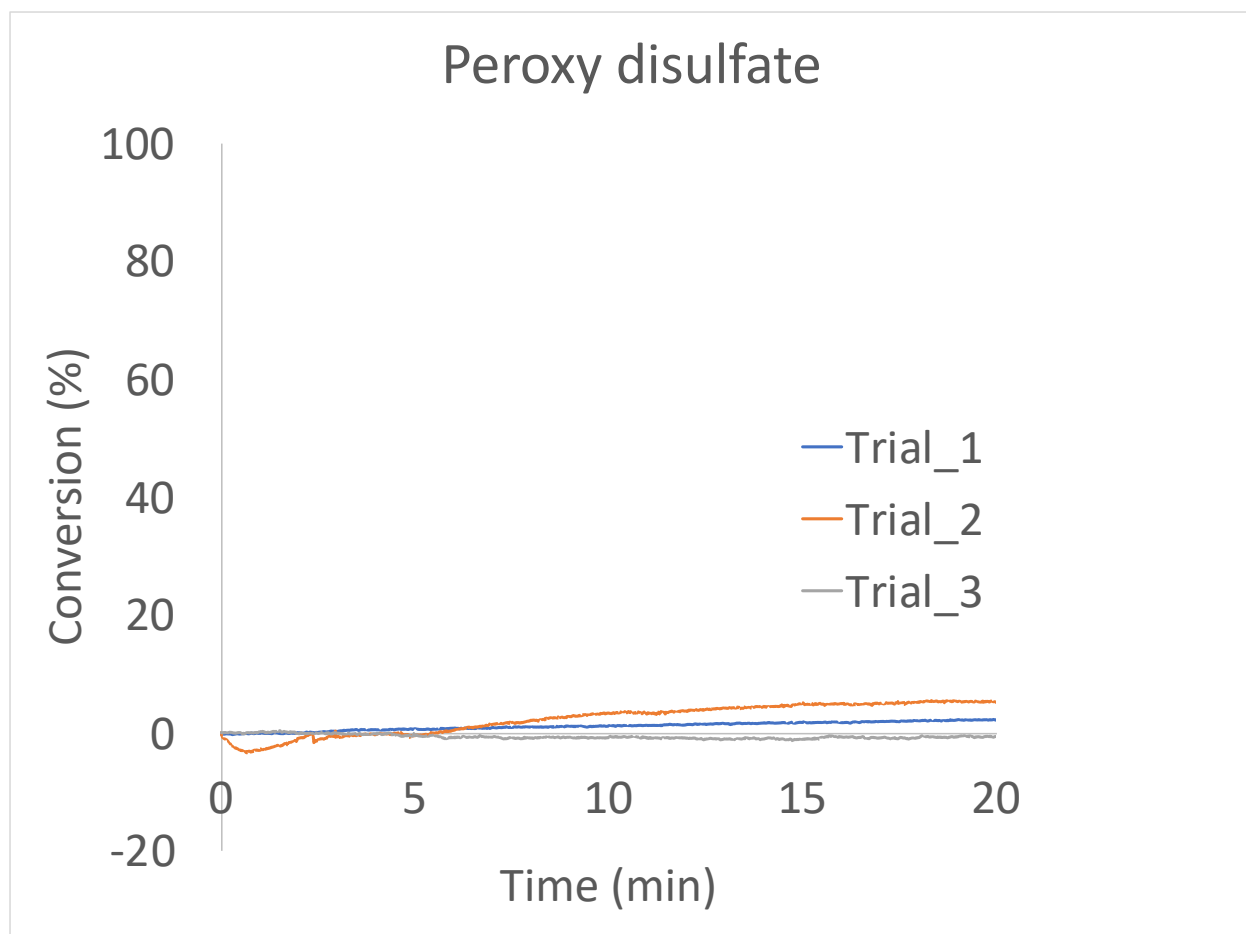


Figure S3.10. Polymerization profiles of peroxy disulfate

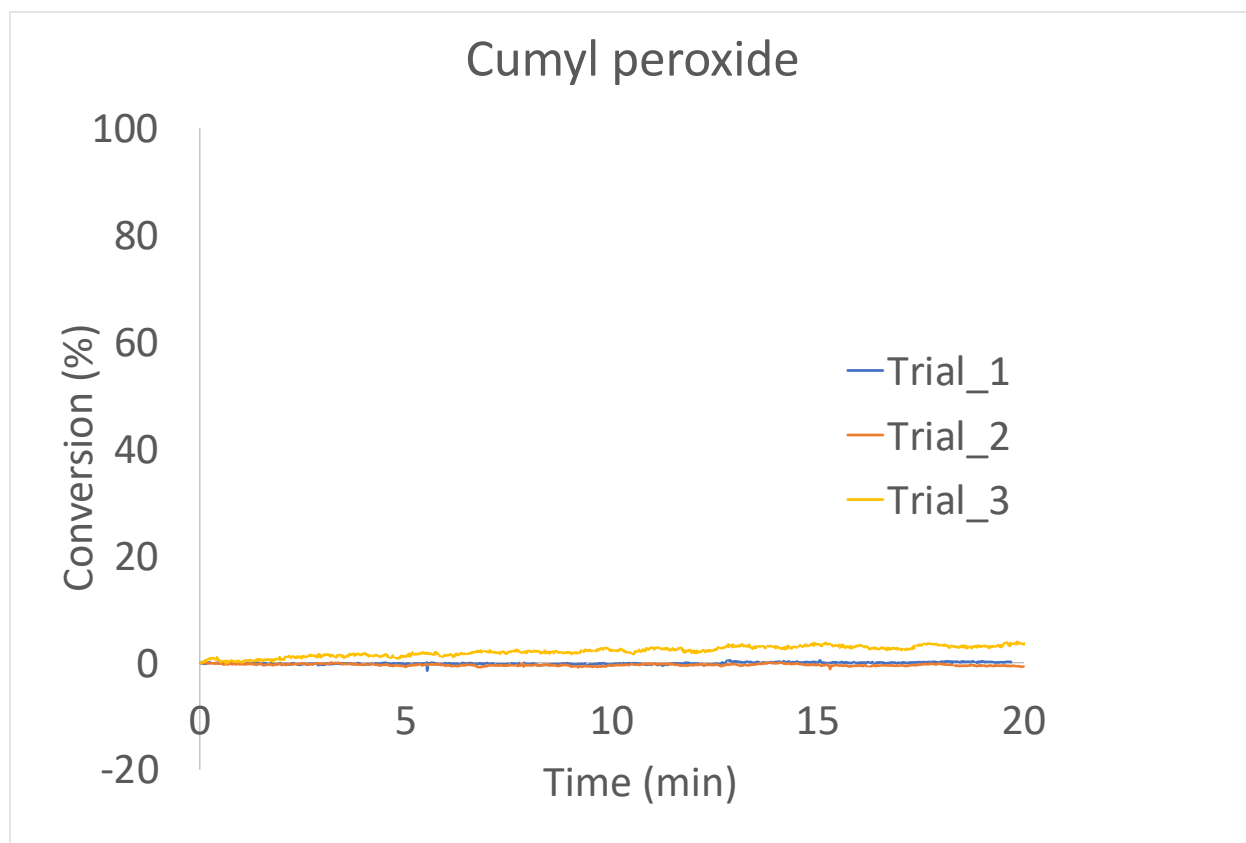


Figure S3.11. Polymerization profiles of cumyl peroxide

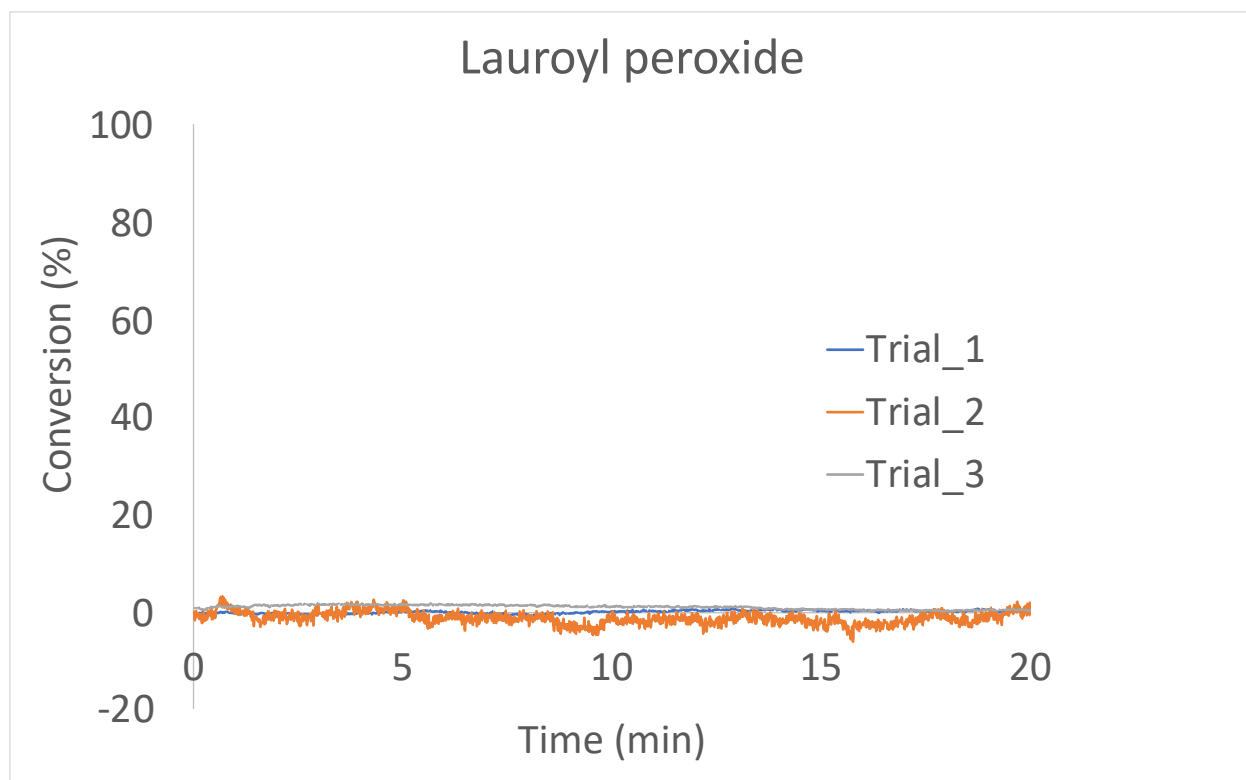


Figure S3.12. Polymerization profiles of lauroyl peroxide

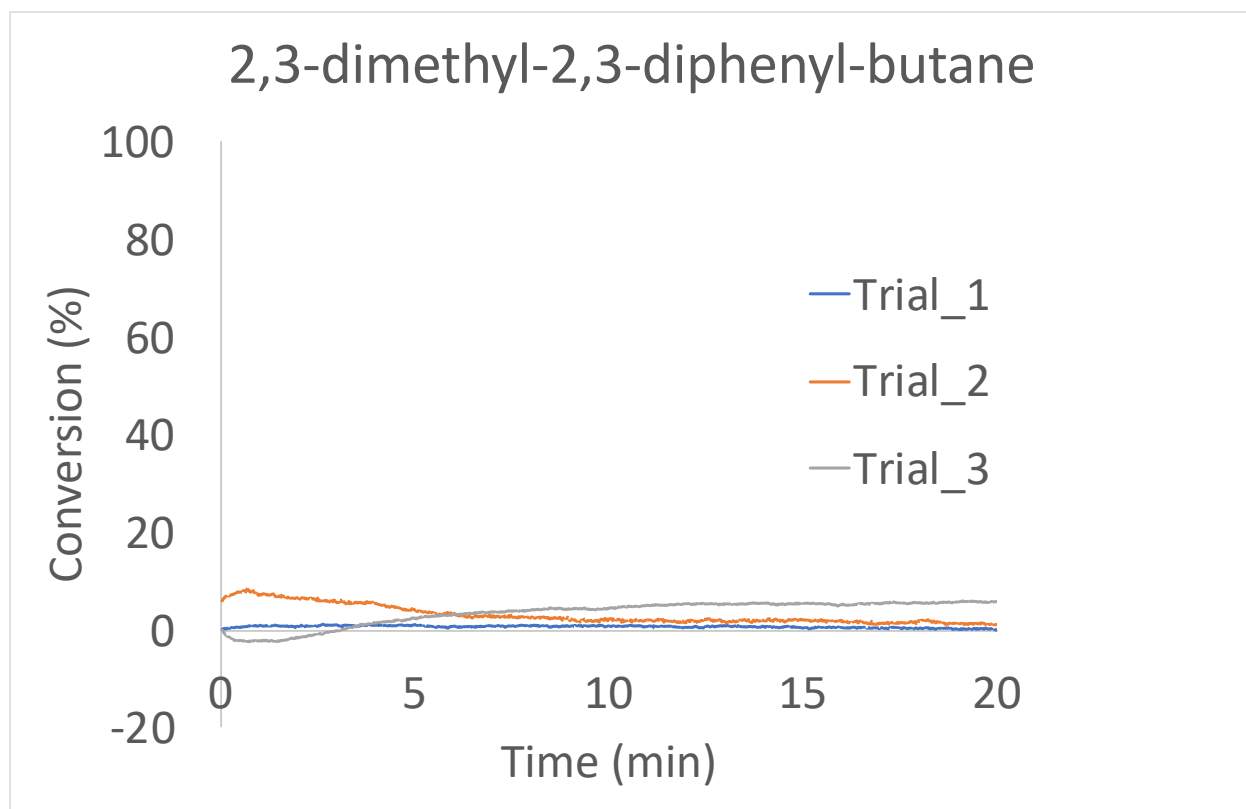


Figure S3.13. Polymerization profiles of 2,3-dimethyl-2,3-diphenyl-butane

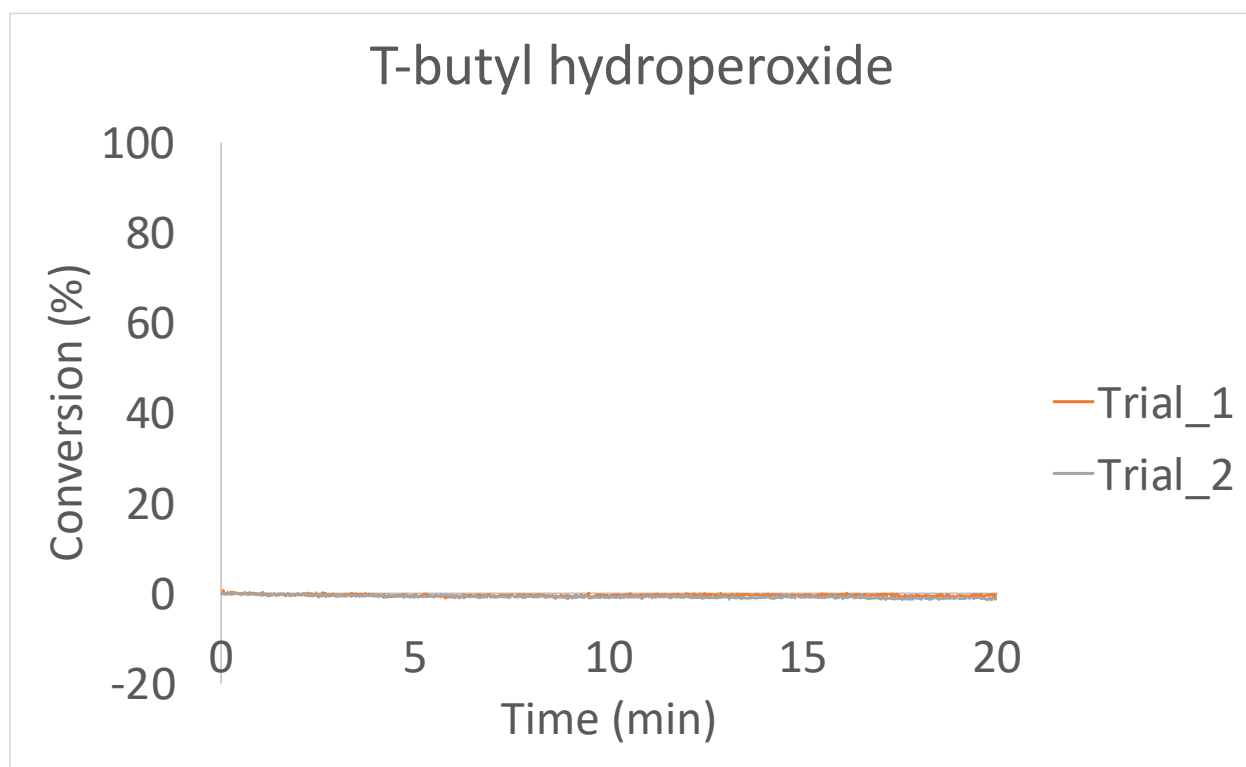


Figure S3.14. Polymerization profiles of t-butyl hydroperoxide

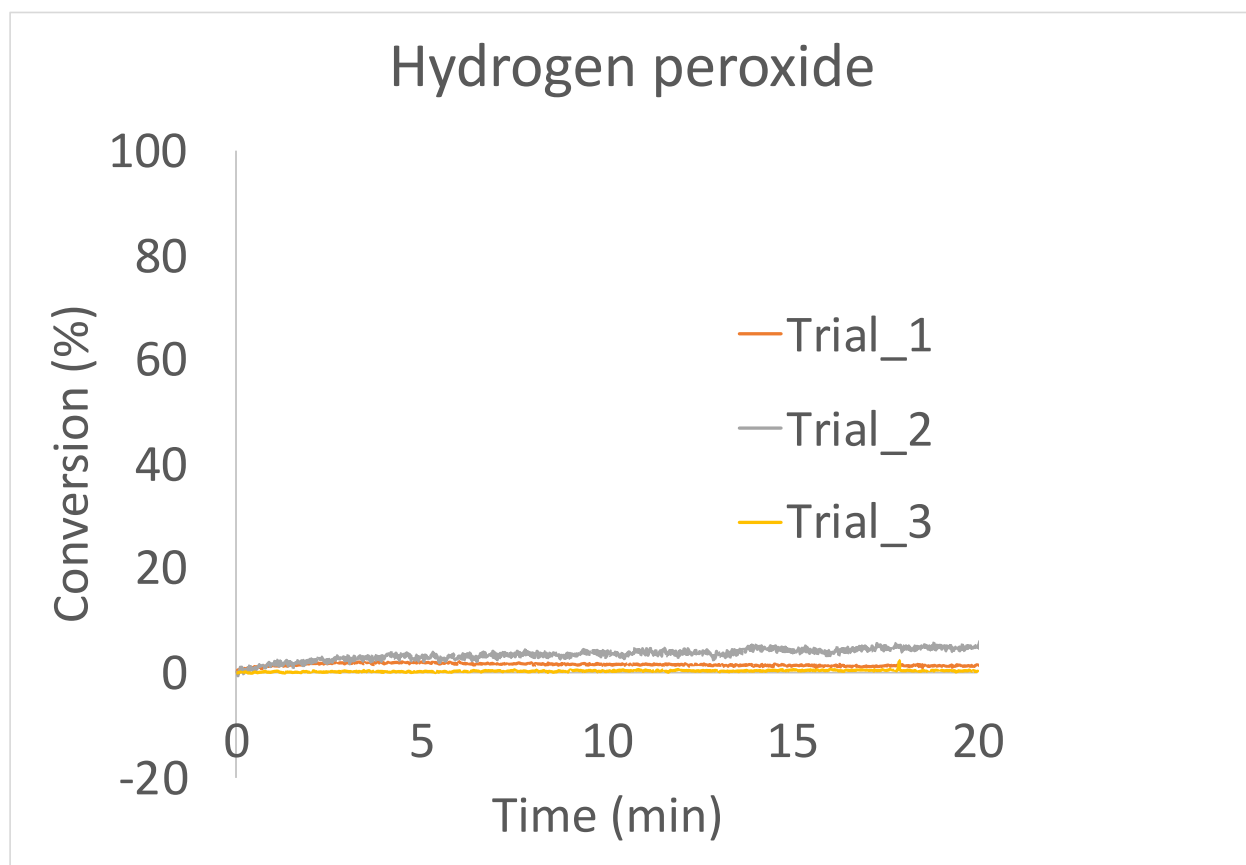


Figure S3.15. Polymerization profiles of hydrogen peroxide

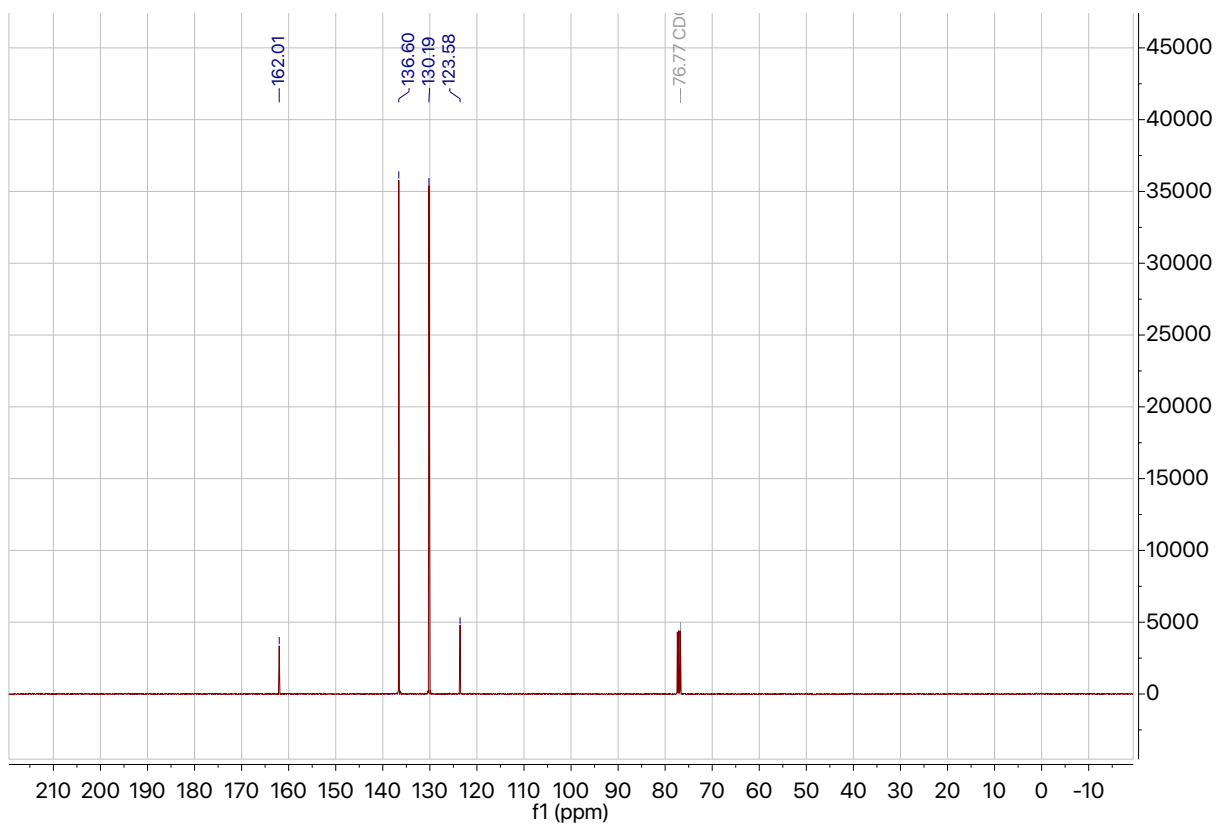


Figure S3.16. ^{13}C -NMR of *N*-(4-Methoxyphenyl)pyrrolidine.

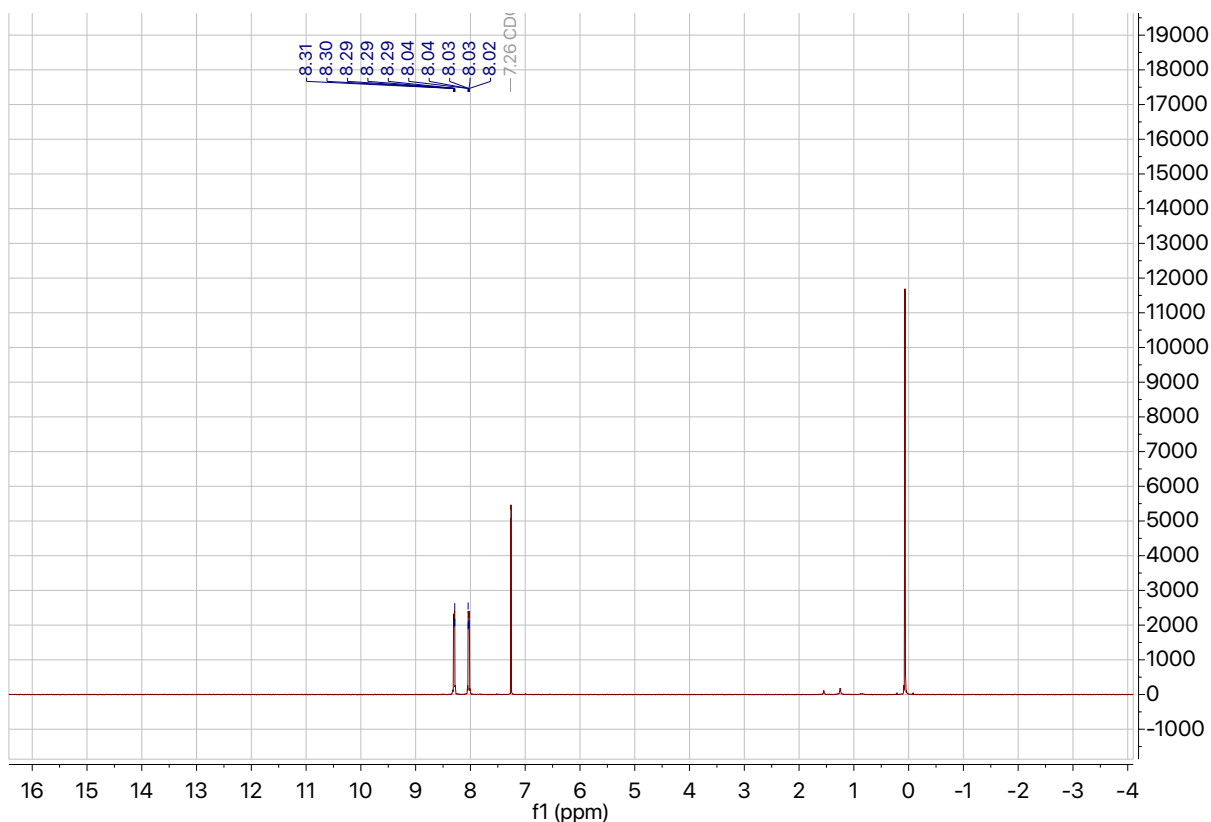


Figure S3.17. ^1H -NMR of *N*-(4-Methoxyphenyl)pyrrolidine.

S3.3. APRP Direct Writing System:

The 3D printer was built with a wooden frame, four stepper motors recycled from CD ROM components, and two 12V DC peristaltic pumps. 3mm ID x 5mm OD silicone tubing was used to flow the resins. A Raspberry Pi 3 model B+ was used as the controller for the printer. A4988 stepper motor controllers and 16 pin L293D drivers were used to control the stepper motors and pumps, respectively. Python scripts were developed to operate the Raspberry Pi and control the printing process.

A major limitation to our specific printer is that the pumps were not consistent enough to deliver a constant flow rate, and thus a consistent printed thickness. The inconsistency in the flow rates also resulted in inconsistent ratios of amine and peroxide resin in the mixing nozzle, which

slowed curing times and further reduced resolution. It is likely that a more sophisticated printer could overcome both of these challenges and print with much finer resolution. Other major challenges to developing this technology further include optimizing curing times and material properties with different resin systems and fillers and transitioning between different resin systems in a single print to obtain variable material properties.

Chapter 4: High Efficiency Radical Photopolymerization ENHANCED by Autonomous Dark Cure

The work described in this chapter is adapted from a publication available at <https://pubs.acs.org/doi/abs/10.1021/acs.macromol.0c01023>: Kangmin Kim, Jasmine Sinha, Guangzhe Gao, Kimberly K. Childress, Steven M. Sartor, Austyn M. Salazar, Sijia Huang, Charles B. Musgrave, Jeffrey W. Stansbury; *Macromolecules* 2020, 53, 13, 5034–5046

4.1 Abstract

Radical photopolymerization (RPP) has grown into a multibillion-dollar technology for reduced energy consumption and waste with increased productivity. However, radical-mediated polymerization ceases almost immediately following discontinuation of irradiation because of rapid termination of reactive centers. This restricts the wider use of RPP in applications that involve light attenuation or irregular surfaces, because uniform polymerization is not guaranteed for these challenging exposure conditions and the resultant under-curing leads to compromised materials properties and harmful leachable monomers. Herein, we developed a unique radical dark-curing photoinitiator (DCPI) that continues its polymerization beyond the cessation of irradiation. DCPI achieved a remarkable 25-60% additional conversion over a 1 hour-period, when light was shuttered at 20% conversion, compared to the 1-3% additional conversion achieved by a Norrish type II control photoinitiator. We elucidated the origin of the high photon efficiency using computational studies and experiments, which suggest that DCPI may be the most-photon-efficient photoinitiator to date. We also demonstrated that the mechanical properties of dark-cured polymer are similar to and even exceed those of the corresponding polymer obtained by extended photo-curing. In particular, the initial 0.1 MPa storage modulus continuously developed to 4.3 MPa

without further irradiation, while also exhibiting ~30% less shrinkage stress than the full exposure control. With its superior photo- and dark-polymerization efficiency, DCPI enhances the performance of many existing RPP processes while extending RPP to heretofore unattainable applications. DCPI accomplishes such performance through an inherent automatic rectification of initially under-cured regions and defies the RPP paradigm that light dosage directly correlates to conversion.

4.2 Introduction

Radical polymerization represents the most investigated and utilized approach for polymer synthesis with 40-45% of the ~300 million metric tons of annual worldwide industrial polymer production based on this chemistry. Radical polymerization's predominance is due to its facile and flexible reaction conditions, its compatibility with solvents and water, as well as its tolerance for a tremendous variety of functional comonomers.¹ In particular, the rapid growth of radical photopolymerization (RPP) as a prevalent green technology relative to conventional thermal polymerization has been fueled by its potential to reduce energy consumption and waste (e.g. no volatile organic compounds), while increasing productivity;²⁻⁴ RPP provides the advantages of ambient temperature processing with fewer side reactions, and a well-controlled onset and rate of polymerization dependent on the light source and photocuring conditions. This has driven the development of a photopolymer market currently estimated to be \$4.8 billion and projected to grow at a rate of 9.4% through 2025 to \$8.3 billion.⁵ RPP's nearly immediate termination of polymerization upon discontinuation of irradiation gives rise to the spatial and temporal control that is highly desirable in 2D and 3D lithography. Yet, such termination behavior also restricts its broad use for a multitude of polymeric materials applications. This is because of the likelihood of

producing highly heterogeneous or under-cured regions, even with careful tailoring of the photopolymerization process to its specific application. Evidence of a well-cured surface of a photopolymer does not guarantee sufficient or homogeneous through-cure, which is also challenging to verify. While trapped radicals can persist in high-conversion, vitrified regions within structurally heterogeneous photopolymer networks,⁶⁻⁸ the low mobility necessary for such radical persistence also restricts free monomer migration from adjacent domains of lower conversion, thus limiting significant post-curing potential.⁹ More critically, any low conversion regions present at the end of the irradiation interval will persist due to very efficient biradical termination that effectively arrests post-curing. As expected, under-curing contributes to compromised properties and leachable monomer, among other issues that cannot be rectified without additional irradiation to produce new initiating radicals. This rapid termination behavior seriously limits or even precludes implementation of RPP in applications that involve dimensionally thick or otherwise light-attenuating systems, including highly filled and pigmented materials, or curved- and irregular-surface coatings.^{10,11}

To combat prematurely terminated polymerization due to inadequate irradiation and resulting poor polymer property, researchers have studied photopolymerization methods in which polymerization continues beyond the cessation of irradiation, which is known as dark-curing. The active centers in cationic photopolymerization offer an intrinsic dark-curing capability due to the lack of a direct termination mechanism and this capability was previously demonstrated to lead to superior mechanical properties in comparison to that of nascent cationic-photo-cured polymer without dark-curing.¹²⁰ However, cationic photopolymers are critically underused in comparison to RPP mainly because of their more limited monomer choice and less predictable copolymerization potential, both of which complicate targeting specific polymer properties.

Therefore, we elected to focus our efforts on facilitating dark-curing via generically effective RPP processes.¹²¹

Over the past five years, radical-based dark-curing has been demonstrated for a few cases, yet these examples suffer from a variety of deficiencies that impose practical limitations. Our group previously reported a photoinitiating system that offered RPP dark-curing to near-completion after a brief light exposure while being the only example in the literature that is uniquely applicable in bulk conditions. However, it suffers from heavily colored products and the absence of concurrent photopolymerization during irradiation.¹² Shanmugam et al. reported a photoinitiating system for controlled radical polymerization (CRP) that utilizes oxygen to generate radical-producing hydrogen peroxide *in situ* in an aqueous environment.¹³ Although this example is a promising green chemistry for CRP, many aforementioned applications require significantly faster and solvent-free initiating systems. He et al. introduced a promising photoinitiation system that immediately generates radicals upon irradiation and also releases amines that react with peroxide to induce latent radical generation. However, only a single demonstration of the photo-activated dark-curing capability of this system was reported in solution with ~ 50 vol% polar dimethyl sulfoxide (DMSO) solvent, while nearly all RPP applications are solvent-free.^{14,15} Additionally, a study of polymer property development was absent in all of these previous examples and this oversight may result in a neglect of potential enhancement of final properties. Hence, recognizing the unrealized potential of radical-based dark-curing photoinitiation in bulk, we examined the mechanism responsible for the latent radical generation phase of the proposed dark-curing scheme and then using the guidance provided by the detailed mechanism and its computed energetics, developed an improved photoinitiator that exhibits extensive dark-curing behavior along with overall high-photon efficiency under typical photopolymer conditions.

Herein, we report the first demonstration of solvent-free radical dark-curing of (meth)acrylate resins that does not rely on a reaction exotherm nor photo-induced thermal assistance. This new radical photoinitiator with unprecedented photon-efficiency enables rapid surface curing and subsequent dark-curing to near vitrification-limited conversion in initially under-cured regions after a brief, partial photocure. We first compared the radical dark-curing photoinitiator (DCPI) to a control Norrish type II photoinitiator (CTPI) using a commercially available 365 nm LED. We then investigated the mechanism and chemistry of the DCPI *via* computational and experiment methods to elucidate the origin of the observed high photon efficiency. Finally, we further probed the hitherto unstudied dark-curing behavior in bulk resins under various conditions. Notably, we demonstrate that the mechanical properties of the dark-cured polymer are similar to, or even exceed in some cases, those of the corresponding polymer obtained by extended photo-curing. We suggest that a practical DCPI with pre-cure thermal stability and highly efficient polymerization could enhance the efficiency of many existing photopolymerization processes and final polymer properties while extending their applicability to currently unattainable light-attenuating samples through an inherent automatic rectification of initially under-cured regions.

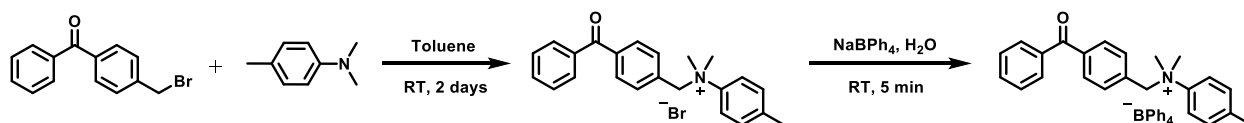
4.3 Experimental Section

4.3.1 Experimental methods

- a. **Materials** 4-(bromomethyl)benzophenone, benzoyl peroxide (BPO), n-butyl methacrylate (BMA), benzophenone (BP), anhydrous toluene, acetonitrile, and dichloromethane were purchased from Sigma Aldrich. *N,N*-dimethyl-*p*-toluidine (DMPT) and sodium tetraphenyl borate were purchased from Alfa Aesar. Triethylene

glycol dimethacrylate (TEGDMA, 95%) and α -methylene- γ -butyrolactone (MBL) were purchased from TCI America with 60 ppm MEHQ. BPO was purified by dissolving in dichloromethane and recrystallizing from methanol. All reagents were purchased in the highest purity available ($\geq 95\%$) and used without further purification.

b. BP-DMPT/BPh₄ Synthesis



1) *Synthesis of ammonium bromide salt. BP-DMPT/Br*

To the solution of 1 g (3.6 mmol) of 4-(bromomethyl)benzophenone in 50 mL of anhydrous toluene was added dropwise 0.5 g (3.9 mmol) of DMPT at room temperature under nitrogen. After the addition, the reaction mixture was then stirred for 2 days at room temperature under nitrogen. After 24 h of stirring, a white precipitate was observed. After 2 days, the reaction mixture was centrifuged to obtain the precipitate, which was washed thrice with toluene followed by washing with hexane and then dried in vacuum oven at 70 °C for 15 min. The desired compound was obtained as white solid. Yield: 35%; ¹H NMR (CDCl₃, δ ppm): 7.73 (d, 2H), 7.62 (m, 2H), 7.48 (t, 1H), 7.41 (d, 2H), 7.33 (d, 4H), 7.21 (m, 2H), 5.88 (s, 2H), 4.02 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H).

2) *Synthesis of ammonium borate salt. BP-DMPT/BPh₄*

To the solution of 0.5 g (1.2 mmol) of BP-DMPT/Br in 5 mL of water was added a solution of 0.45 g (1.3 mmol) sodium tetraphenyl borate in 5 mL of water dropwise at room temperature. The white

precipitate was immediately observed. The reaction was stirred for 5 min and then diluted with water and subjected to centrifuge followed by washing with water. The white solid hence obtained was dried in vacuum oven at 70 °C for 4-5 h to obtain the desired compound. The white solid hence obtained was then dissolved in a minimum amount of hot acetonitrile and recrystallized from cold diethyl ether. The white solid hence obtained was subjected to dry under vacuum resulting in the desired compound. Yield: 78%; ¹H NMR (CD₃CN, δ ppm): 7.76 (m, 4H), 7.56 (m, 1H), 7.48 (m, 2H), 7.42 (d, 2H), 7.30 (m, 8H), 7.19 (d, 2H), 7.02 (t, 8H), 6.87 (t, 6H), 4.86 (s, 2H), 3.49 (s, 6H), 2.43 (s, 3H).

c. Characterization

Polymerization Kinetics The conversion of vinyl functional groups in monomers by photopolymerization and dark-curing was monitored in real time with FT-IR spectrophotometer (Nicolet Magna-IR Series II, Thermo Scientific, West Palm Beach, FL) by monitoring the peak area of the =CH₂ overtone band at 6165 cm⁻¹ in horizontal transmission mode (**Figure S34**).¹²² Irradiation was performed using a LED (ThorLabs M365L2-C5) after 1 min of acquiring a baseline, and continued for 40-60 min. The light intensity was maintained at 30 mW/cm² unless otherwise specified, which was measured by a ThorLabs PM100D optical power meter with a S120VC photodiode power sensor (200 - 1100 nm). In full-irradiation experiments, resins were continuously irradiated until the obvious inflection point in the functional group conversion was observed, defined here as the vitrification conversion under ambient isothermal condition,¹²³ assuming the PI concentration remained sufficiently high to refrain from being limiting. On the other hand, to demonstrate the dark-curing capability, partial cure studies were conducted for

which the irradiation was terminated before the inflection point. Specifically, we identified the signal intensity at which the irradiation should terminate by calculating the percentage conversion from the initial total absorbance. For example, for a 20% partial cure, we stopped the irradiation at an absorbance of 8, if the initial total absorbance was 10, which hence signifies the conversion of 20% of functional groups at the time of irradiation termination. Additionally, factors that influence photopolymerization rates were chosen to achieve such partial cure studies, including concentrations, irradiation intensity, and methacrylate resin system. In turn, such control permits the appropriate termination of irradiation to successfully investigate the dark-curing effect. For most of our studies, we elected to use a comonomer resin of TEGDMA and MBL¹²⁴ to replicate a highly crosslinking polymer while ensuring solubility of our ionic photoinitiators. The resin choice is noteworthy as TEGDMA is commonly used crosslinking monomers and MBL is a non-fossil fuel-based monomer from a renewable feedstock that exhibits similar or better polymerization reactivity and materials properties than analogous methyl methacrylate.^{124–126} Samples were prepared by solubilizing BPO into TEGDMA and a photoinitiator into MBL, and then mixing the two solutions together. Prepared samples were kept at room temperature without an obvious change in appearance nor performance except occasional recrystallization of photoinitiator that was resolved by sonication. Circular laminated samples were prepared between glass slides with a 1.1 mm rubber gasket. The surface temperature of a glass slide was measured to estimate polymerization exotherm and resultant temperature change of the sample with an IR thermometer (Sper Scientific).

UV-Vis Spectroscopy The UV-Vis spectra of photoinitiators in dimethylformamide were recorded in PMMA cuvettes with 1 cm optical path lengths in a UV-Vis spectrophotometer (Thermo-Fischer Scientific) after baseline correction with a blank run.

Electrochemical Analysis Cyclic Voltammetry (CV) measurements were performed using a 3-electrode technique at room temperature, which employed a 0.01 M Ag/AgNO₃ reference electrode, a platinum working electrode, and a platinum counter electrode in a CH Instruments 601C electrochemical analyzer. Acetonitrile was used as solvent and 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The vial containing the sample was sparged with argon in order to remove oxygen. Potentials versus the standard calomel electrode (SCE) were determined by employing the oxidation of ferrocene as an internal standard and then adding 380 mV.¹²⁷ The scan rate was 100 mV/s with the initial scan direction being negative.

NMR ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, as indicated in the respective measurement. For quantitative NMR, ethylene carbonate was used as an internal standard.

Mechanical Property Storage modulus (E') and corresponding functional group conversion were measured in real-time with an oscillatory photo-rheometer (ARES-G2, TA Instruments) that is coupled with the FT-IR spectrophotometer. Resins were placed between two 20 mm parallel quartz disc plates with a gap of 0.5 mm and evaluated at a frequency of 1 Hz and 0.5% strain in ambient temperature after irradiation at 4.4 mW/cm² with a mercury-lamp (Acticure 4000) with a 365 nm bandgap filter. To test stability of resins, thermal ramp from 20 to 100 °C at a rate of 2 °C/min was performed to identify the onset temperature of polymerization.

Shrinkage Stress dynamic shrinkage stress and corresponding functional group conversion were measured in real-time with a cantilever beam-based tensometer (Volpe Research Center, American Dental Association Foundation, Gaithersburg, MD) that is coupled with the FT-IR spectrophotometer.¹²⁸ Shrinkage stress was evaluated with 30 mW/cm² irradiation from a mercury-

lamp (Acticure 4000) with a 365 nm bandgap filter while conversion measurement proceeded as described above. Each specimen was sandwiched between two silanized glass rods (silane fusion: George Taub Products & Fusion Co., Inc.) in disc shape (6 mm diameter and 1 mm thickness).

4.3.2 Computational Methods

All calculations were performed using the GAUSSIAN 16 (Revision A.03) software package⁵⁹ at density functional theory of the M06-2X density functional¹²⁹ and 6-31+G(d,p) basis set.⁶¹ The M06-2X functional was chosen because it excelled for calculating the thermochemistry and kinetics of organic molecules as well as for their excited state calculations.¹²⁹ Vibrational frequencies were computed to verify that the stationary states were optimized to the correct structures and to compute vibrational entropies, zero-point energies and thermal corrections to enthalpies at 298 K. Solvent effects were described using the universal solvent model⁶⁷ with solvent parameters for ethyl acetate (EtOAc) because of its structural similarity to (meth)acrylate monomers.¹³⁰ Furthermore, the dielectric constant of EtOAc⁵⁹ of ~6 is suitable for describing the dielectric environment produced by common bulk (meth)acrylate monomers with dielectric constants ranging from 2.5 to 11.^{68,69} Gibbs free energies were corrected using bulk-resin environment simulation, according to a previous reference.¹³⁰ The monomer used in the computational investigation of the monomer addition kinetics was ethyl methacrylate. Reductional potential calculations were performed based on the methodology adopted by Tossell.^{131,132}

4.4 Results and Discussion

4.4.1 Dark-curing photoinitiator development

Previous studies^{12–15} of radical-based dark-curing photoinitiators involved *in-situ* photogeneration of redox initiators that latently generate radicals without the further need of light

after initial irradiation. These strategies are only possible because excited photoinitiators and initiating radicals have limited lifetimes, while photo-generated redox initiators are inherently stable and persist until encountering a counter redox partner. This class of photoinitiators produce radicals over an extended period, relying on the intrinsic thermodynamic driving force for redox reactions (**Figure 1**). However, none of these cases fulfill the following requirements to be a practical DCPI. An effective DCPI should: 1) be stable as a one-component formulation prior to irradiation and exhibit polymerization only after irradiation; 2) exhibit rapid photopolymerization during irradiation and extensive dark-curing following irradiation with vinyl-based monomers including common (meth)acrylates in bulk at ambient temperatures; and 3) produce polymer that exhibits mechanical properties comparable or superior to those produced by extended photo-curing, while being without distinctive coloration or bubble formation from photo-decarboxylation. In considering these characteristics, we elected to study amine-peroxide redox polymerization (APRP) as a potential photo-activated latent initiating system. Since its discovery in the 1950s⁵⁶ APRP's advantages of room-temperature activation, biocompatibility, and solvent-free bulk polymerization have led to its extensive use in cementation processes in dental and orthopedic applications³¹ and APRP has proved its usefulness in various emerging applications such as frontal polymerization,³⁴ self-healing materials,³⁵ interfacial polymerization,³⁷ adhesives,³⁸ nanocomposites,³⁹ and microfluidic chips.⁴⁰ In order to make this redox chemistry photo-activated, we incorporated a photoactive compound that performs as both photo-radical generator for rapid photopolymerization and photo-base-generator (PBG) to release amine reductants that undergo ground-state redox reaction with peroxide for prolonged post-irradiation conversion.

Photopolymerizations initiated by a PBG have typically used strong bases to provide effective initiation activity for anionic-mediated polymerizations.^{133,134} However, our earlier study

suggested that highly basic photocleaved amines are not ideal reductant partners for reactions with oxidants such as benzoyl peroxide (BPO).¹³⁰ For instance, the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) amine used in He's studies^{14,15} fails to undergo efficient redox reactions and hence exhibits limited potential for dark-curing. Our results from bulk polymerization experiments activated by combining an amine and peroxide in a typical redox application showed that DBU (red in **Figure 2**) does not undergo redox reaction with BPO as readily as dimethyl aniline (DMA, green in **Figure 2**) or dimethyl-p-toluidine (DMPT, blue in **Figure 2**). In particular, DBU exhibits a polymerization profile with an early plateau at 5 – 20% conversion, while both DMA and DMPT achieve >90% conversion under identical conditions (e.g. initiator concentrations) (**Figure 2**). The inferior redox performance of DBU results because the two active *N*-sites in DBU exhibit different redox capacities; One *N*-site that is more reactive towards BPO generates no radicals at room temperature. This suggest that DBU should not be considered as the amine component of an amine-peroxide redox system.¹³⁰ Additionally, DBU undergoes undesired side-reactions with common monomers that are prone to Michael reactions, including acrylate and acrylonitrile, limiting the use of DBU in generic resin formulations.¹³⁵ (See **Figure S4** for inactive chain-growth polymerization with DBU vs. DMPT). Our previous study also showed that primary and secondary amines react with BPO to form stable intermediates that do not produce initiating radicals at room temperature while amines with high reduction potentials were much more effective in generating radicals via reaction with BPO.¹³⁰ For these reasons, we elected to investigate DMPT as the photo-releasable amine in this DCPI study. Consequently, the restriction on photo-releasable bases - tertiary aromatic amines - and the requirement of concurrent photo-radical generation narrowed our search for photo-base-generator structures. Furthermore, in order to meet the pre-irradiation stability requirement, we selected a PBG platform introduced by Neckers and coworkers that possesses a chemically stable

yet photo-cleavable covalent linkage between the chromophore and amine while lacking a reactive lone pair.¹³⁶ The combination of covalent linkage and masked lone pair makes the formulation inherently stable by preventing ground-state reactions with BPO in our formulation. By contrast, other PBG platforms commonly have a reactive lone pair or bind to an amine via non-covalent ionic interaction that involves an acid-base equilibrium. The Neckers-type PBG with UV-absorbing benzophenone-chromophore and photo-releasable DMPT (BP-DMPT/BPh₄) was conveniently synthesized in two steps with isolation achieved by recrystallization. The deliberate selection of molecular components that meet the specific requirements identified for a practical DCPI allowed us to develop a new and effective dark-curing photoinitiator that we demonstrate in this contribution (**Figure 3**).

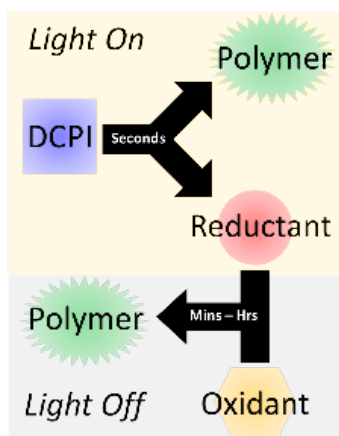


Figure 1. General strategy of radical dark-curing mechanisms. The DCPI reported in this study generates initiating radicals during irradiation as well as the reductant amine (dimethyl-p-toluidine, DMPT), which undergoes redox reactions with oxidant peroxide (benzoyl peroxide, BPO) to generate latent radicals over extended periods following irradiation.

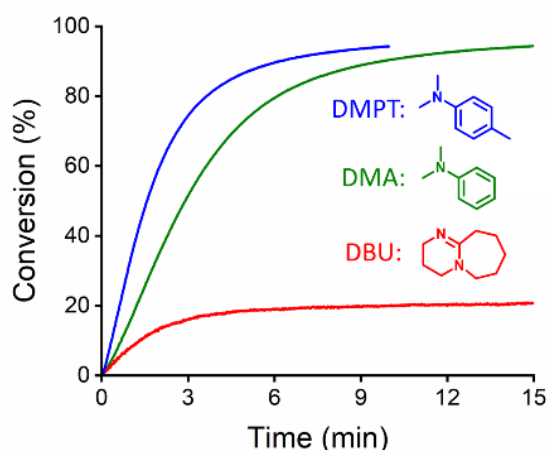


Figure 2. Redox polymerization kinetic profiles with amines as reductants and benzoyl peroxide (BPO) as the oxidant under identical conditions of di(ethylene glycol) ethyl ether acrylate resin, 3 mol% BPO and amine concentrations. Note that DBU exhibits slower and incomplete polymerization which can be attributed to its inadequate redox capacity.

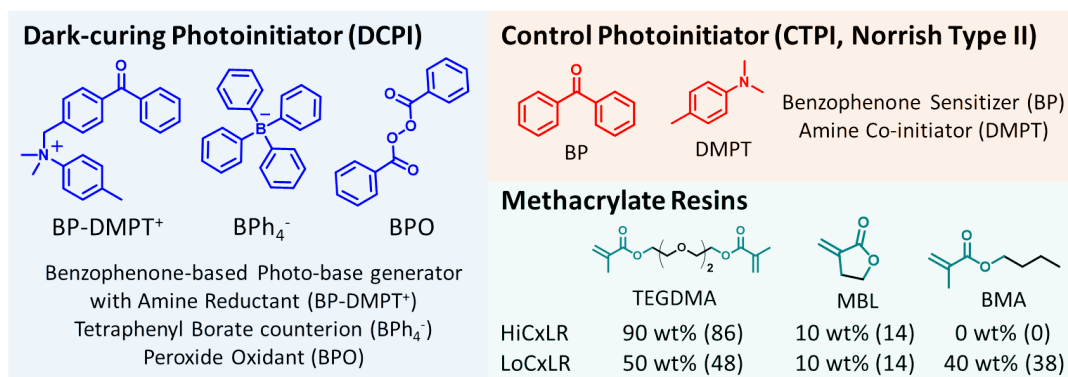


Figure 3. Molecular structures of dark-curing photoinitiator (DCPI), control photoinitiator (CTPI), and methacrylate resins used in the study. The DCPI design incorporates carefully chosen molecular components to fulfill practicality requirements, while CTPI was selected as a control due to its similar photophysics. The resins were comprised of di- and mono-functionalized methacrylates with MBL (α -methylene- γ -butyrolactone) as the cyclic analog of methyl

methacrylate to assist the solubility of the BP-DMPT/BPh₄. HiCxLR and LoCxLR represent high and low crosslinking resins with mol% reported in parentheses.

4.4.2 Comparison between dark-curing and control photoinitiators

To demonstrate the dark-curing capacity of DCPI relative to a control photoinitiator (CTPI), we briefly irradiated two samples of HiCxLR resin containing each respective photoinitiator with a 365 nm LED to achieve partial conversions in optically thin films (**SI. Thin Film Approximation**). The thin films in full and partial cure regimes along with controlled irradiance provide a well-controlled model for through-cure of light-attenuated or optically thick samples, where the full and partial cures simulate surface- and deep-cures that depend on the amount of irradiance. Real-time monomer conversion was observed during and subsequent to photopolymerization with FT-IR. Both DCPI and CTPI initiated the resins with irradiation, which was shuttered when the conversion reached 20% (**Figure 4**). Irradiation was ceased at different exposure time intervals, resulting in different light doses for each sample, because DCPI exhibited faster photopolymerizations than CTPI (**Figure S5**) at equivalent overall initiator concentrations. After irradiation, the conversion of the DCPI resin continued in the dark, albeit at a slower rate than during active photopolymerization, and gained an additional $23\% \pm 5\%$. The 10 minutes immediately following irradiation exhibited the most prominent dark-curing due to the thermodynamic driving force provided by the presence of the maximum number of available amine reductants upon light termination. We suspect that the overall redox radical count is largely affected by consumption of the limiting amine reagent and the diffusion rate of both redox initiators, which precipitously drop as polymerization progresses. However, the conversion of the CTPI resin rapidly halted, resulting in an additional $2.5 \pm 2\%$ dark cure conversion over 1 h. Such plateauing behavior is expected for all free radical polymerizations, especially in low to moderate

conversion regimes wherein the mobility of radical active centers leads to highly efficient bimolecular termination. **Figures S6 and S7** show the plateauing behavior of Type I and II photoinitiators) The dark-curing of DCPI, as shown in **Figure 4**, effectively doubled the initial conversion present when irradiation was discontinued. On the other hand, the photo-base-generator BP-DMPT/BPh₄ without the addition of BPO behaves similarly to CTPI in that it exhibits no dark-curing and its conversion plateaued immediately due to the lack of ground state amine-peroxide redox activity post-irradiation (**Figure S8**). A steady state analysis of the photopolymerization kinetics based on **Figure S5** indicated that the rate of polymerization during irradiation is 0.68 for CTPI, 3.40 for BP-DMPT/BPh₄, and 4.50 M⁻¹s⁻¹ for DCPI. This yields initiator efficiencies for these respective photoinitiators of 0.02, 0.43, and 0.75 as calculated from the free radical photopolymerization kinetic equation. (**SI. Kinetic Property Calculation**). These results suggest that DCPI may be the most photon-efficient photoinitiator to date, even before considering additional redox-derived radicals generated in the dark phase.

Polymerization initiated by DCPI is the first demonstration of photo-activated curing that occurs concurrently with irradiation and with subsequent radical dark-curing that does not rely on elevated temperature for thermolysis of BPO (ΔT of samples < 1 °C) nor on the addition of a solvent that enhances redox pair mobility or provides a more favorable polar environment for ionic-mediated photo-base-generation and redox reaction (*vide infra* and ref 27). Although DCPI does not achieve a vitrification-limited conversion within an hour, the observed dark-curing has promising implications such as producing materials with more robust and homogeneous mechanical properties, shortened irradiation times, and reduced levels of leachable monomer. The remediation of poor conversion in the under-cured regions that leads to more uniform properties is assisted by the high diffusivity of the redox initiators in these regimes. Furthermore, DCPI not

only increases apparent photon efficiency but it also introduces two polymerization routes that act independently over drastically different time scales: seconds for photopolymerization vs. minutes to hours for dark-curing. This unique mechanism may lead to lower radical-radical recombination as the generation of radicals required for a full conversion is distributed over an extended period, as opposed to conventional photopolymerization that compresses the radical production process into the active irradiation period. Such extended radical generation may also result in less shrinkage stress and better mechanical properties,^{137–139} while being initiated by a single convenient brief stimulus of light.

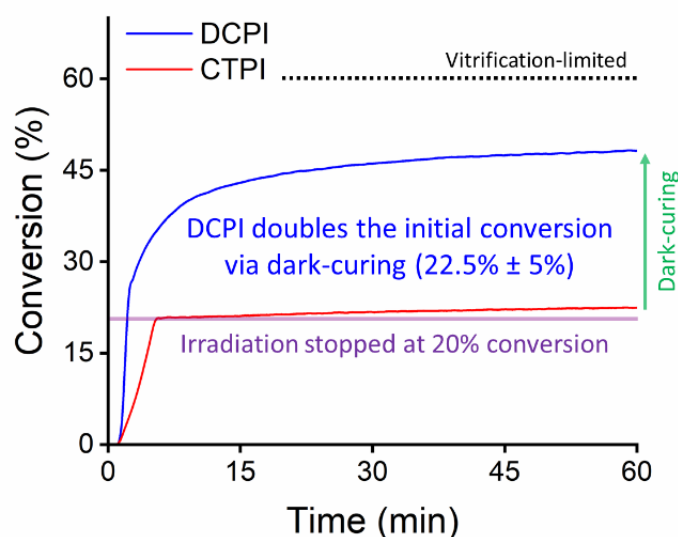


Figure 4. Polymerization kinetic profiles of dark-curing photoinitiator (DCPI) and control photoinitiator (CTPI) under partial cure conditions monitored for 1 h. Upon discontinuation of irradiation at 20% conversion, the conversion in the resin containing DCPI continued to polymerize with $22.5\% \pm 5\%$ additional conversion within 1 h, more than doubling the initial conversion. In contrast, polymerization of the resin containing CTPI immediately halted and plateaued with marginal post-polymerization conversion of $2.5 \pm 2\%$. The conditions of these polymerizations included illumination with a 30 mW/cm^2 365 nm LED with $[\text{BP}] = [\text{BP-}$

DMPT/BPh₄] = 7.7 μmol/g of resin and [DMPT] = [BPO] = 23.1 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

4.4.3 Dark-curing photoinitiator mechanism

The unusual behavior of DCPI shown in **Figure 4** originates from a combination of two radical generation processes (photo- and redox-initiations), both of which are initially activated by light. The overall DCPI mechanism occurs in two distinct stages during which each initiation mechanism predominantly operates: photo-induced near-instantaneous radical generation during irradiation and redox-induced latent radical generation during the dark. DCPI produces two radicals and an amine by photo-base-generator photolysis; the liberated amine subsequently undergoes redox reaction with a peroxide, largely after the irradiation phase has concluded, thereby generating two additional radicals latently over extended periods (**Figure 5**). A close examination of the photoexcitation process reveals that the initial step involves the promotion of an electron from the highest occupied molecular orbital of BP-DMPT⁺ to a higher-energy unoccupied orbital to produce a hole. We used a 365 nm ($E_{365nm} = 78.1$ kcal/mol) LED, which is just sufficiently energetic to excite BP-DMPT⁺ to its first singlet excited state ($\Delta G_{S_1}^{\circ} = 77.0$ kcal/mol). None of the other initiator components (BPh₄⁻, BPO, and DMPT) or monomers absorb at 365 nm while the parent benzophenone chromophore of BP-DMPT⁺ exhibits an essentially identical UV-Vis spectrum to benzophenone with the molar absorption coefficient of 80.1 L/cm/mol at 365 nm, which was used as a control photoinitiator with free DMPT co-initiator as described above (also see **Figure S11** for UV-Vis spectra). The high-energy hole of the excited chromophore ([BP-DMPT⁺]^{*}) is strongly oxidizing and thus facilitates an intra-ion-pair electron transfer (ET₁) from the borate anion (BPh₄⁻) to [BP-DMPT⁺]^{*}. The thermodynamic feasibility of the ET₁ was predicted

from the difference in the calculated reduction potentials of the excited and ground states of BP-DMPT⁺ ($E^0 = 1.5$ V vs. -1.9 V vs. SCE in acetonitrile). The electrostatically induced proximity of the photo-redox pair in the non-polar monomer environment motivated our hypothesis that ET₁ can be operational in both the excited singlet or triplet states (¹ or ³[BP-DMPT⁺]^{*}), as the excited singlet state is not limited by its short lifetime and the first triplet excited state ($\Delta G_{T_1}^{\circ} = 67.2$ kcal/mol) is still sufficiently oxidizing to induce spontaneous ET₁ ($\Delta G_{ET_1}^{\circ} = 56.0$).^{140,141} ET₁ produces a reduced chromophore (²BP-DMPT^{*}) and an oxidized borate (BPh₄^{*}), both of which are transient intermediates destined to undergo homolysis via separate pathways. BPh₄^{*} degrades by homolysis (HM₁) into triphenyl borane (BPh₃) and a phenyl radical that efficiently initiates monomer with a large exergonicity of -51.9 kcal/mol.^{140–142} Similar photo-radical-generation mechanisms with redox pairs of photosensitizers and borates have been exploited in various photopolymer applications.^{141,143–147} As previously shown, photopolymerization rates can also be controlled by utilizing different borate anions with various reduction potentials.^{143,144,146–148}

Our examination of the nature of the transient intermediates after ET₁ involved computing the structures of BP-DMPT⁺ and ²BP-DMPT^{*} which revealed that the length of the C-N covalent bond between the BP and DMPT moieties increased from 1.54 Å to 1.58 Å. This results because upon reduction the additional electron occupies the C-N antibonding orbital which drives homolysis of ²BP-DMPT^{*} to release anionic 4-methylbenzophenone (BP⁻) and amine radical cation (DMPT⁺⁺). The BP⁻ and DMPT⁺⁺ products form a contact ion-pair within a viscous solvent cage¹⁴⁰ ($\Delta H_{Complexation} = -50$ kcal/mol). A subsequent intra-ion-pair electron transfer (ET₂) between this charge-transfer complex only requires a small enthalpic penalty of 6.4 kcal/mol. Formation of this complex involves the transfer of free radical electron density (spin density), rationalizing the unusually large complexation energy. (See **Figure S14**). As a result, 4-methylbenzophenone

radical (BP[•]) is generated, which we predict efficiently adds to a monomer with a exergonicity of -29.1 kcal/mol. BP[•] behaves similarly to an electron-rich styrene-like radical that reacts efficiently with an electron-poor monomer such as (meth)acrylate.^{136,149} Bi-phenyl, 4-methyl benzophenone, and bis-(4-methyl benzophenone) species were experimentally observed, indicating the generation of a phenyl radical and 4-methyl benzophenone radical.¹³⁶ The final product of the photochemical process following ET₂ is an amine species with a regained lone pair (DMPT) that can react with benzoyl peroxide (BPO) via inner-sphere electron transfer (ET₃), generating two additional initiating radicals: a benzoyloxy radical (BzR[•]) and alpha-aminoalkyl radical (AAR[•]). Because ET₃ is considerably slower than the preceding photochemical reactions that lead to the generation of DMPT (minutes - hours vs. seconds), it accounts for the observed latent polymerization following irradiation.

The detailed mechanism of ET₃ is not described here because of its complexity, which involves four reactions with reactive intermediates.¹³⁰ We hypothesized that within an ideal DCPI framework, a single photon reliably generates four separate initiating radicals. When compared to Norrish type I and II photoinitiators that generate one or two initiating radicals per photon absorption event, DCPI significantly outperforms other photoinitiators, possibly making it the most photon-efficient photoinitiator for radical polymerization to date, especially considering the auxiliary initiating abilities of the products of the DCPI chemistry.^{136,150} In particular, the chain-end groups from 4-methylbenzophenone and alpha-aminoalkyl radicals can be recycled to function as a tethered photoinitiator and an amine initiator to provide additional radicals through additional photo- and redox cycles.¹⁴⁵ Such recycling ability of tethered amines enhances their dark cure potential within the APRP framework, especially in regions of limited light access where the free amine, relative to the formulated BPO concentration, is the limiting redox reagent. (See **Figure**

S15 for comparison of amine and tethered amine undergoing redox reaction). We contend that the additional radical-generating chemistry of the chain-ends further increases the photon efficiency of DCPI.

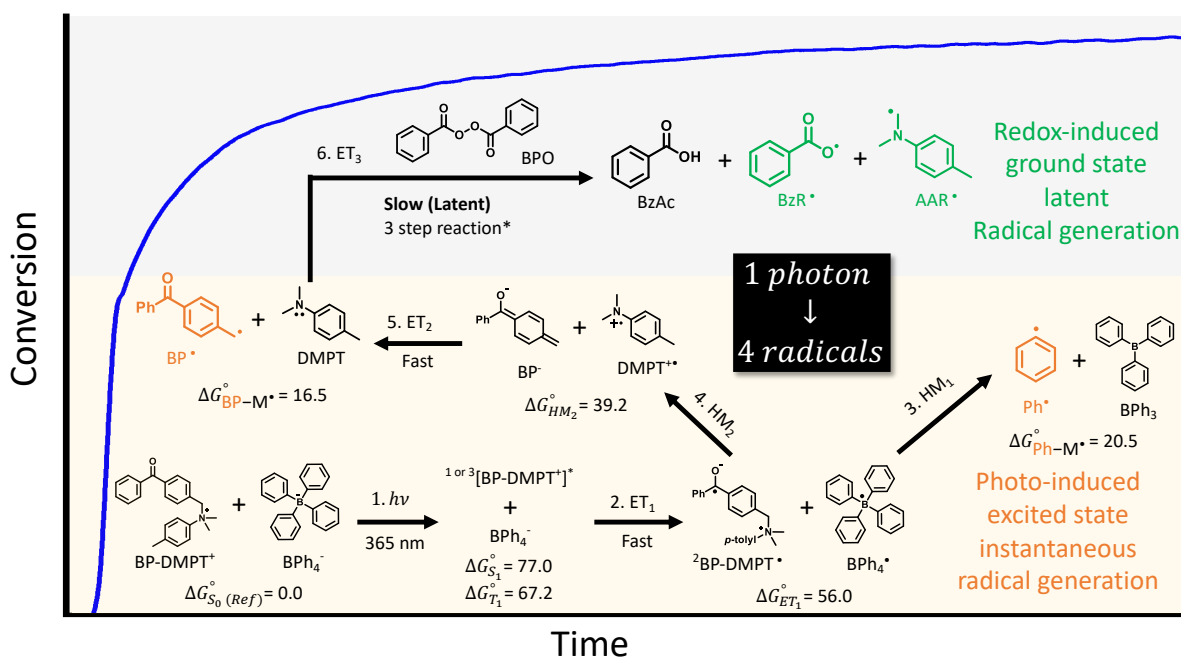


Figure 5. Proposed dark-curing photoinitiation mechanism divided into photo-induced and redox-induced radical generation stages superimposed over a dark-curing polymerization kinetic profile. Photo-induced stage: Irradiation excites BP-DMPT⁺ to ¹ or ³[BP-DMPT⁺]^{*}, whose hole is backfilled by electron transfer (ET₁) from BPh₄⁻ counterion, generating the two transient radical species, BPh₄[•] and ²BP-DMPT[•]. The boranyl radical (BPh₄[•]) dissociates into triphenyl borane (BPh₃) and phenyl radical (Ph[•]), while the chromophore radical (²BP-DMPT[•]) undergoes homolysis to produce BP[•] and DMPT^{••}, which exchange an electron to become benzophenone radical (BP[•]) and DMPT. Ph[•] and BP[•] are the initiating radicals that immediately result from

irradiation and lead to the initial rise in the polymerization profile and rapid conversion. Redox-induced stage: Over an extended period following irradiation, free DMPT diffuses to react with BPO throughout the sample to generate two additional radicals; $\text{BzR}^\bullet$ and $\text{AAR}^\bullet$. Thus, within the DCPI framework, a single photon generates two sets of two radicals on drastically different time scales. Free Energies in kcal/mol computed at the M062X/6-31+g(d,p)/SMD-EtOAc level of theory predict that this mechanism is rapid at room temperature as photoexcitation provides sufficient energy for the ensuing reactions. *The full extent of amine peroxide redox reaction is not illustrated in this figure.

4.4.4 Additional details of the DCPI photochemistry

To probe whether photogeneration of redox-active DMPT from BP-DMPT/BPh₄ is indeed occurring, we studied the evolution of ¹H-NMR peaks specific to BP-DMPT and DMPT (**Figure 6**). Following irradiation with a 365 nm LED, the peak associated with the *p*-tolyl hydrogens of BP-DMPT at 2.17 ppm diminishes while three sets of methyl hydrogen peaks of DMPT (N-CH₃ at 2.88 ppm and Ph-CH₃ at 2.25 ppm) emerge, indicating that DMPT is absent prior to irradiation and is photo-generated from BP-DMPT/BPh₄. This indicates DCPI's potential to induce dark-curing with BPO within the amine-peroxide redox polymerization framework. Furthermore, we conducted quantitative NMR to study the dose-dependence of photo-base-release from BP-DMPT/BPh₄ by varying irradiation time at a fixed irradiance of 2.5 mW/cm². Below a moderate dose of 600 mJ/cm², ~75% of BP-DMPT/BPh₄ degradation yielded DMPT amine generation. However, while the degradation continues at the larger dose of 1200 mJ/cm², the DMPT generation rate decreases and is accompanied by the visible appearance of a by-product peak at 3.08 ppm. This results from the subsequent photoreaction of 4-methyl benzophenone product with DMPT.

BP derivatives can act as a Norrish type II photoinitiator with an amine co-initiator. As a result, DMPT is consumed via this secondary photochemical reaction while BP-DMPT continues to degrade. Overall, the quantum yield of photodegradation of BP-DMPT/BPh₄ is 0.40,¹³⁶ and 75% of this photodegradation results in amine generation. We estimate that nearly one of three absorbed photons successfully leads to selective photochemical reaction to release DMPT amine ($\phi_{Amine-Release} = 0.40 * 0.75 = 0.30$). Considering that the quantum yield of the commonly used o-nitrobenzyl photo-base generators' photo-decomposition (not photo-base-generation) ranges from 0.001 to 0.201,¹⁵¹ our dark-curing system exhibits a higher efficiency of photo-base-release while also achieving photopolymerization with immediate radical generation. However, we note that the estimated quantum yield was derived using parameters from acetonitrile solution conditions while practical application conditions impose both a lower dielectric constant and higher viscosity than acetonitrile that inevitably influences BP-DMPT/BPh₄ behavior.

To further investigate the photoelectrochemical aspects of our hypothesized DCPI mechanism (namely, ET₁), we studied the electrochemical properties of BP-DMPT/BPh₄ with cyclic voltammetry (**Figure S16**). The cyclic voltammogram (CV) of BP-DMPT/BPh₄ possesses a peak at -1.29 V vs. SCE, which we interpret as the single-electron reduction of BP-DMPT⁺ because an analogous compound with bromide counterion (BP-DMPT/Br) exhibits a similar peak at -1.33 V vs. SCE (**Figure S17**) while BPh₄⁻ is highly unlikely to undergo further reduction. Notably, this peak proved to be irreversible, indicating that degradation followed reduction. This supports our mechanistic assertion that following *photochemically* induced reduction (ET₁), ²BP-DMPT^{*} undergoes rapid homolysis (HM₂) because *electrochemically* reducing BP-DMPT⁺ produces the identical species (²BP-DMPT^{*}) with the same electronic configuration. The irreversible reduction of BP-DMPT⁺ consequently contributes to efficient photo-base-generation

with no back-electron transfer. Additionally, the CV of BP-DMPT/BPh₄ possesses a peak at 0.82 V vs. SCE (**Figure S16**), which we interpret as the single-electron oxidation of BPh₄⁻ because BP-DMPT/Br exhibits peaks at 0.70 V and 0.99 V vs. SCE (**Figure S17**), eliminating the oxidation of electrochemical products of BP-DMPT⁺ as possibilities. Coincidentally, the oxidation peak also proved to be irreversible, which indicates degradation following oxidation and thus also supports our mechanistic assertion that photochemically oxidized BPh₄[•] undergoes rapid homolysis (HM₁) by similar reasoning to that described above. The irreversibility of BPh₄⁻ oxidation benefits the generation of radicals that cause polymerization during irradiation, consistent with the previously reported utilization of borate salts in RPP.^{141,143–147} We suggest that such irreversible ET reactions contribute to the fast photopolymerization rates that benefit rapid surface cure and minimize oxygen inhibition while also contributing to extensive dark-curing that gives rise to further polymer property development even after the cessation of irradiation (*vide infra*)

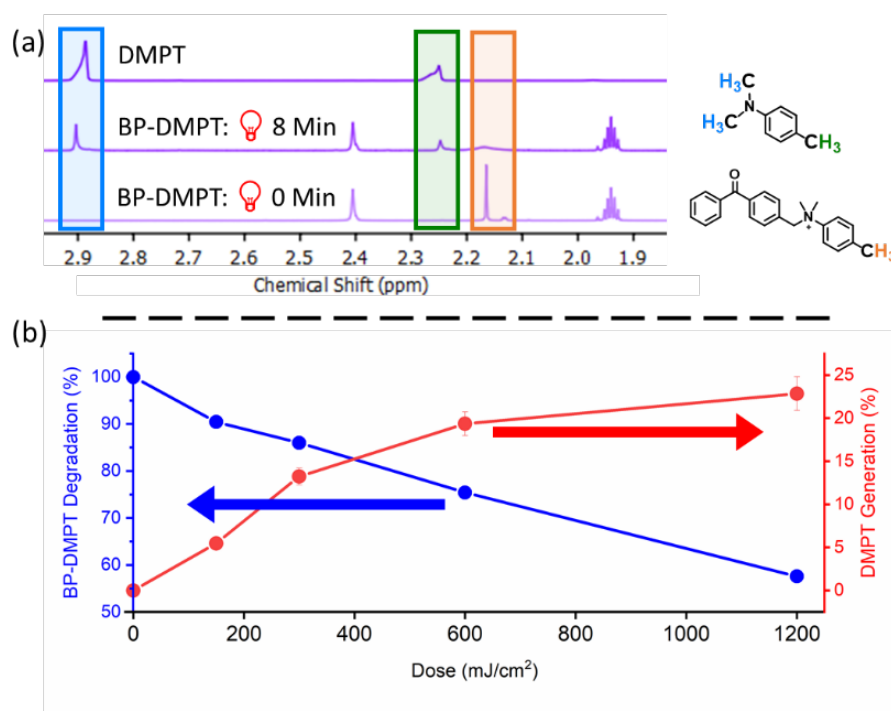


Figure 6. NMR evidence of photo-base-generation and its dose-dependence. (a) With no exposure, BP-DMPT exhibits no peaks indicative of DMPT. However, irradiation of BP-DMPT results in the emergence of two peaks corresponding to DMPT while one peak of BP-DMPT diminishes. This demonstrates DMPT generation in response to irradiation and resultant BP-DMPT degradation. The identity of the peaks is color-coordinated to the hydrogens of the molecule structures. (b) Using an internal standard, BP-DMPT degradation and DMPT generation were quantitatively traced. Up to 600 mJ/cm^2 , $\sim 75\%$ of the degradation results in DMPT generation, showing the high selectivity of these photochemical reactions. The experimental conditions include 2.5 mW/cm^2 365 nm LED exposure in deuterated acetonitrile at a BP-DMPT/BPh₄ concentration of 12.8 mM.

4.4.5 Dark-curing photoinitiator behavior under various conditions

After confirming the successful design of DCPI, we further studied its behavior under various conditions including varying concentrations, resin compositions, and irradiation intensities in order to gain insight into its bulk radical dark-curing processes. As expected, we found that increasing BP-DMPT/BPh₄ concentration leads to faster photopolymerization (**Figure S18**), which limited our ability to reliably shutter the illumination at desired lower-conversion intervals. Assuming that the quantum yield of photo-base-generation remains constant relative to radical generation (1 amine to 2 radicals during irradiation), such an increase in photopolymerization rates should not lead to any notable change in dark-curing behavior. On the other hand, we hypothesized that increasing oxidant concentration will lead to an increase in dark-curing rates as higher concentrations will result in greater bimolecular collisional rates and thermodynamic driving forces that are particularly critical to the amine-peroxide redox chemistry because its rate-

determining step proceeds under thermodynamic control.¹³⁰ As hypothesized, increased oxidant concentration indeed led to higher dark-curing rates (**Figure 7.A.**). Shuttering irradiation at 20% partial conversion, and at BPO concentrations of 0.56, 1.12, and 1.68 wt%, led to the observation of initial respective dark-curing rates of 4.8, 5.5, and 8.3 %/min; this is because redox radical production rates are directly correlated to BPO concentrations as propagating radicals that originate from the preceding photolysis reactions rapidly terminate. Additionally, increased dark-curing rates also led to higher short-term post-conversions (41, 48, and 56 %, respectively) within a 40 min measurement interval. As concentrations are easily adjusted at the formulation stage of the application, such changes enable facile modulation of dark-curing rates for specific applications.

To understand the effects of redox-initiator mobility on dark-curing behavior under various bulk conditions, we varied crosslinking density using different divinyl to monovinyl comonomer ratios (**Figure 7.B.**). Considering bulk polymerization conditions, mobility of photo-generated amines and formulated peroxides is central to promoting dark-phase redox reactions. While a study of initial formulation viscosities is relevant to understand the effects of mobility, we chose to examine varying crosslinking density because workable initial viscosity in practice varies only up to 2 orders of magnitude and this difference is quickly exceeded during polymerization which raises viscosity ~8 orders of magnitude in many crosslinked polymers. In order to isolate the effects of crosslinking density, we ensured that the change of resins did not significantly impact the initial viscosity, secondary interactions between monomers and reactive group density (See **SI Details of Resin Design**). Thus, we used formulations of varying crosslinking densities: HiCxLR with 90 wt% (86 mol%) crosslinker and LoCxLR with 50 wt% (48 mol%) crosslinker. Despite these attempts, vitrification, which dramatically slows polymerization still occurs at different

conversions during pseudo-isothermal photocuring.¹²³ Thus, we observed vitrification-limited conversions of ~60% in HiCxLR and ~80% in LoCxLR at ambient temperature and under full irradiation (**Figure S5 and S24**). The low cross-linking case was particularly noteworthy as LoCxLR exhibits a continuous polymerization profile with a nearly indistinguishable transition from photo-radical-generation to redox-radical-generation indicating that the rate of redox radical-generation that is responsible for dark-curing is comparable to that of photo radical-generation under these conditions.

Lastly, we investigated the dependence of dark-curing rates on irradiation intensity because high irradiation intensities (1000 - 3000 mW/cm²) are often used to elicit rapid polymerization rates.¹⁵² However, we elected to span a relatively modest range of incident irradiance (5, 30, 50 mW/cm²) where exposure-conversion reciprocity,¹⁵³ thermal excursion, and the practical issue of controllably targeting the 20% partial cure point for shuttering the light source did not impose any significant experimental complications. We found that increased irradiation intensity increases apparent dark-curing efficiency (**Figure 7.C.**). However, this likely does not indicate that additional photons lead to greater dark-curing efficiency. In fact, the irradiation times used were sufficiently long so that the driving force for second-stage redox initiation is concurrently consumed during irradiation. For example, the longer irradiation time to reach 20% conversion at 5 mW/cm² intensity due to slower photopolymerization results in more redox initiator consumption relative to the 50 mW/cm² condition. For higher intensity conditions, the conversion to 20% is primarily due to photopolymerization, which conserves a larger quantity of redox initiators to be available for latent curing. Therefore, relatively short irradiation times with higher irradiance levels likely offer an enhanced dark-curing effect, which is advantageous under commonly utilized practical conditions. Despite the limited study of the effects of concentrations,

resins, and intensities, we surmise that the various circumstances imposed by specific applications will lead to widely varying radical dark-curing behavior in bulk, including conditions where the initial photopolymerized conversion might be quadrupled or more in less than an hour (**Figure 7.B.**). The unique capabilities of this DCPI as well as the lack of published reports of radical dark-curing in bulk suggest that additional condition-dependent studies are warranted.

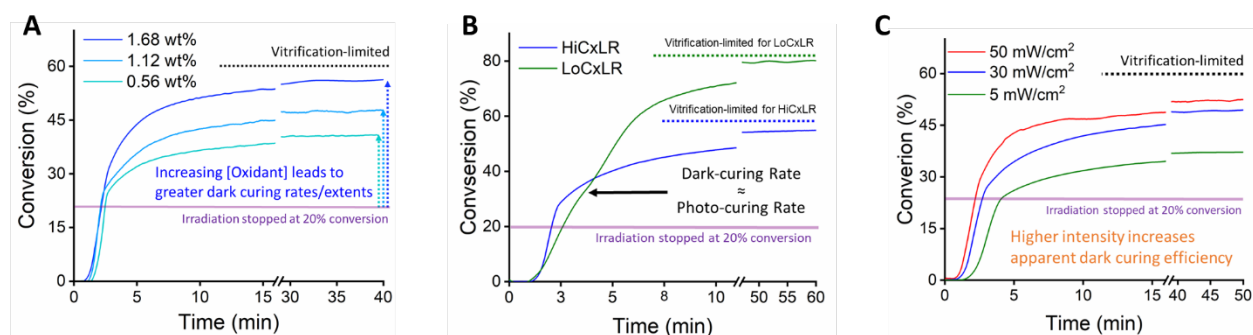


Figure 7. Bulk polymerization profiles of dark-curing photoinitiator (DCPI) under various conditions and initial 20% partial conversion conditions. **A.** Increasing the concentration of benzoyl peroxide (BPO) oxidant leads to greater dark-curing rates and extents due to increasing the thermodynamic driving force for the redox reaction. With 1.68 wt% BPO, the 20% partial cure conversion nearly reaches the conversion of the vitrified polymer within 40 mins. **B.** Lower crosslinking density leads to greater dark-curing and overall conversion. LoCxLR exhibited extensive dark-curing with an additional 60% conversion achieved following irradiation to quadruple its initial conversion. **C.** Due to the reduced consumption of amine via redox reactions during irradiation, higher light intensities resulted in greater dark-curing. The total concentration of photo-generated amine is similar to when light was terminated at 20% conversion in all three conditions. The experimental conditions include a 365 nm LED with $[BP\text{-}DMPT/BPh_4] = 7.7$

$\mu\text{mol/g}$ of resin. HiCxLR was used for **A** and **C**; $[\text{BPO}] = 46.2 \mu\text{mol}$ or $1.12 \text{ wt\%/g}$ of resin was used for **B** and **C**; and 30 mW/cm^2 was used for **A** and **B**.

4.4.6 Enhanced mechanical properties from dark-curing photoinitiation

Material properties of bulk-cured polymer networks are primarily dependent on the conversion achieved during polymerization.¹⁵⁴ Therefore, we initially expected that dark-cured polymers would exhibit similar properties to photo-cured polymers at a given conversion. However, the rate at which monomers are incorporated into the polymers (i.e. polymerization kinetics) also affects resultant material properties to a modest extent by changing internal polymer architecture.^{155,156} Due to the unusual polymerization kinetic regimes that result from the two drastically different radical generation time scales of DCPI produced polymers, divergence in material properties from the internal polymer architecture might arise. Consequently, we examined two select properties that are relevant to bulk photopolymerization: storage modulus and shrinkage stress.¹⁵⁴ First, we examined storage modulus development with respect to conversion in photo-cured and dark-cured samples using an oscillatory photo-rheometer coupled with FT-IR. Within the 20% partial cure regime, we demonstrated (**Figure 8.A.**) that the storage modulus (E') of dark-cured polymer is comparable to that of photo-cured polymer at the vitrification conversion ($\sim 4 \text{ MPa}$ at 60% conversion), where over an hour DCPI transformed the initially partially cured polymer with a storage modulus of 0.1 MPa to the vitrified polymer with E' of 4.3 MPa . Such a large increase in modulus from underdeveloped polymers is of practical significance, where user errors in in-situ applications are commonplace or where irradiation conditions are not ideal.¹⁵⁴ For example, emission intensity of a light source is non-uniform, which is a maximum in the center of common light sources and decreases outwards towards the boundary of irradiation due to

Lambert's cosine law, in addition to other intensity-related issues from inconsistencies between and degradation of light sources.^{157,158} Such uneven irradiation results in conversion gradients from over-cured to under-cured resins over an area of the surface. In addition, inherent light attenuation leads to depth-wise gradients, where conversion decreases with distance from the surface. DCPI formulations prevents this common problem and produces more uniformly polymerized samples by evolving undercured regions in the dark while simultaneously avoiding energy-wasting over-curing of other areas. Similarly, photopolymerization of samples with irregular surfaces (e.g. uneven or curved) likewise undergo disproportionate irradiation that may also benefit from our proposed DCPI strategy.¹⁵⁹

In addition to the DCPI-promoted continuous development of polymer properties following irradiation, we also found that the internal stress commonly induced by photopolymerization of bulk samples was reduced in dark-cured polymer (**Figure 8.B.**). This internal stress results from volumetric shrinkage during polymerization and often leads to micro-/macro-fractures, inferior mechanical properties, distortion, or detachment from the substrate.¹⁵⁴ Although conversion and shrinkage stress are generally correlated, higher rates of and later stage polymerization typically result in greater shrinkage stress.¹⁵⁴ Based on this phenomena, we hypothesized that the transition from rapid photopolymerization to relatively slower redox-polymerization reduces internal stress from polymerization shrinkage. Using CTPI under full irradiation as a control, we found that DCPI shuttered at 35% conversion resulted in ~30% less shrinkage stress (0.73 MPa vs. 1.06 MPa) as each process achieves an equivalent vitrification conversion. Interestingly, the transition of the polymerization mode of the DCPI mechanism can be identified from **Figure 8.B.** DCPI initially exhibited a higher shrinkage stress for 20% to 40% conversions due to its faster photopolymerization kinetics relative to CTPI, although this higher

stress during the early stages of polymerization did not contribute significantly to the overall stress at vitrification. When the light was shuttered at 35% conversion, the dominant curing mode of DCPI transitioned to dark-curing redox polymerization that is slower than photopolymerization by CTPI and correspondingly, a lower rate of stress development was observed beyond 45% conversion (**Figure S31**). The switch to slower polymerization rates in DCPI resins during late-stage polymerization led to an overall lower stress in the DCPI resin than in the CTPI-polymerized resin. We note that a similar, but more complex strategy to reduce shrinkage stress with conventional photoinitiators by manipulating light intensity and the corresponding polymerization rates as polymerization progresses, has been extensively utilized in practice.¹³⁹ DCPI achieves this result without the use of light intensity management beyond stopping irradiation after partial curing.

Finally, we investigated the thermal response of HiC_xLR resins with CTPI and DCPI as a surrogate benchmark for shelf stability in the dark. We used a temperature ramping protocol to identify temperature ranges at which the mechanical behavior of a resin shifts from liquid to viscoelastic solid. Both resins began to show signs of polymerization near 100 °C (**Figure S32**), confirming that DCPI composed of BP-DMPT/BPh₄ and BPO does not compromise shelf-stability of fully formulated DCPI resins. This property results from our molecular design which ensures high thermal stability not only as an isolated solid ($T_{Degradation}^{Solid} = 189\text{ °C}$),¹³⁶ but also as a dissolved component to prevent inadvertent degradation of stored formulations. Recognizing that degradation is especially detrimental to DCPI relative to conventional photoinitiators, we specifically designed the DCPI reported herein to have slow degradation kinetics by possessing a sufficiently high C-N bond strength (48.6 kcal/mol) so that it would not thermally dissociate to initiate undesired radical polymerization in storage on a reasonable time-scale ($t_{1/2,298K} \cong 10^{15}$ years). On the other hand, BPO appears to be the only potentially stability-limiting component

here and it has sufficient thermal stability to be included in many two-part redox-curable commercial resins.²⁶ Under refrigeration at 4 °C, the storage time of BPO-containing methacrylate solutions exceeds 12 months.¹⁶⁰

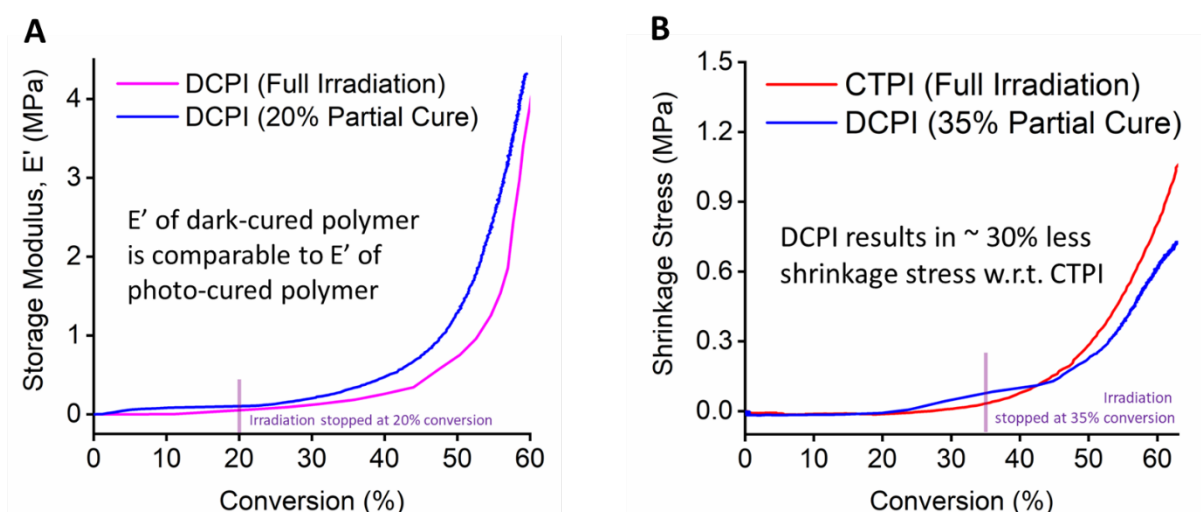


Figure 8. Mechanical property development of bulk polymers initiated by DCPI and CTPI. **A.** The storage modulus (E') of photo-cured polymer is comparable to that of dark-cured polymer (~4 MPa) at the vitrification conversion (~60%), which dark-curing developed from 20% partial conversion with an initial E' of 0.1 MPa over 1 h. **B.** Dark-cured polymer with its light shuttered at 35% conversion has ~30% less shrinkage stress than photo-cured polymer (0.73 MPa vs. 1.06 MPa) at vitrification, which we attribute to lower internal stress produced by slower crosslinking development in late-stage polymerization. The experimental conditions include a 365 nm-filtered Hg arc lamp with $[BP\text{-}DMPT/BPh_4] = 7.7 \mu\text{mol/g}$ and $[BPO] = 23.1 \mu\text{mol/g}$ of HiC_xLR resin at ambient temperature. The rotational rheometer was used with 0.5% strain and 1 Hz oscillation frequency while intensities of 4.4 mW/cm² and 30 mW/cm² were used for **A** and **B**, respectively.

4.5 Conclusion

In this work, we report a radical dark-curing photoinitiator (BP-DMPT/BPh₄ + BPO) that defies the conventional RPP paradigm that light dosage must correlate to conversion by enabling substantial dark-phase polymerization activated by light. We used quantum chemical modeling to elucidate a foundational mechanistic understanding of light-phase photochemistry and dark-phase redox-chemistry and then exploited this understanding to design DCPI that also satisfies the practical constraints imposed by its potential applications. With a successful DCPI design, we then demonstrated that DCPI could achieve an additional 25-60% monomer conversion in the dark after light exposure was ceased at 20% conversion, far exceeding the marginal 1-3% dark conversion observed for a conventional photoinitiator (Norrish type II control). Our computational study and electrochemical and spectroscopic experiments elucidated the origin of high photopolymerization and dark-curing efficiency of DCPI while a steady-state kinetic analysis suggested that DCPI may be the most photon-efficient photoinitiator to date. DCPI with such high photon efficiency results in four or more initiating radicals per photon while conventional photoinitiators make one or two viable radicals. The resulting dark-cured polymers exhibit properties similar to, or in some cases superior to, polymers obtained by conventional photo-curing. This potential enhancement of polymer properties cannot be achieved by any other photoinitiators in a typical photopolymer condition. This new class of photoinitiators represents a new and higher standard in energy-efficient photopolymerization, while enabling both the improvement of existing photopolymerization applications and new applications that were previously unattainable because conventional photoinitiators are limited by their inability to cure in depth or with light attenuation. The dark-curing ability of DCPI automatically corrects initially under-cured regions within a

specimen by raising the conversion levels of all regions that received different light exposures. This homogenizes the polymer properties and increases the reliability of photocuring processes. As a result, DCPI, which can be readily substituted for conventional photoinitiators in pre-existing formulations, minimizes potential user errors and facilitates higher throughput, higher energy-efficiency, more reliable, and lower cost production of superior polymers with less internal stress.

4.6 Supporting Information

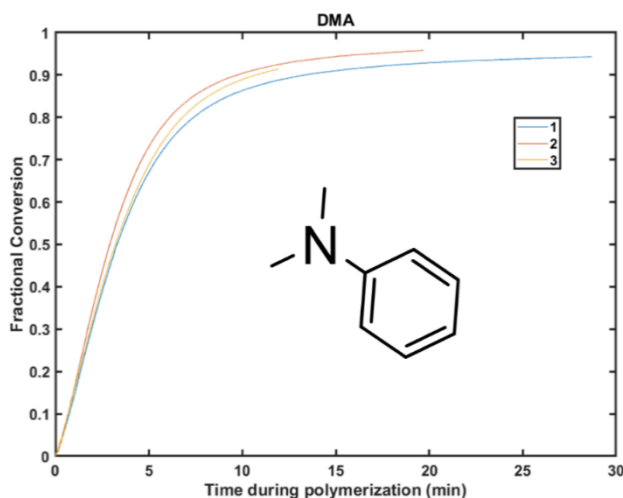


Figure S4.1. Redox polymerization profiles of *N,N*-dimethylaniline (DMA) for **Figure 2**. The experimental conditions include 3 mol% concentrations of both DMA and BPO in di(ethylene glycol) ethyl ether acrylate.

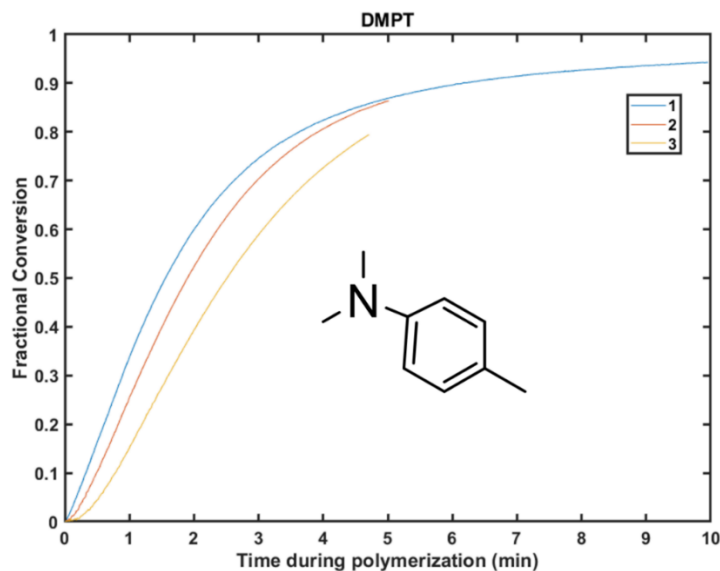


Figure S4.2. Redox polymerization profiles of N,N-dimethyl-p-toluidine (DMPT) for **Figure 2**. The experimental conditions include 3 mol% concentrations of both DMA and BPO in di(ethylene glycol) ethyl ether acrylate.

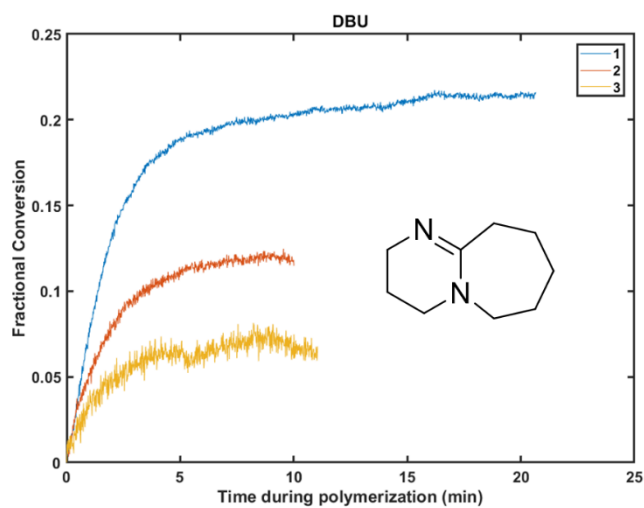


Figure S4.3. Redox polymerization profiles of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for **Figure 4.2**. The experimental conditions include 3 mol% concentrations of both DMA and BPO in di(ethylene glycol) ethyl ether acrylate.

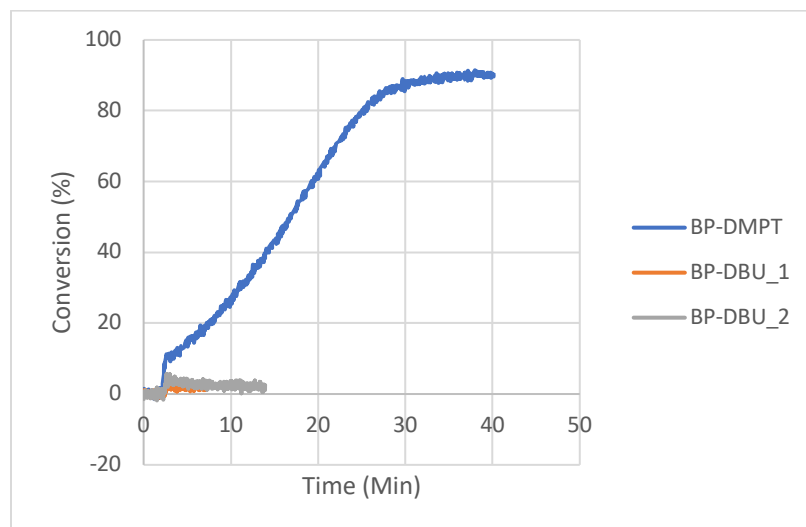


Figure S4.4. Polymerization profiles of two DCPIs that release DMPT (BP-DMPT) and DBU (BP-DBU), respectively. The resin composition is 90% TEGDMA and 10% acrylonitrile with 2 mol% BPO and 1 mol% respective photoinitiators. As acetonitrile is susceptible to Michael addition, more nucleophilic DBU attacks acetonitrile and limits the radical-mediated chain growth polymerization while non-nucleophilic DMPT avoids such side reactions and proceeds to react with BPO to induce dark-curing.

S11. Thin Film Approximation

According to Beer-Lambert, $A = \epsilon cl$ where ϵ is molar absorptivity, c is molar concentration of photochemical species, l is path length.

The UV-Vis spectra (**Figure S11** and **S13**) indicate that DCPI and CTPI absorb light with a similar absorptivity ($\epsilon = 80.1 \text{ L/cm/mol}$). The molar concentration (c) in our experiments was 0.007 mol/L while the path length (l) of the samples were 0.11 cm.

Hence, $A = 80.1 \times 0.007 \times 0.11 = 0.062$

Reorganizing $A = -\log T$ yields $10^{-A} = T$

Plugging in A value, $T = 10^{-0.062} = 0.87$.

Therefore, the minimal irradiance gradient introduced across the sample pathlength here effectively validates the optically thin film approximation.

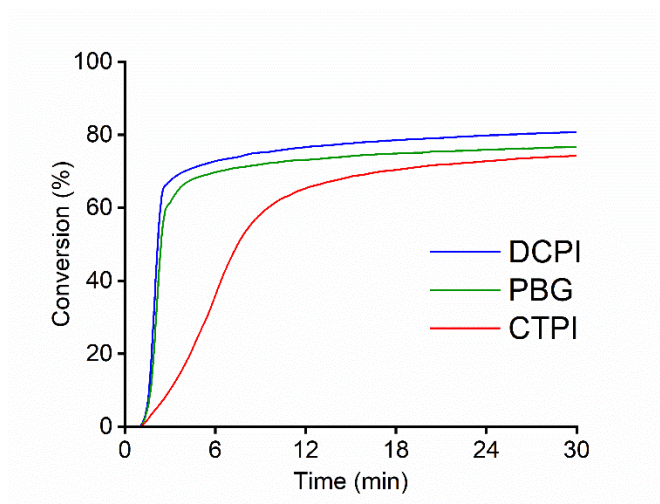


Figure S4.5. Photopolymerization kinetic profiles of DCPI, PBG, and CTPI under full cure. DCPI and PBG have similar kinetics while CTPI is slower. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP] = [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [DMPT] = [BPO] = 23.1 μmol/g of resin in HiCxLR with a TEGDMA/MBL (9:1 mass fraction) composition.

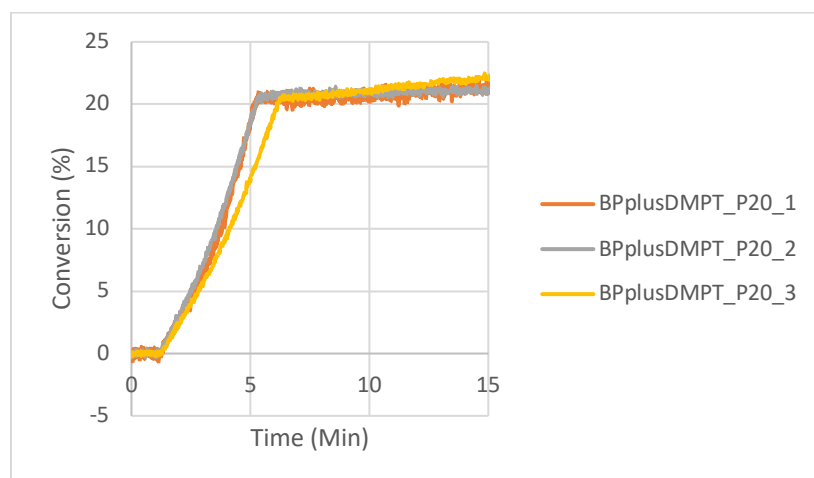


Figure S4.6. Partial cure polymerization profiles of CTPI composed of BP sensitizer and DMPT co-initiator. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP] = 7.7 μ mol/g of resin and [DMPT] = 23.1 μ mol/g of resin in HiCXL[®] with a TEGDMA/MBL (9:1 mass fraction) composition.

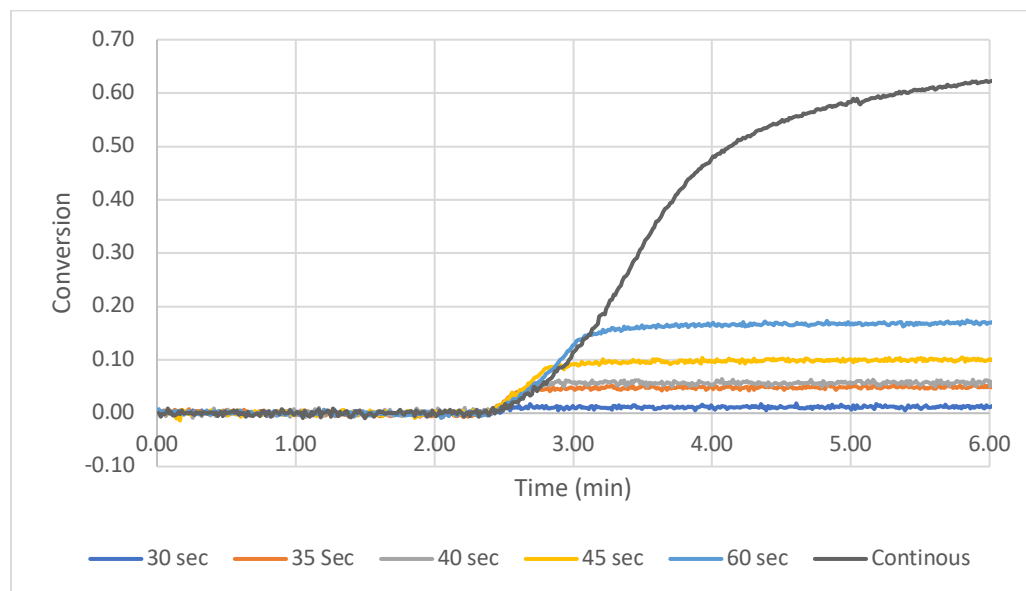


Figure S4.7. Polymerization profiles of DMPA (2,2-dimethoxy-2-phenylacetophenone) with varying irradiation durations. The conditions of these polymerizations included illumination with a 10 mW/cm² 320-390 nm filter arc lamp with [DMPA] = 0.025 mol% in TEGDMA.

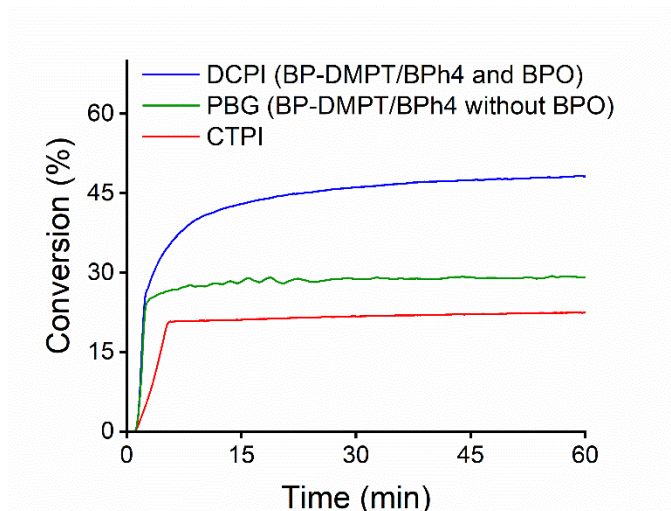


Figure S4.8. Photopolymerization kinetic profiles of DCPI, PBG, and CTPI under 20% partial cure. DCPI shows dark-curing while PBG and CTPI does not. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP] = [BP-DMPT/BPh4] = 7.7 μmol/g of resin and [DMPT] = [BPO] = 23.1 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

SI2. Kinetic Property Calculations

Based on a steady-state analysis, the rate of methacrylate free radical polymerization (R_p) can be expressed as¹⁶¹

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](\epsilon I_0 \Phi [I])^{1/2}} \quad \text{Eq. 1}$$

Whereas k_p is propagation kinetic constant, k_t is termination kinetic constant. The molar concentration of monomer is represented by $[M]$, the initiator molar absorption by ϵ , light intensity by I_0 , initiator efficiency by Φ , and the initiator concentration by $[I]$. Therefore, the initiator efficiency can be calculated by reorganizing **Eq. 1**

$$\Phi = \frac{k_t R_p^2}{\epsilon I_0 [I] ([M] k_p)^2} \quad \text{Eq 2}$$

Based on **Figure S5**, R_p for each system was calculated based on the time that it took the reaction proceed from 10% to 20% conversion. $\frac{k_p}{k_t^{1/2}}$ for TEGDMA was obtained from the previous literature, where k_p is $516 \text{ M}^{-1}\text{s}^{-1}$ and k_t is $5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.¹⁶¹ From **Figure S11**, the molar absorptions for BP, PBG, and DCPI at 365nm are nearly identical ($\epsilon = 0.8 \text{ L/m/mol}$). Initiator concentration $[I]$ is 0.007 mol/L . Light intensity I_0 is 300 W/m^2

Hence, Φ for DCPI can be determined as

$$\Phi = \frac{k_t R_p^2}{\epsilon I_0 [I] ([M] k_p)^2} = \frac{5 \times 10^5 \times 4.5^2}{0.8 \times 300 \times 0.007 \times (5.5 \times 516)^2} = 0.75$$

Similar calculations were done with PBG and CTPI.

Table S4.1. Rate of polymerization and initiator efficiency of photoinitiators

	CTPI	PBG	DCPI
$R_p \text{ (M}^{-1}\text{s}^{-1}\text{)}$	0.68	3.40	4.50
Φ	0.02	0.43	0.75

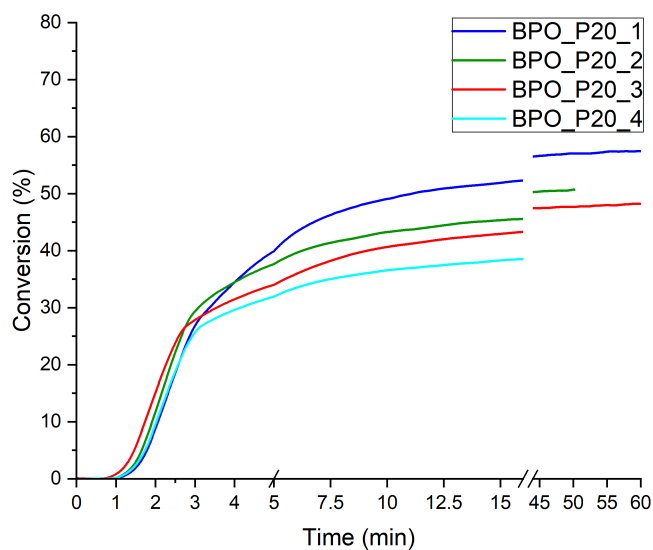


Figure S4.9. Polymerization profiles of DCPI under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [BPO] = 23.1 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

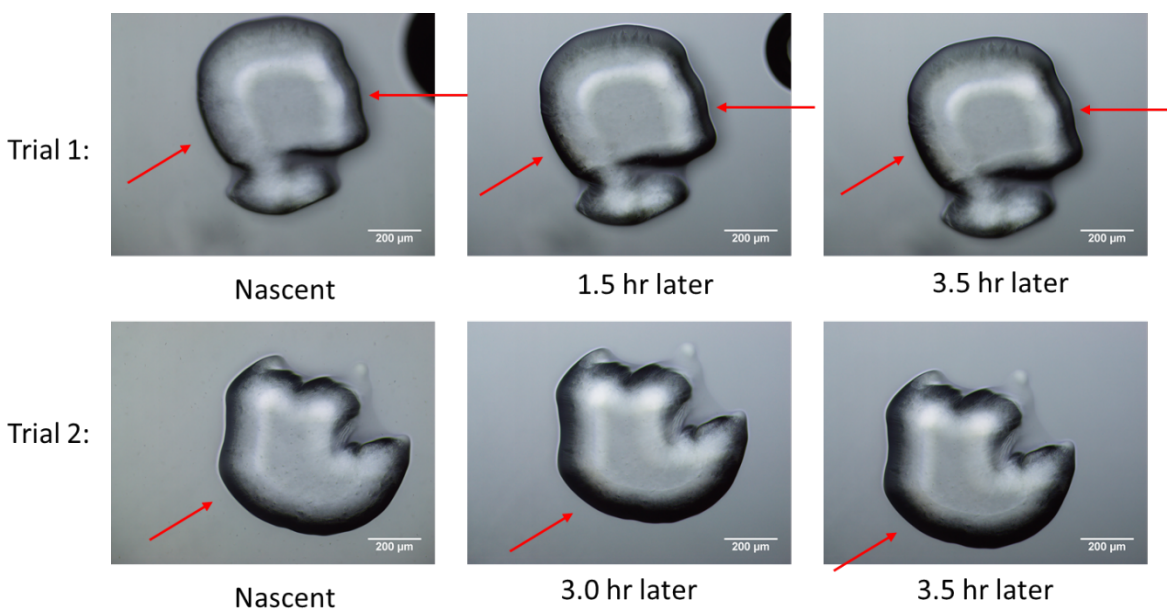
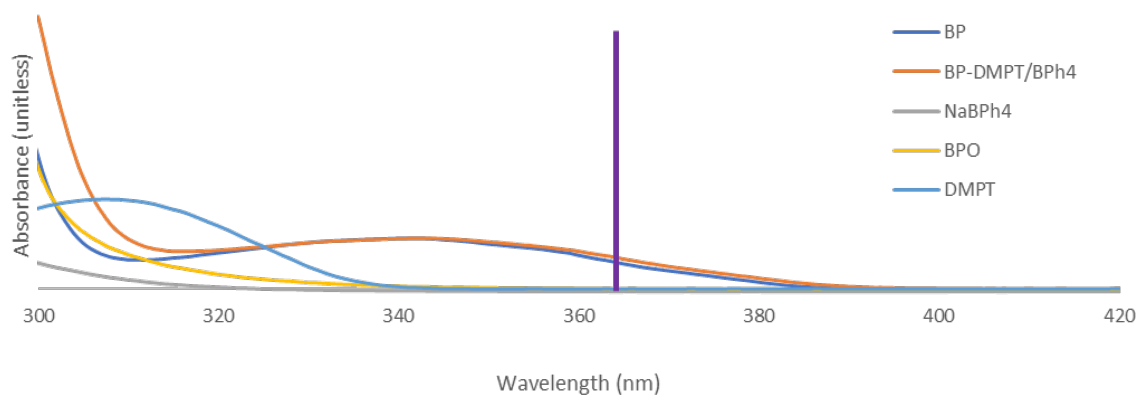


Figure S4.10. Visual development of dark-cured polymer using a microscope. As polymerization proceeds further by dark-curing and the refractive index of polymer changes, the edges of a pin-hole polymer become darker.

A



B

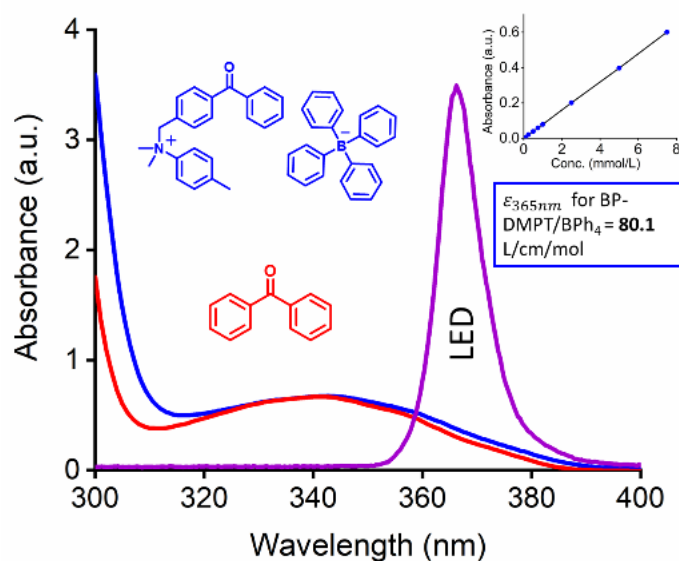


Figure S4.11 A and B. UV-Vis spectra of initiating components of DCPI and CTPI in dimethylformamide (DMF). The concentrations are 0.5 mM DMPT, 5 mM BP, 5 mM BP-

DMPT/BPh₄, 50 mM NaBPh₄, and 50mM BPO. BP-DMPT/BPh₄ and BP essentially have the same molar absorptivity at 365 nm while other components do not absorb at 365 nm. The Inset shows concentration-dependent absorbance of BP-DMPT/BPh₄ at 365 nm, resulting in molar absorption coefficient (ϵ) = 80.1 L/cm/mol at 365 nm. the photophysical properties of these photoinitiators based on benzophenone chromophore do not significantly differ in regards to intersystem crossing efficiency, excited state energies, or absorbance.^{162–164}

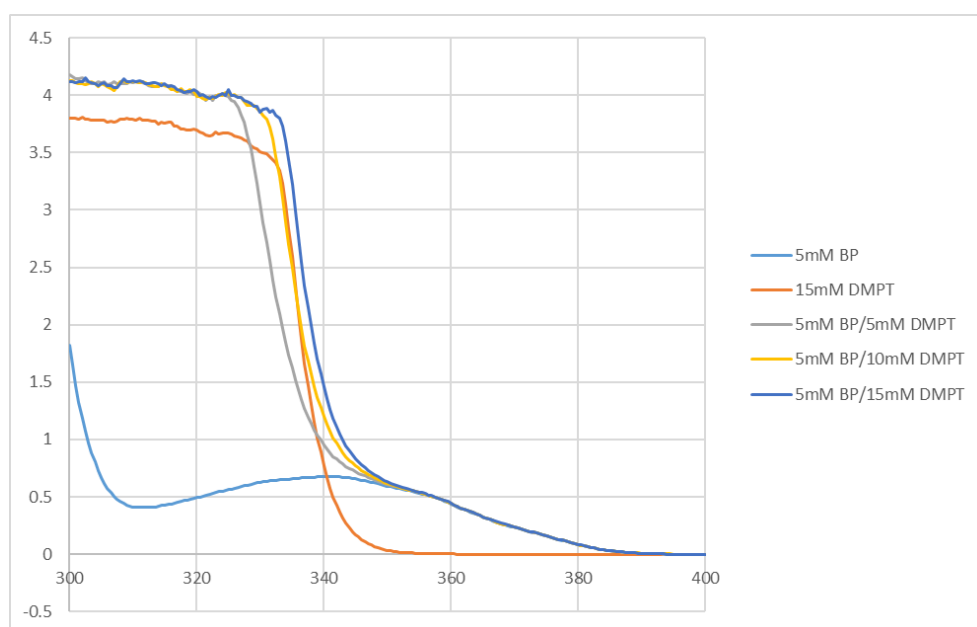


Figure S4.12. UV-Vis Spectra of BP with varying concentrations of DMPT. When BP and DMPT are added, a new spectrum is identical to the two spectra of BP and DMPT added to each other, which means a lack of ground state interaction (e.g. charge transfer complex) between BP and DMPT.

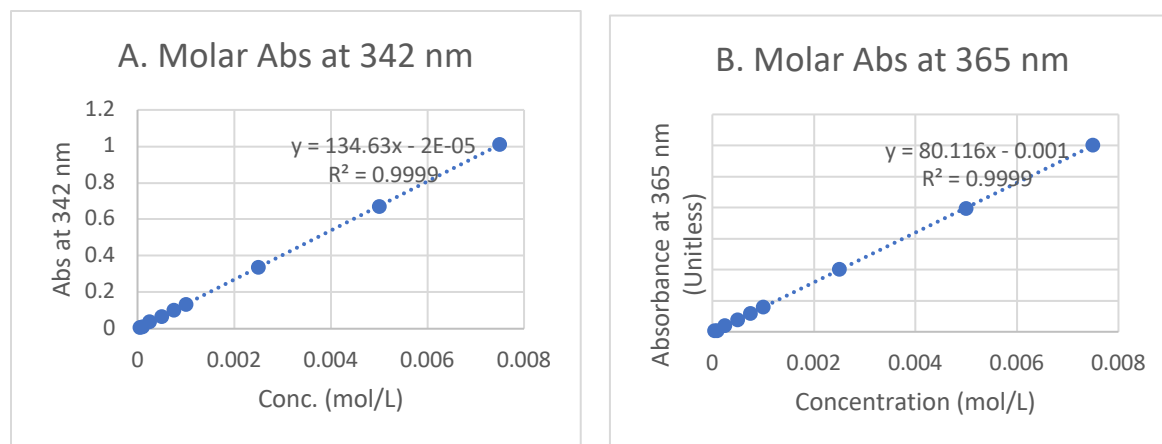


Figure S4.13 A and B. Molar Absorptivity of BP-DMPT/BPh4 in DMF at lambda max of 342 nm and irradiation wavelength of 365 nm.

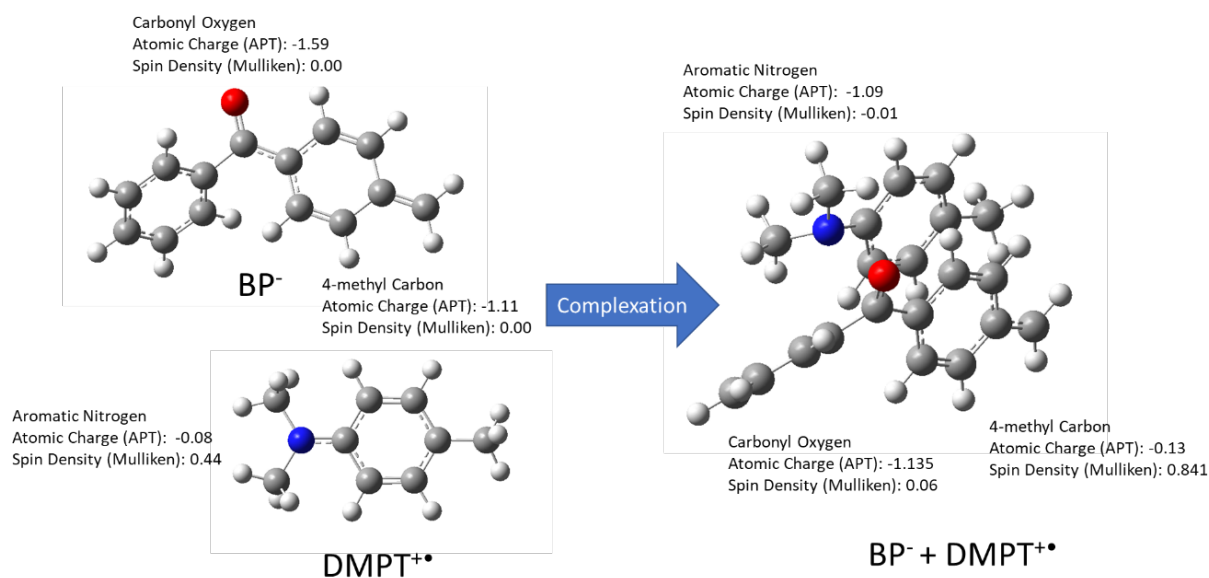


Figure S4.14. Charge-transfer complex formation between BP⁻ and DMPT^{+•}. Anionic charges of BP⁻ were transferred to DMPT^{+•} while spin density of DMPT^{+•} was transferred to BP⁻.

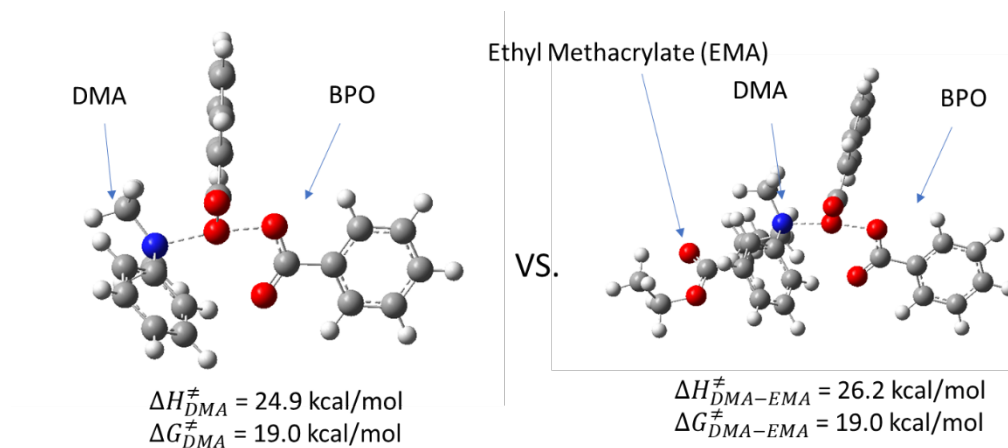


Figure S4.15. Transition states of DMA attacking BPO and DMA tethered to methacrylate attacking BPO. Activation barrier difference between these two initiators are marginal. See reference 5 (Kangmin Kim, 2019, JACS) for the detailed nature of the transition state.¹³⁰

SI3.Details of Quantitative NMR for Figure 6.

In order to account for the amine photogeneration in our system, three sets of hydrogens can be tracked via H-NMR. Hydrogens at para-methyl group of DMPT are a singlet with an integration of 3 at 2.22 ppm (DMPT-p-methyl-H). Hydrogens at N,N-dimethyl group of DMPT are a singlet with a integration of 6 at 2.85 ppm. (DMPT-N,N-dimethyl-H) Hydrogens in the aromatic regions of DMPT are doublet with a integration of 2 at 6.68 ppm and another integration of 2 at 7.02 ppm. Using aromatic hydrogens would be intractable due to the presence of numerous aromatic hydrogens in vicinity from BP moiety and BPh4 counterion. Also, we soon realized that DMPT-p-methyl-H overlaps with the methyl hydrogen of the photolyzed BP-moiety from BP-DMPT. Therefore, we decided to track the appearance of DMPT-N,N-dimethyl-H signal to quantify the amine photogeneration. We also tracked the disappearance of the analogous peak signals (BP-DMPT-N,N-dimethyl-H) from the caged amine species in the PBG in order to confirm that the

appearance of DMPT and disappearance of PBG are making up 100% of DMPT in either form. If we found that 100% of DMPT are present, then it can indicate that the undesired side reactions that may destroy the amine are minimal. Such reactions may be imine formation by losing a N-methyl group. For the reference peak to use as a constant integration, we initially tried to use aromatic signals but their integration was found to be unreliable due to a short recycle delay that prevent the nuclei relaxation after a pulse. Instead, we chose to use ethylene carbonate peak for the internal standard.

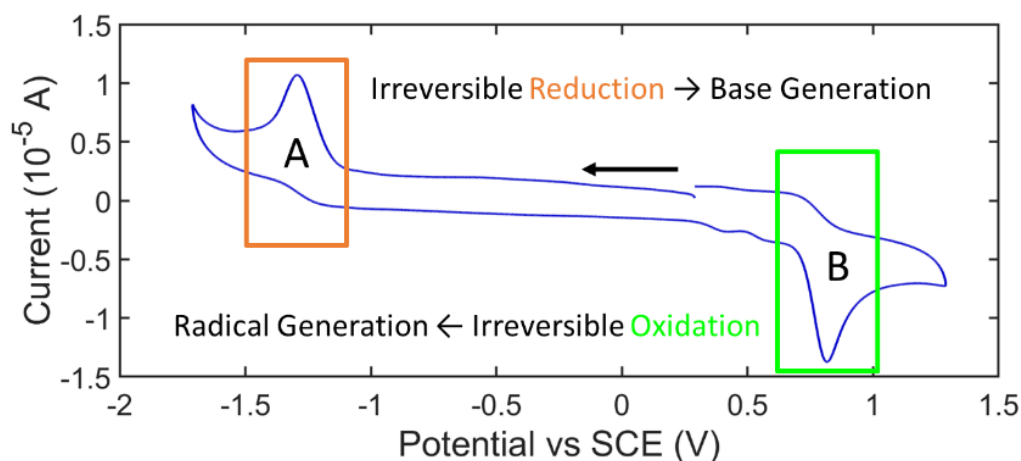


Figure S4.16. Cyclic voltammogram of BP-DMPT/BPh₄. Both reduction of BP-DMPT and oxidation of BPh₄ are irreversible under our experimental conditions, which contributes to efficient photopolymerization and dark curing. The initial scan direction was negative, as indicated by the arrow, and CVs were collected in room temperature acetonitrile under Ar with a 0.01 M Ag/AgNO₃ electrode and 0.1 M tetrabutylammonium hexafluorophosphate, and scanned at a rate of 100 mV/s.

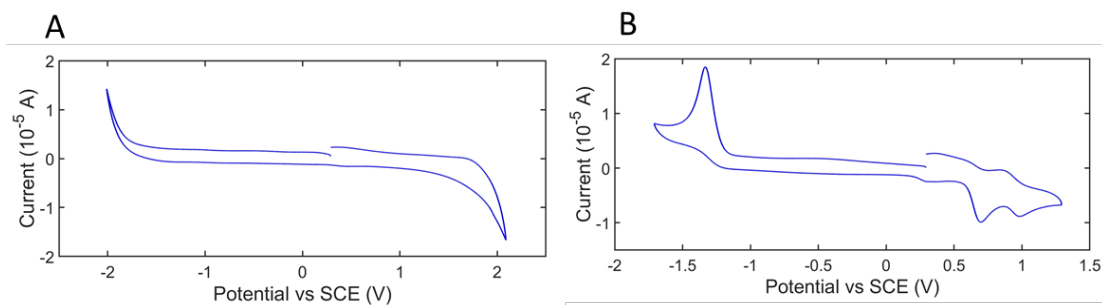


Figure S4.17.A. Cyclic voltammogram of acetonitrile at room temperature under argon atmosphere, taken at a scan rate of 100 mV/s. The initial scan direction was negative. Acetonitrile provides a sufficiently wide range of voltage for our experiments. **B.** Cyclic voltammogram of BP-DMPT/Br in room temperature acetonitrile under argon atmosphere, taken at a scan rate of 100 mV/s. The initial scan direction was negative. The reduction peak corresponds to the reduction of BP-DMPT, similar to what was discussed in the manuscript. However different oxidation behaviors were observed regarding bromide counter ion.

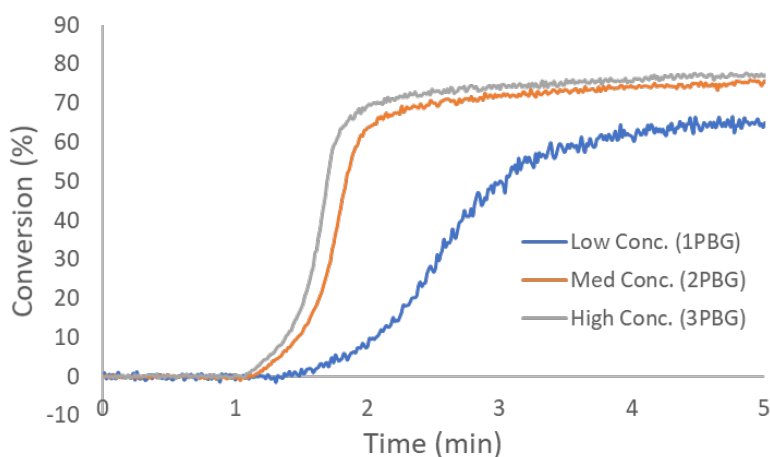


Figure S4.18. Photopolymerization profiles of photo-base-generator (PBG, BP-DMPT/BPh₄) with its various concentrations under full irradiation conditions. Low (1PBG), Med (2PBG), and High (3PBG) corresponds to [BP-DMPT/BPh₄] = 7.7; 15.4; and 23.1 $\mu\text{mol/g}$ of resin with 90 wt% TEGDMA and 10 wt% MBL composition. With higher concentrations of PBG, polymerization

rates are too rapid which limited our ability to reliably shutter the illumination at desired intervals.

The experimental conditions include 30mW/cm² 365nm LED.

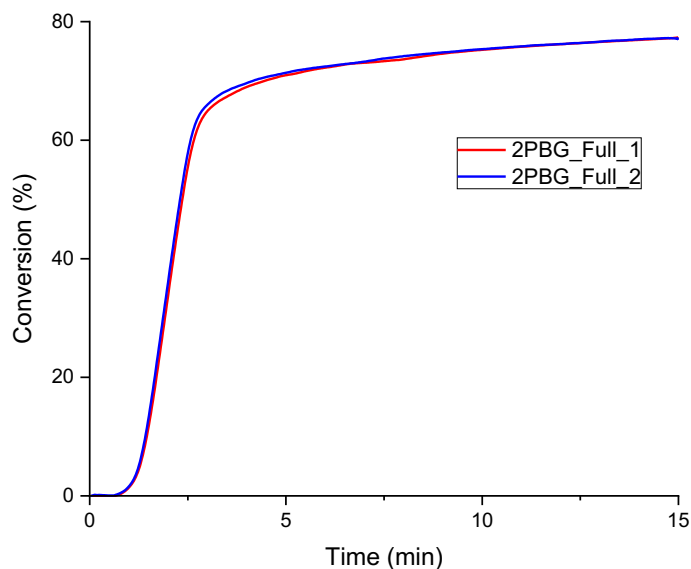


Figure S4.19. Photopolymerization profiles of medium concentration photo-base-generator (PBG, BP-DMPT/BPh₄) under full irradiation conditions. medium (2PBG) corresponds to [BP-DMPT/BPh₄] = 15.4 μ mol/g of resin with 90 wt% TEGDMA and 10 wt% MBL composition. The experimental conditions include 30mW/cm² 365nm LED.

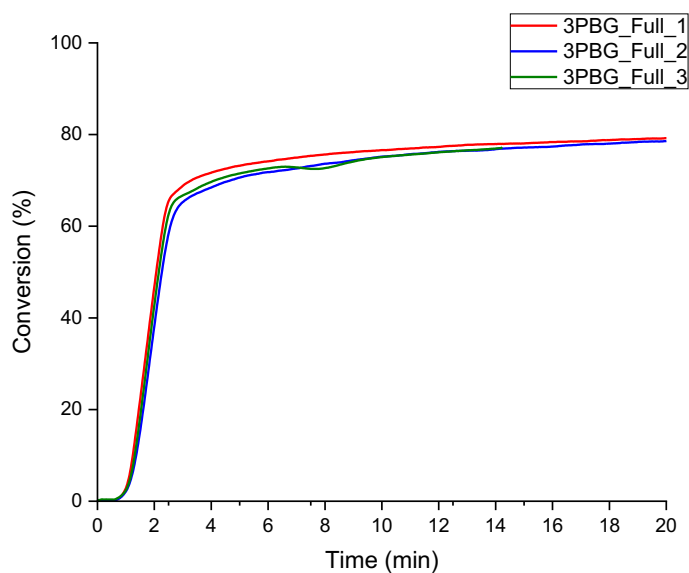


Figure S4.20. Photopolymerization profiles of high concentration photo-base-generator (PBG, BP-DMPT/BPh₄) under full irradiation conditions. High (3PBG) corresponds to [BP-DMPT/BPh₄] = 23.1 $\mu\text{mol/g}$ of resin with 90 wt% TEGDMA and 10 wt% MBL composition. The experimental conditions include 30mW/cm² 365nm LED.

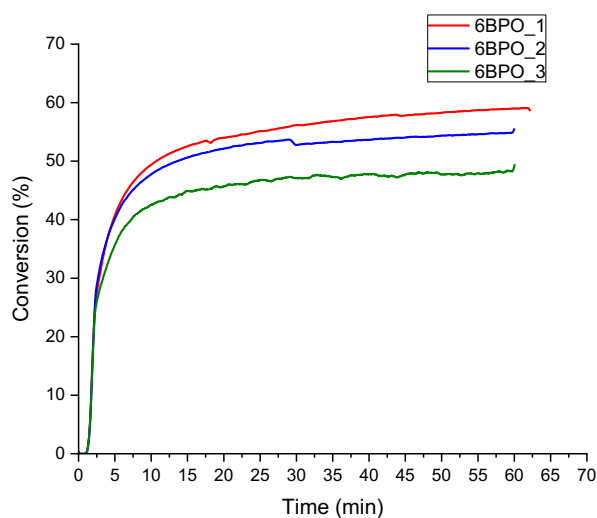


Figure S4.21. Polymerization profiles of DCPI with medium concentration of BPO under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 30

mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and 6BPO = [BPO] = 46.2 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

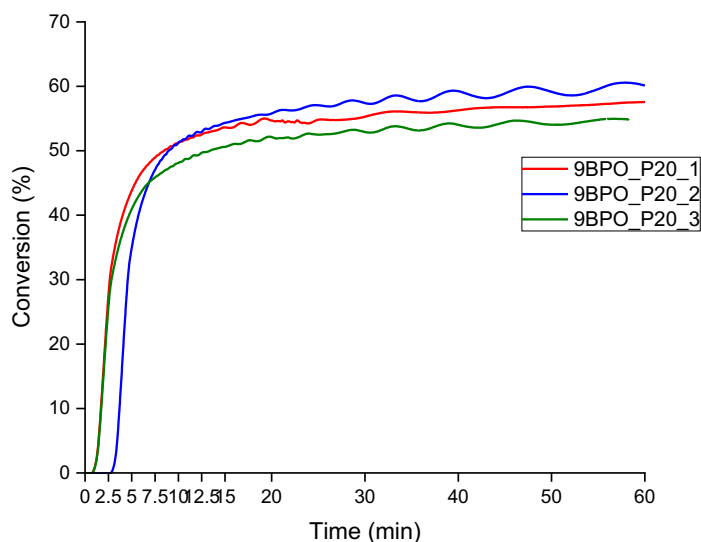


Figure S4.22. Polymerization profiles of DCPI with high concentration of BPO under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and 9BPO = [BPO] = 69.3 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

*SI4.4 Details of Resin Design for **Figure 8.B***

We refrained from introducing any confounding components that may change coordination (e.g. hydrogen bonding), ensuring that, between samples, no drastic initial viscosity differences were observed as well as minimizing the influence of such coordination changes on polymerization kinetics.¹⁶⁵ Additionally, because larger monomers/oligomers can induce unexpected changes in polymerization behavior, we maintained an approximately constant reactive group density by

combining n-butyl methacrylate (BMA) with triethylene glycol dimethacrylate (TEGDMA) because BMA has approximately half the molecular weight of the di-vinyl TEGDMA.

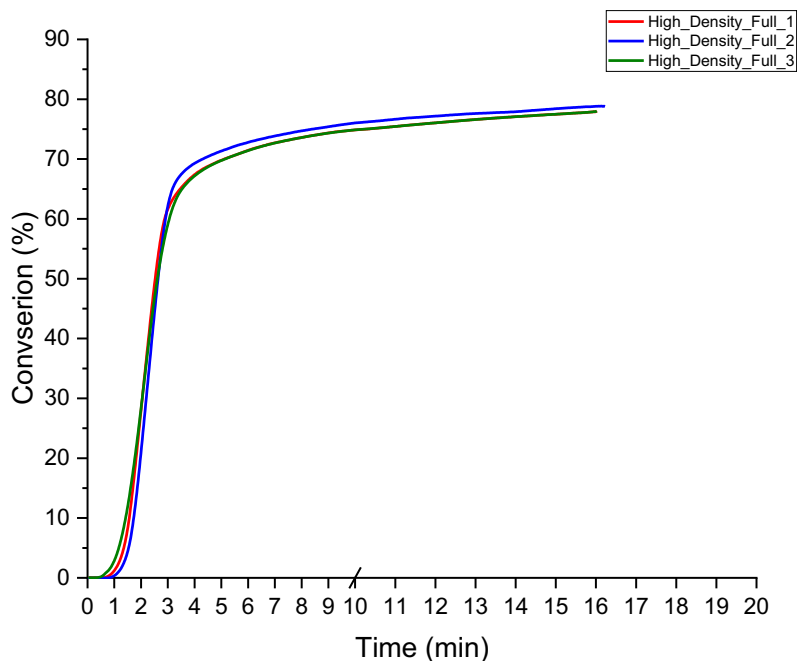


Figure S4.23. Polymerization profiles of DCPI in HiCxLR under full cure regimes. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [BPO] = 46.2 μmol/g of resin.

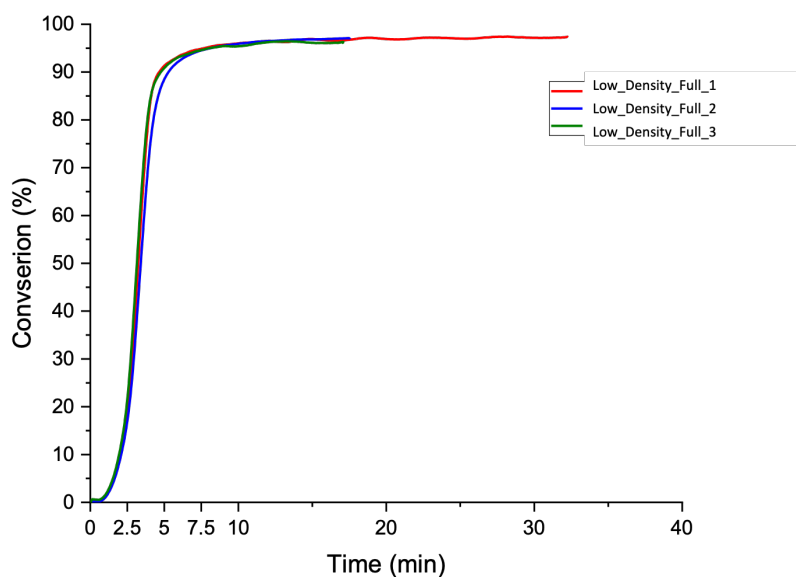


Figure S4.24. Photopolymerization profile of LoCxLR under full irradiation condition. LoCxLR is composed of 50wt% TEGDMA, 10wt% MBL, and 40 wt% BMA. The experimental conditions include 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [BPO] = 46.2 μmol or 1.12 wt%/g of resin.

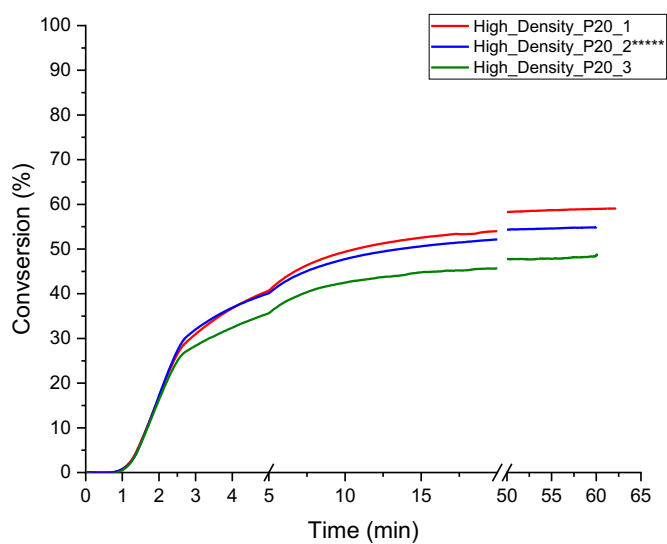


Figure S4.25. Polymerization profiles of DCPI with low concentration of BPO under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [BPO] = 46.2 μmol/g of resin in HiCxLR with a TEGDMA/MBL (9:1 mass fraction) composition.

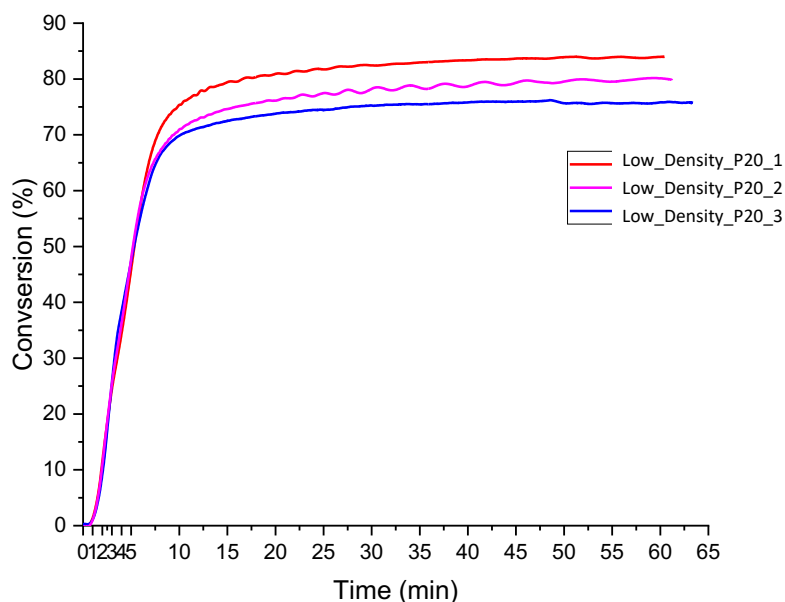


Figure S4.26. Polymerization profiles of DCPI in LoCxLR under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 30 mW/cm² 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and [BPO] = 46.2 μmol/g of resin.

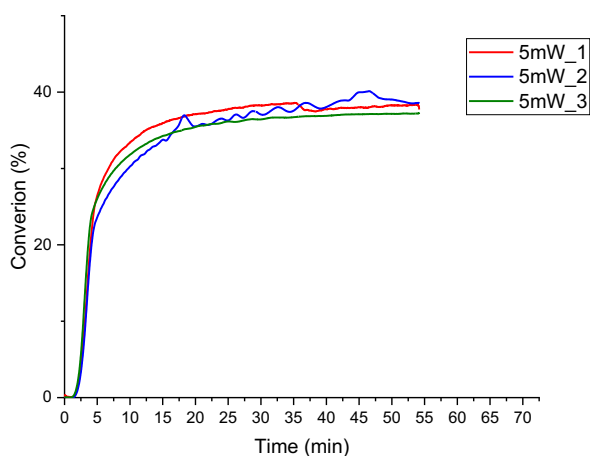


Figure S4.27. Polymerization profiles of DCPI with 5 mW/cm² under 20% partial cure regimes.

The conditions of these polymerizations included illumination with a 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and 6BPO = [BPO] = 46.2 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

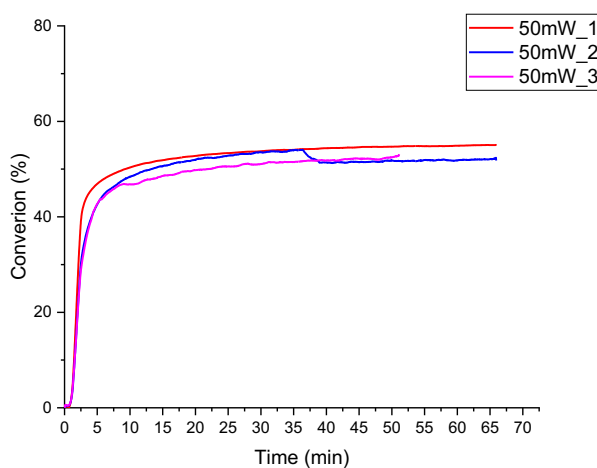


Figure S4.28. Polymerization profiles of DCPI with 50 mW/cm² under 20% partial cure regimes. The conditions of these polymerizations included illumination with a 365 nm LED with [BP-DMPT/BPh₄] = 7.7 μmol/g of resin and 6BPO = [BPO] = 46.2 μmol/g of resin in HiC_xLR with a TEGDMA/MBL (9:1 mass fraction) composition.

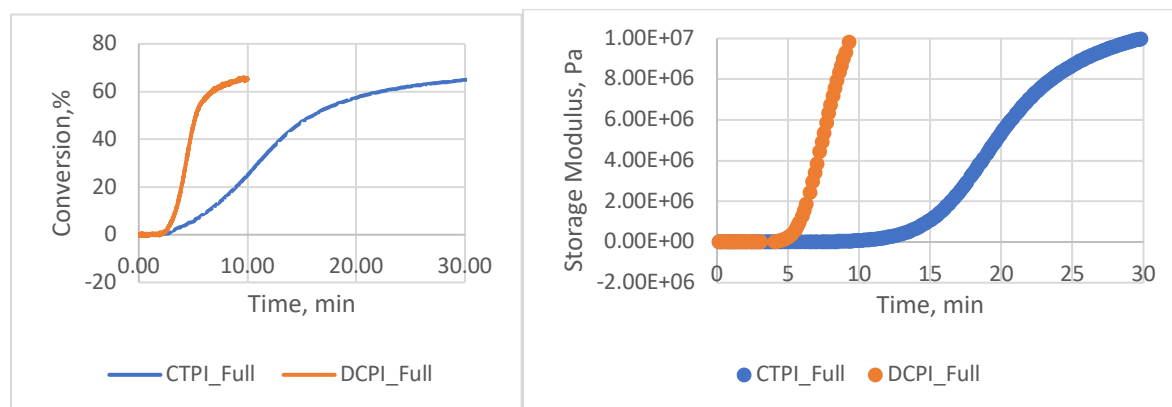


Figure S4.29. Polymerization profile and corresponding storage modulus development of CTPI and DCPI under full cure protocol, using a photo-rheometer coupled with FT-IR. Despite different photopolymerization rates, CTPI and DCPI reached similar storage modulus at vitrification, as expected. The experimental conditions include a 365 nm-filtered Hg arc lamp with $[BP\text{-}DMPT/BPh_4] = 7.7 \mu\text{mol/g}$ and $[BPO] = 23.1 \mu\text{mol/g}$ of HiCxLR resin at ambient temperature. The rotational rheometer was used with 0.5% strain and 1 Hz oscillation frequency while intensities of 4.4 mW/cm^2 was used.

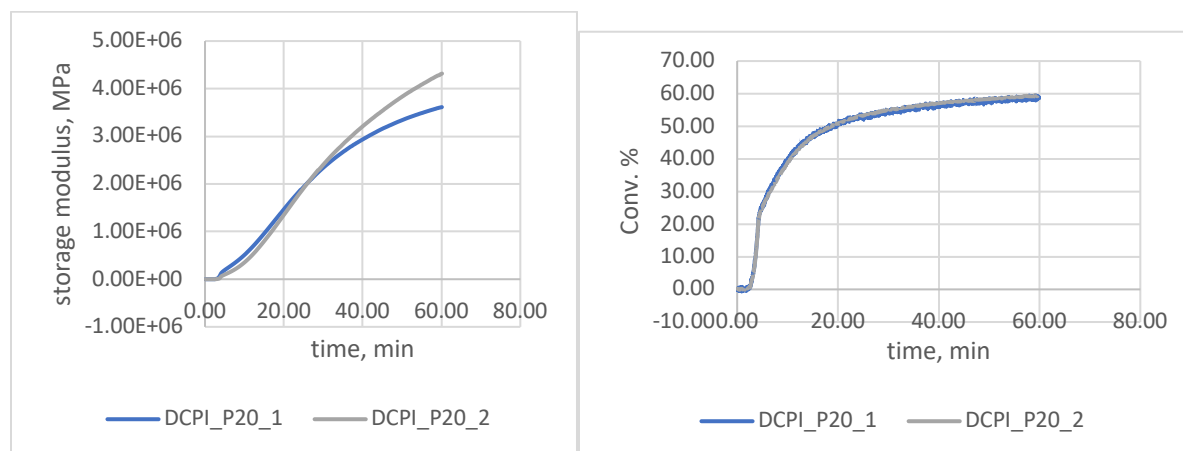


Figure S4.30. Polymerization profile and corresponding storage modulus development of DCPI under 20% partial cure protocol, using a photo-rheometer coupled with FT-IR. The experimental conditions include a 365 nm-filtered Hg arc lamp with $[\text{BP-DMPT/BPh}_4] = 7.7 \mu\text{mol/g}$ and $[\text{BPO}] = 23.1 \mu\text{mol/g}$ of HiC_xLR resin at ambient temperature. The rotational rheometer was used with 0.5% strain and 1 Hz oscillation frequency while intensities of 4.4 mW/cm^2 was used.

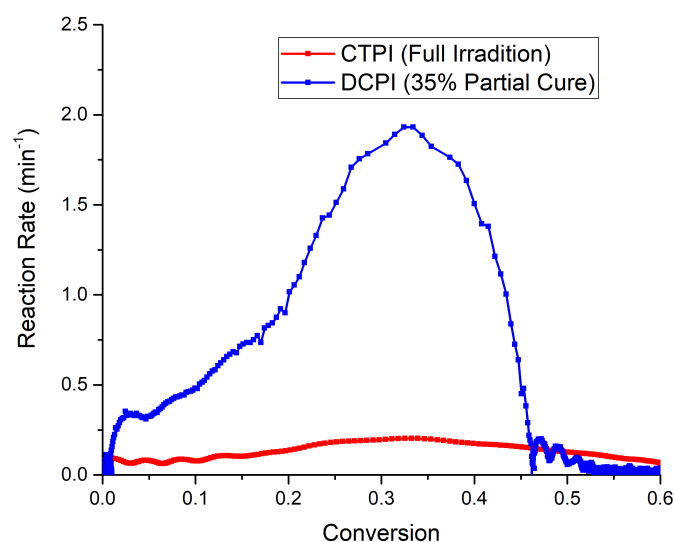


Figure S4.31. Polymerization rate changes with respect to conversion in experiments for Figure 9.B. Initially, a higher photopolymerization rate of DCPI results in higher stress, relative to that of CTPI. However, at ~45% conversion, CTPI has a higher photopolymerization than a dark-curing rate of DCPI. As a result, CTPI's stress surpasses DCPI's.

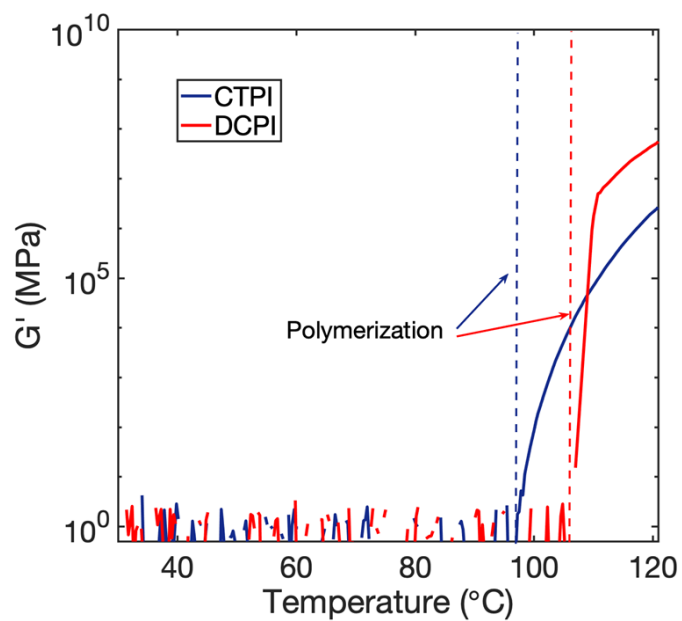


Figure S4.32. Thermal response of CTPI and DCPI resins measured by rheometer. Both resins started to polymerize around 100 °C.

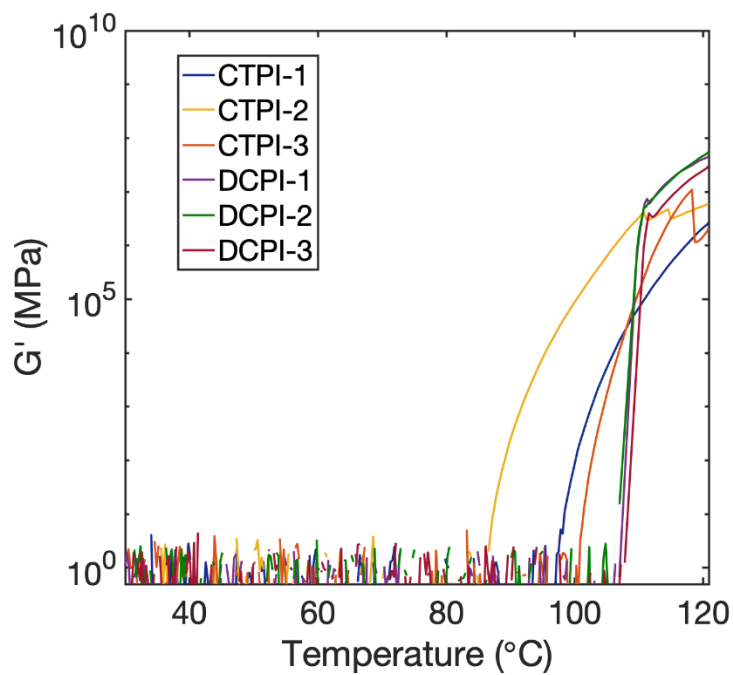


Figure S4.33. Thermal response of CTPI and DCPI resins measured by rheometer. Both resins started to polymerize at approximately 100 °C.

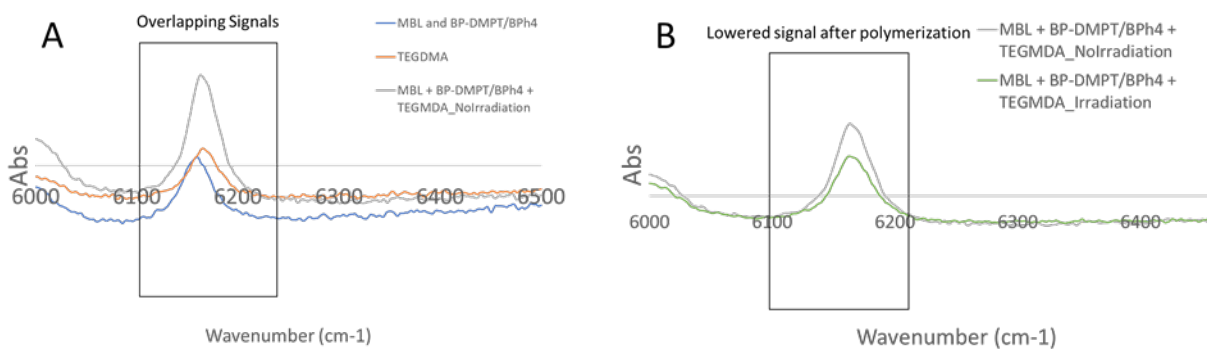


Figure S4.34. **A.** IR spectra of MBL and TEGDMA. **B.** lowered IR signal after polymerization.

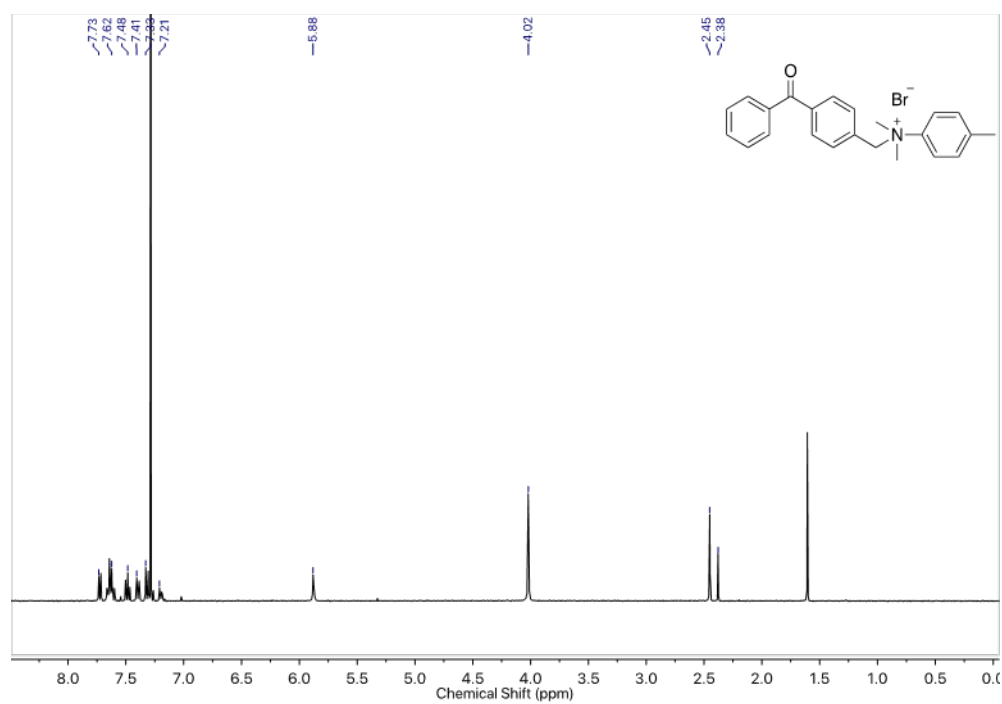


Figure S4.35. ^1H -NMR of BP-DMPT/Br

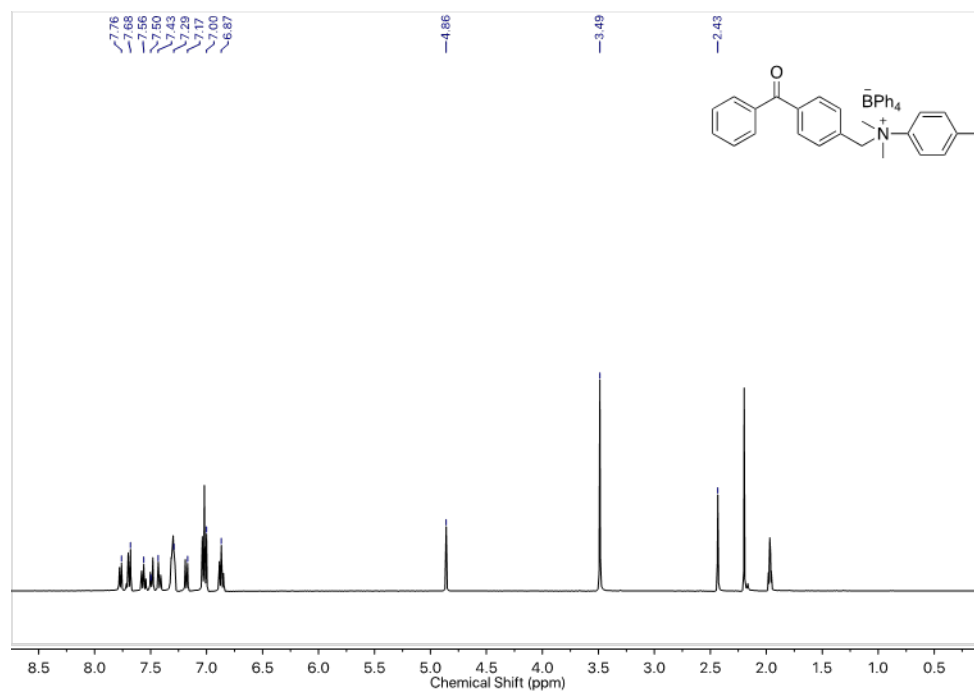


Figure S4.36. ¹H-NMR of BP-DMPT/BPh₄

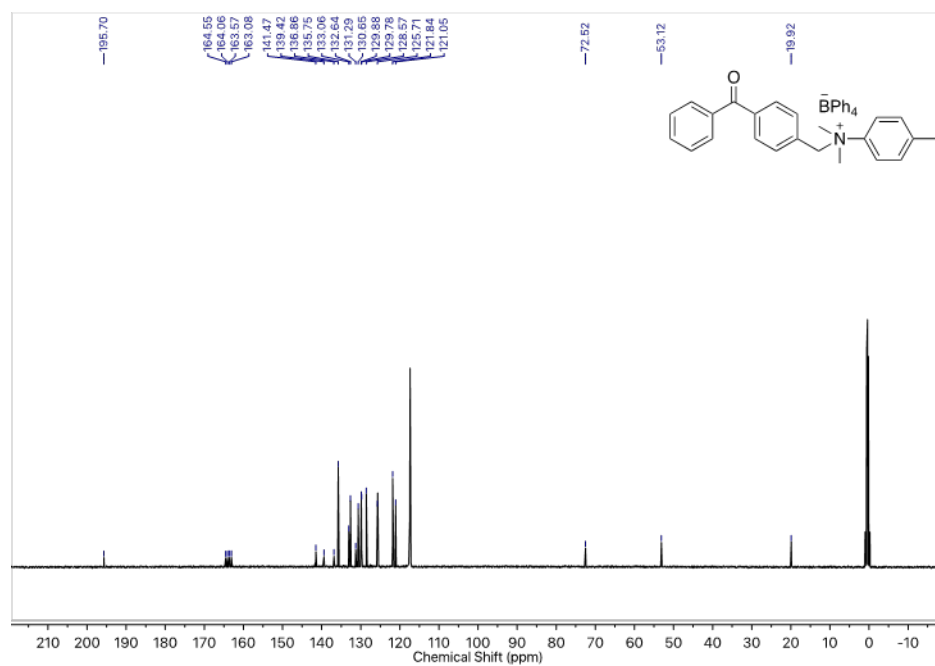


Figure S4.37. ¹³C-NMR of BP-DMPT/BPh₄

Chapter 5: Visible-light photoinitiation of (meth)acrylate polymerization with autonomous post-conversion

The work described in this chapter is adapted from a manuscript in preparation: Kangmin Kim, Jasmine Sinha, Jeffrey W. Stansbury, Charles B. Musgrave.

5.1 Abstract

Radical photopolymerization (RPP) ceases its conversion almost immediately following discontinuation of irradiation because of rapid termination of reactive radicals, which restricts the wider use of RPP in applications that involve light attenuation or irregular surfaces. Based on our recent report of a radical dark-curing photoinitiator (DCPI) that continues polymerization beyond the cessation of irradiation by enabling latent redox initiation with photo-released amine, we developed a new DCPI that extended its absorption into the visible range. Our design process involved a series of computational investigations of candidate molecules, including a systematic study of substituents and their position-dependent effects on absorption characteristics, electronic transitions, and the photochemical mechanism and its associated energetics. Our quantum chemical computations identified the target compound 5,7-dimethoxy-6-bromo-3-arylcoumarine-DMPT/BPh₄ and predict that it facilitates the dark-curing mechanism by concurrent photo-radical-generation and photo-induced release of an efficient redox reductant under visible irradiation. This reductant-tethered chromophore was then synthesized and optically examined with UV-Vis spectroscopy that revealed its strong visible light absorption with molar absorptivity of 5710 M⁻¹ cm⁻¹ at 405 nm and 50 M⁻¹ cm⁻¹ at 455 nm. We then demonstrated extensive dark-curing (>35% additional conversion over 25 min) following activation by brief irradiation with a 455 nm LED when irradiation was ceased at 20% conversion. In comparison, when irradiation was shuttered at that same point for the control formulation, its conversion immediately plateaued at 20%. We determined a remarkable initiator efficiency of 2.82 that results from the additional redox-generated radicals with a 77% photo-reductant-generation quantum yield. The superior photo- and dark-curing efficiency of this new visible DCPI will open new application opportunities in radical photopolymerization, especially those involving resins that are light attenuating or that possess irregular-surfaces.

5.2 Introduction

Photopolymerization (PP) is one of the most environmentally friendly methods to produce materials due to its ambient temperature processing, absence of volatile organic compounds, reduced energy consumption, and increased productivity with a well-controlled onset and rate of polymerization dependent on the light source and photocuring conditions.¹⁶⁶ This has driven the development of a photopolymer market currently estimated to be \$4.8 billion and projected to grow at a rate of 9.4% through 2025 to \$8.3 billion.⁵ The most commonly used PP is radical-based (>90% of all PP), which uniquely exhibits nearly immediate termination of polymerization upon discontinuation of irradiation due to highly reactive radical intermediates leading to efficient bi-radical termination. Such termination behavior increases the likelihood of producing highly heterogeneous or under-cured regions, even with careful tailoring of the photopolymerization process to its specific application. Therefore, solving this issue will broaden PP for a multitude of polymeric materials applications that involve dimensionally thick (> 100 μm) or otherwise light-attenuating systems, including highly filled and pigmented materials, or curved- and irregular-surface coatings.^{10,11}

In response to such limitations, we recently reported radical-mediated photopolymerization that exhibits extensive post-polymerization after cessation of irradiation.¹⁶⁷ This demonstration was enabled by an innovative design of a dark-curing photoinitiator (DCPI) that incorporated photo-reductant-generation concurrent with a direct photo-radical-generation process during irradiation. Radicals resultant of photolysis initiated photopolymerization in a similar manner to conventional photoinitiator while the same photolysis led to photo-released amines that function as reductants in reactions with formulated peroxide oxidant.¹⁶⁷ Such a redox reaction leads to initiating radicals via the mechanism of amine-peroxide redox reaction, which effectively extends polymerization beyond the temporal termination of irradiation.^{130,167} The demonstrations of this DCPI include quadrupling of the conversion initially achieved by irradiation, where the resin was photopolymerized to 20% conversion and dark-polymerized to 80% conversion. Also, the mechanical properties of dark-cured polymer, including its storage modulus and shrinkage stress, were equal to or exceeded those of the continuously photo-cured polymer.

This prior DCPI with a benzophenone chromophore (BP-DMPT/BPh₄) absorbs up to 390 nm and hence is activated only by UV that has a few disadvantages in comparison to visible-light activation. In particular, shorter-wavelength UV photons undergo drastic intensity attenuation through the depth of the material or media, which are detrimental to many industrial and

biomedical applications that involve thick, pigmented, or filled resins. Although our UV-based DCPI can chemically mitigate such depth-of-curing issues by raising the conversion at the deepest depth reached by photons, greater light attenuation of UV physically limits the curing depth in comparison to longer wavelength visible light. Additionally, highly energetic UV photons present significant occupational safety and health issues (particularly to vision) as well the higher cost of UV LEDs.⁷ With the potential of dark-curing photoinitiators being particularly suitable for the difficult-to-cure resins, an analogous photoinitiating system with visible light activation will be exceptionally useful in enabling or improving existing and future high-value photopolymerization applications. Additionally, such visible-light DCPI may allow autonomous annealing in photo-activated 3D printing, as the dark-curing mechanism can continue curing of 3D printed structures under ambient conditions without additional light or heat input. Most 3D printed parts require time-consuming and costly post-processing of “green parts”, such as by thermal or light annealing, as these green parts are only cured to a gel that holds its shape but not sufficiently to ultimately possess viable mechanical properties. Therefore, the development of visible-light activated DCPI will enable many applications of light-attenuated resins with greater productivity, safety, and energy efficiency.

Herein, we report the first demonstration of visible-light activation of solvent-free radical dark-curing that does not rely on a reaction exotherm nor photo-induced thermal assistance. The design of this new visible-light absorbing DCPI was enabled by an extensive computational quantum chemical study to target the desired compound before synthesis. We chose 3-aroylcoumarin as the chromophore scaffold to create candidate DCPIs because of its potential to accommodate synthetic diversity and the dark-curing mechanism and thus conducted a systematic study of its substituted derivatives where we computationally examined its absorption characteristics. We identified 5,7-dimethoxy-6-bromo-3-aroylcoumarin as a target compound and conducted a mechanistic study of this chromophore to confirm that its energetics allow concurrent photo-reductant- and -radical-generation as a visible light DCPI. Following synthesis, this new dark curing photoinitiator was demonstrated to be activated by 365, 405 and 455 nm LEDs, absorbing up to 470 nm, which resulted in rapid photocuring during irradiation and substantial dark-curing following irradiation when the initiator package includes a peroxide oxidant to enable redox radical production pathways. The new development we report herein presents a valuable

tool for polymer scientists to use visible light to synthesize industrial and biomedical materials that commonly involve light attenuating resins or resins with irregular-surfaces.

5.3 Results and Discussion

5.3.1 Dark curing mechanism

This study aims to enable visible light absorption that facilitates the reaction cascade shown in **Figure 5.1**. Aryl groups allow tuning of absorption characteristics while methylene ammonium groups release an amine upon photoexcitation. The borate salt is involved in both photo-radical- and -reductant-generation. The photo-released amine reacts with formulated peroxide to produce latent radicals after irradiation is ceased. My previous UV-absorbing DCPI is based on a benzophenone chromophore and undergoes a complex mechanism composed of 3 homolysis, 3 electron transfer (2 outer-sphere and 1 inner-sphere), and 1 proton transfer reactions, whereby direct photolysis and latent redox reaction produce initiating radicals over two time-scales (**Figure 5.1**).¹⁶⁷ I will exploit our understanding of the DCPI mechanism to enable an analogous set of reactions with a new DCPI that is efficiently activated by visible light. The dark curing mechanism begins with photoexcitation from irradiation, as do all photoinitiators. After photoexcitation, the chromophore, which is covalently bound to a photo-releasable amine, accepts an electron from tetraphenyl borate (BPh_4) anion (ET_1). The resultant oxidized borate radical homolyzes into triphenyl borane and a phenyl radical that efficiently initiates monomers (HM_1), while the reduced chromophore-ammonium radical undergoes homolysis on its own into chromophore anion and amine radical cation (HM_2). The chromophore anion donates an electron back to the amine radical cation (ET_2), producing chromophore radical and amine with the restored lone pair. The chromophore radical adds to a monomer with efficiency similar to a styrenic radical. Such dissociative electron transfers to generate initiating radicals are an effective strategy here¹⁶⁸ because visible light photons typically are not sufficiently energetic to directly cleave C-C bonds to create carbon-centered radicals.¹⁶⁹

The dark-curing mechanism proceeds with the photo-released amine then attacking formulated benzoyl peroxide (BPO). It should be noted that the photo-protected amine species in the form of chromophore-ammonium cation does not contain any reactive lone pair, which consequently prevents ground state interactions with BPO, resulting in a relatively stable one-component formulation until the thermal degradation of BPO exceeds the capacity of the inhibitors included in the formulation.¹⁶⁷ Attack of BPO by amine results in ammonium species and benzoate anion, where the amine is singly oxidized and the benzoate anion is singly reduced via inner-sphere electron transfer (ET₃).¹³⁰ The ammonium species homolyzes into another amine radical cation and benzoyloxy initiating radical (HM₃). When the benzoate anion abstracts a proton from the amine radical cation, an initiating aminoalkyl radical is generated along with benzoic acid. Essentially, a single photon can generate two radicals via photolysis during irradiation and two more radicals via redox reaction, which occurs either during irradiation or post-irradiation. Therefore, a design of a new DCPI that enables this complex dark-curing mechanism and absorbs visible-light (>400 nm) involves the development of visible-light-absorbing photo-base-generator that can release a tertiary aromatic amine that is a weak base but an effective reductant and initiating radicals by photoexcitation. In this approach, prior to irradiation there is no potential of reactions with any component of the formulation including peroxide. I designed such a photoinitiator that fulfills all the requirements by conducting an extensive quantum chemical study prior to undertaking the initiator synthesis.

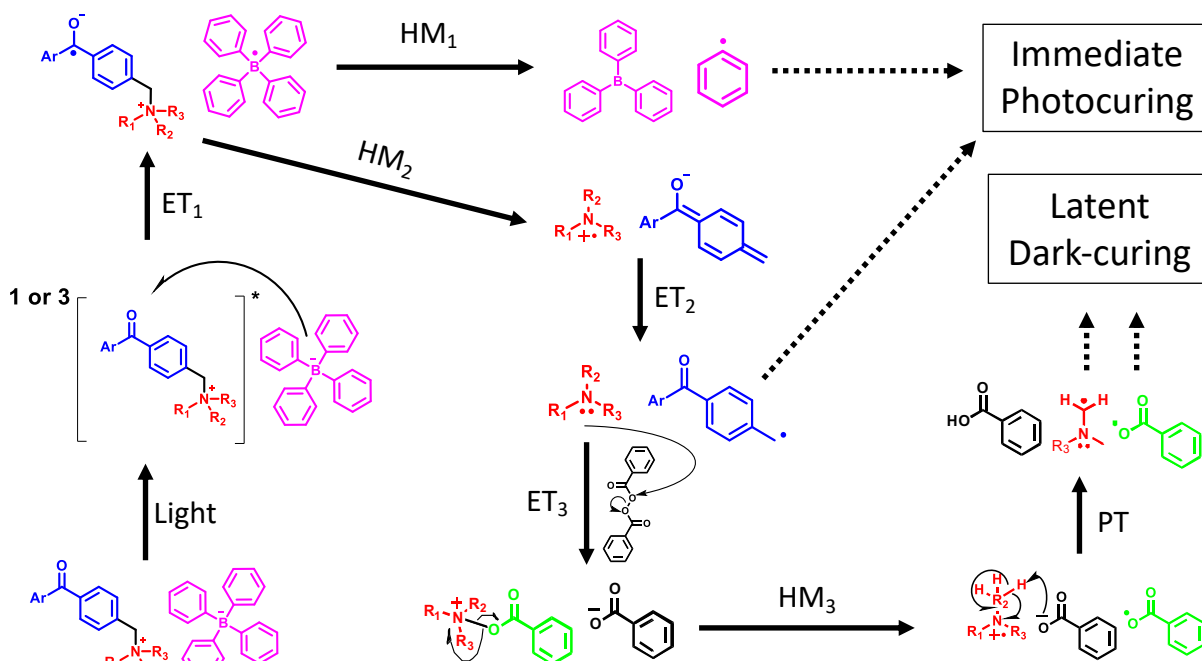


Figure 5.1. light- and dark-curing mechanism. The proposed DCPI undergoes a complex mechanism composed of 3 homolysis (HM), 3 electron transfer (ET), and 1 proton transfer (PT) reactions, whereby direct photolysis and latent redox reaction produce initiating radicals over two time-scales.

5.3.2 Chromophore Scaffold

I first considered various aryl ketone chromophores to enable an analogous photo-base/radical-generation, as the notable feature of benzophenone-based DCPI is diaryl ketone. None of these molecules have their maximum absorption (λ_{max}) in the visible light range. For example, the λ_{max} of benzophenone (BP), xanthone, thioxanthone, and anthraquinone occur at 335, 340, 360, and 326 nm, respectively. Furthermore, modification with various functional groups does not red-shift λ_{max} . BP derivatives with several functional groups, including dianhydride, biphenyl, dihydroxy, and (di)alkyl essentially exhibit a similar λ_{max} (~335 nm), although such

functionalization is often accompanied by higher molar absorptivity (ϵ) relative to the unfunctionalized BP. On the other hand, some functionalization was shown to achieve an ~ 30 nm of red-shift ($\lambda_{\text{max}} = \sim 370$ nm) as in Michler's ketone that is a BP derivative with para-bis-dimethyl-amino functionality. Lastly, a few of these chromophores with λ_{max} located in the UV range are currently used in industry as a visible photoinitiators (e.g. thioxanthenes) due to their low but extended absorption in the visible range. As such, our targeted chromophore needn't have λ_{max} in the visible range to act as a visible photoinitiator and judicious selection of functional groups could lead to desirable absorption characteristics (vide infra). Besides, the photo-base-generation mechanism requires that the desired chromophore contain a para-tolyl group to furnish a tertiary amine via benzylic bromination. Based on such restrictions, I decided to pursue 3-aryl coumarins (ARC) as our chromophore scaffold among many aryl ketone chromophores due to the synthetic accessibility of the coumarin moiety for tuning absorption characteristics and of the tolyl group for accommodating a tertiary amine (**Figure 5.2**).¹⁷⁰

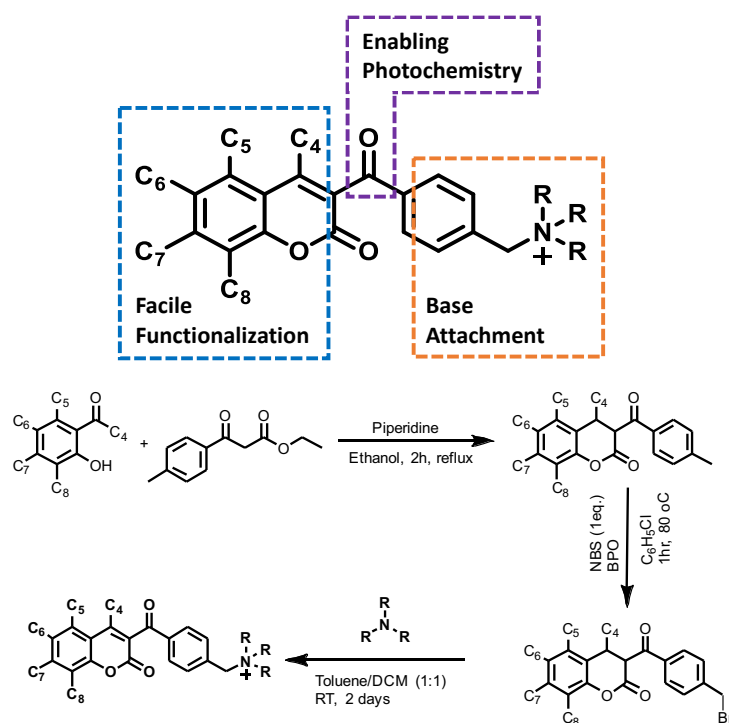


Figure 5.2. 3-Aroylcoumarin structural moiety and its potential synthetic route that facilitates facile functionalization to tune absorption. The design components of visible light-absorbing dark curing photoinitiators include diaryl ketone that mediates photochemistry, coumarin moiety with functionalization opportunities that modify light-absorption characteristics and the methylene phenyl group that attaches to a tertiary amine as ammonium.

5.3.3 Benzophenone vs 3-aroylcoumarin

I then computationally examined the photo-absorption of 3-aroylcoumarin and its derivatives to aid the discovery process for new visible-light absorbing chromophores. Primarily, time-dependent density functional theory (TD-DFT) was used at the level of M06-2X/6-311++g(d,p)/SMD-acetonitrile with geometries optimized with DFT at the level of M06-2X/6-31+g(d,p)/SMD-acetonitrile. TD-DFT provided photophysical properties of λ_{max} , its corresponding molar absorptivity (ϵ_{max}), and changes in the electron occupation of active orbitals upon photoexcitation of each new chromophore structure. In this examination to understand how ARC functionalization affects these photophysical properties and to narrow the set of potential target compounds, I truncated the size of the studied molecules to only the para-tolyl-functionalization, excluding ammonium functional groups to reap the reduction in computational cost.

In addition to the absorption of visible light (≥ 400 nm), we sought ideal molar absorptivity of the potential visible DCPI to be $1000 \text{ M}^{-1} \text{ cm}^{-1}$ or higher at 405 nm for a balance of mild coloration and fast reaction for implementation in thin-film applications such as coatings, inks, adhesives, and photolithography,¹⁷¹ as well as $\sim 100 \text{ M}^{-1} \text{ cm}^{-1}$ or lower at 450 nm to reduce optical

density and increase light transmission for increased depth of cure for thick film and bulk applications.¹⁷² For instance, in the case of dental composite applications, $\sim 50 \text{ M}^{-1} \text{ cm}^{-1}$ at 470 nm would be highly desirable to replace camphorquinone/amine system that remains the state-of-the-art for commercial dental resin composite applications due to an appropriate molar absorptivity level for deep curing.^{173,174} The difference in the criteria of desirable molar absorptivity for the given application is due to the intrinsic competitive effects where higher ϵ provides an increased rate of initiation and faster rates of polymerization, yet low ϵ may result in higher light transmission through the material because photon absorption is decreased, which reduces filtering of the active wavelengths.¹⁷² Lastly, rapid photo-bleaching is also desired in order to further facilitate increased depth of cure.¹⁷²

The benzophenone chromophore utilized for our UV-activated DCPI is computed to have λ_{max} at 329 and 250 nm, which closely agree with the observed values of 335 and 248 nm (**Table 5.1**).^{175,176} Additionally, ϵ_{max} derived from our quantum calculations are $19029 \text{ M}^{-1} \text{ cm}^{-1}$ for 250 nm absorption and $69 \text{ M}^{-1} \text{ cm}^{-1}$ for 329 nm absorption, also in close agreement with the experimentally observed values of 19400 and $121 \text{ M}^{-1} \text{ cm}^{-1}$, respectively (**Figure S5.1**).¹⁷⁵ The close agreement validates our computational method for reliably computing absorption characteristics of various chromophores in search of a chromophore that enables a visible DCPI. The unfunctionalized 3-aryl coumarin (ARC) possesses a computed $\lambda_{\text{max},1}$ at 331 nm with $\epsilon_{\text{max},1}$ of $733 \text{ M}^{-1} \text{ cm}^{-1}$ and $\lambda_{\text{max},2}$ at 295 nm with $\epsilon_{\text{max},2}$ of $13361 \text{ M}^{-1} \text{ cm}^{-1}$ (**Table 5.1**). The $\epsilon_{\text{max},1}$ of ARC was greater by a factor of ~ 10 with a similar $\lambda_{\text{max},1}$ to BP while the $\lambda_{\text{max},2}$ of ARC was red shifted to near 300 nm whereas $\lambda_{\text{max},2}$ of BP lies at 250 nm, indicating that 3-aryl coumarin is a more strongly absorbing chromophore scaffold than benzophenone. In addition to λ_{max} and its associated ϵ_{max} , UV-Vis spectra were simulated using gaussian profiles that take collision and proximity

broadening into account.^{177,178} Thanks to a relatively high $\epsilon_{\max,1}$ of $733 \text{ M}^{-1} \text{ cm}^{-1}$ at 331 nm, unfunctionalized ARC had some visible range absorption with an $\epsilon_{400\text{nm}}$ of $47 \text{ M}^{-1} \text{ cm}^{-1}$ (**Figure 5.3a**). On the other hand, the simulated absorption spectrum of benzophenone is such that the absorptivity of $47 \text{ M}^{-1} \text{ cm}^{-1}$ is found only at 350 nm while its $\epsilon_{400\text{nm}}$ is barely $3 \text{ M}^{-1} \text{ cm}^{-1}$. Although BP and ARC have a similar $\lambda_{\max,1}$, a significant difference in $\epsilon_{\max,1}$ makes ARC a more suitable scaffold for a visible DCPI ($733 \text{ vs. } 69 \text{ M}^{-1} \text{ cm}^{-1}$). Ultimately, unfunctionalized 3-aryl coumarin does not fulfill the photophysical property requirements with $\lambda_{\max,1}$ of $\sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$ or higher at 405 nm, and thus is predicted to not be a high-performing visible light chromophore for our purposes. Therefore, we proceeded by instead investigating the absorption of various substituted ARCs.

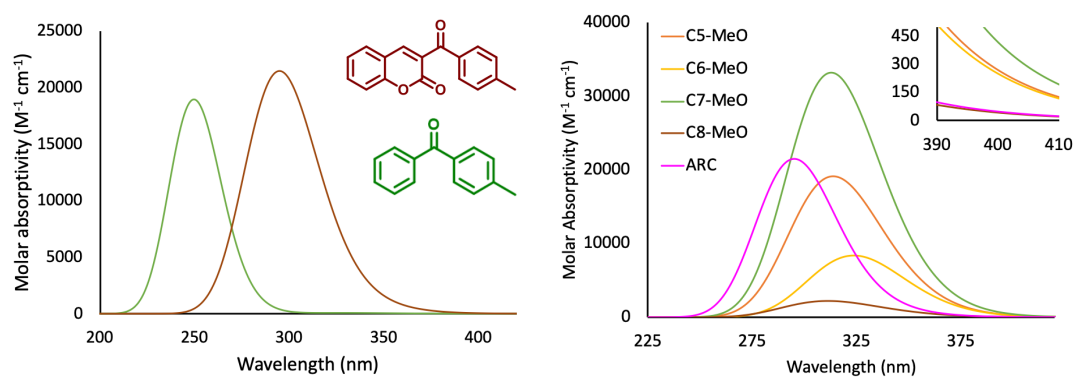


Figure 5.3. (a) Simulated UV-Vis spectra of benzophenone (BP) and 3-aryl coumarin (ARC). Despite their $\lambda_{\max,1}$ being similar at $\sim 330 \text{ nm}$, the $\epsilon_{\max,1}$ of ARC is much greater than that of BP ($733 \text{ vs. } 69 \text{ M}^{-1} \text{ cm}^{-1}$), making ARC a superior scaffold for visible light absorption. (b) Simulated UV-Vis spectra of ARC and its methoxy-substituted derivatives. Methoxy substitutions at the C₅ and C₇ positions increased molar absorptivity more efficiently than those at the C₆ and C₈ positions. The substitution positions are described in **Figure 5.2**. Relevant photophysical constants were computed from TD-DFT.

5.3.4. Functionalization of 3-aryl coumarin

With the predicted weak absorption in the visible range for unfunctionalized ARC, I computationally screened various functional groups to enhance visible light absorption. Synthetic access of functionalization at the C₅, C₆, C₇, and C₈ positions of 3-aryl coumarin is easily achieved with many commercially available salicylaldehyde precursors (**Figure 5.2**). I first examined how the nature of functionalization and the location of such functionalization affected the absorption characteristics. ARC was subjected to single substitution with methoxy and chlorine groups that respectively represent an electron-donating and an electron-withdrawing group (EDG and EWG), which were chosen based on the commercially available salicylic aldehydes. It should be noted that amino-functional groups as an EDG was excluded due to its potential ground-state interactions with benzoyl peroxide in the absence of light via a spontaneous amine-peroxide redox mechanism while the nitro group as an EWG was also excluded because of its potential to act as a radical polymerization inhibitor.^{179,180}

My select EDG and EWG single substitution at all positions retain the same $\lambda_{\max,1}$ at 331 nm as the unsubstituted ARC. However, other absorption characteristics such as $\epsilon_{\max,1}$, $\lambda_{\max,2}$, and $\epsilon_{\max,2}$ all improved to cause further red-shifting (**Table 5.1**). Compared to the $\epsilon_{\max,1}$ of 733 M⁻¹ cm⁻¹ of ARC, functionalization at the C₅ position with an electron-donating methoxy group increased $\epsilon_{\max,1}$ to 2729 M⁻¹ cm⁻¹, to 2020 for functionalization at the C₆ position, and 4741 at the C₇ position. In contrast, methoxy group substitution at the C₈ position decreased $\epsilon_{\max,1}$ to 632 M⁻¹ cm⁻¹. Furthermore, these substitutions resulted in significant changes of $\lambda_{\max,2}$ and $\epsilon_{\max,2}$. While the unfunctionalized ARC has $\lambda_{\max,2}$ of 295 nm with $\epsilon_{\max,2}$ of 21362 M⁻¹ cm⁻¹, methoxy substitution at the C₅ and C₇ positions both increased $\lambda_{\max,2}$ to 311 nm with $\epsilon_{\max,2}$ of 17289 and 30002 M⁻¹ cm⁻¹,

respectively. Although $\lambda_{\text{max},2}$ is still 20 nm shorter than $\lambda_{\text{max},1}$, such second absorptions with very large molar absorptivities may contribute to visible light absorption. The methoxy substitution at the C₆ position increased $\lambda_{\text{max},2}$ to an even longer wavelength of 321 nm, but with a greatly reduced absorptivity of 6482 M⁻¹ cm⁻¹. On the other hand, the methoxy substitution at the C₈ position performed poorly with $\lambda_{\text{max},2}$ of 307 nm with $\epsilon_{\text{max},2}$ of a mere 1777 M⁻¹ cm⁻¹.

The methoxy substituents are predicted to affect the light-absorbing characteristics through the change in orbital energies and dipole strengths. The $\lambda_{\text{max},1}$ remained unchanged because the corresponding electronic transition is mostly $n \rightarrow \pi^*$ in character, where both the n and π^* orbitals are not significantly affected by the methoxy substitution. The unsubstituted ARC possesses n and π^* orbitals at -9.36 eV and -1.59 eV, respectively. The resultant energy changes in these orbitals from methoxy substitution are less than 0.1 eV for all positions, and most are < 0.05 eV (~1 kcal/mol) due to the orthogonally oriented n orbital that prevents overlap with the lone pairs of the methoxy groups (**Figure 5.4**). In contrast, $\lambda_{\text{max},2}$ was bathochromically shifted from 295 nm to ~310 nm, where the corresponding electronic excitation is a $\pi \rightarrow \pi^*$ transition. Unlike the unaffected n and π^* orbitals, the energy of the π orbital increased by 0.28 to 0.50 eV (6.5 – 11.5 kcal/mol). This is because electron donation increases electron density in the coumarin moiety and raise its π orbital energy. The three relevant orbitals of chromophores that result from chlorine substitutions are less affected than those from the methoxy substitutions. The energetic change in the n orbitals are less than 0.1 eV, similar to the methoxy substitutions, while energies of the π and π^* orbitals decreased slightly and to a comparable degree so that its calculated effect on $\lambda_{\text{max},2}$ is

marginal.

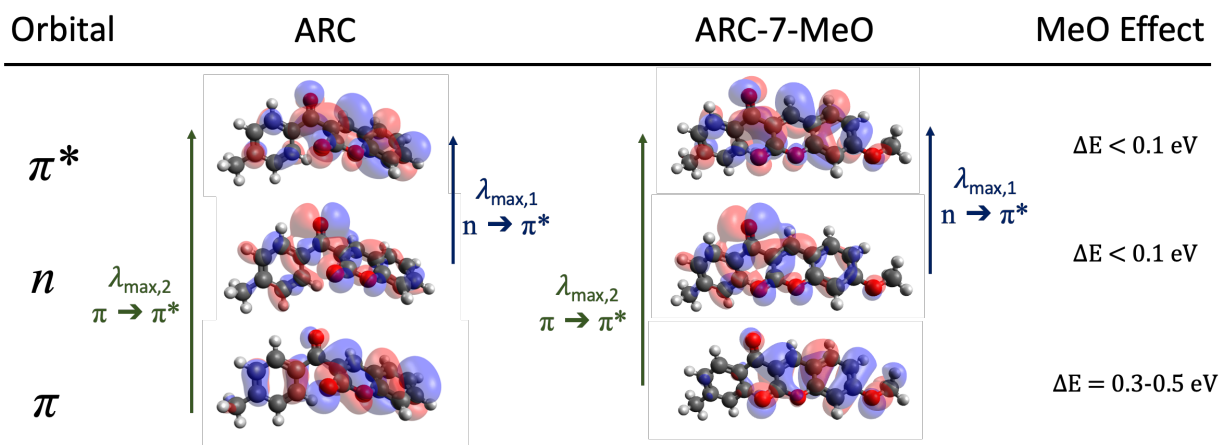


Figure 5.4. Molecular orbitals of 3-aryl coumarin (ARC) and 7-methoxy-3-aryl coumarin (ARC-7-MeO). $\lambda_{\max,1}$ remained unchanged because the participating orbitals (n and π^*) are only marginally affected by the methoxy substituent while $\lambda_{\max,2}$ was bathochromically shifted from 295 nm to ~310 nm due to the higher energy of the π orbital caused by the methoxy substituents

I attribute the change of molar absorptivity predicted by my study to the push-pull effect that mediates intramolecular charge transfer. Absorption of electromagnetic (EM) radiation by organic molecules occurs along particular directions within the molecular framework, where each electronic transition process corresponds to oscillation of an electric dipole. Increases in the dipole strength by a substituent indicates that the electric field of the photon interacts more strongly with the electron cloud of the molecule. Therefore, a molecule with a higher polarizability possesses a higher molar absorptivity.^{181–184} Based on literature reports on coumarin as a chromophore for dye-based solar cell applications,^{185–188} we expected that 3-aryl coumarin also absorbs EM by polarization along the long molecular axis for the $S_0 \rightarrow S_1$ transition that corresponds to both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. (**Figure 5.5**). When ARC is substituted with either an EWG or EDG, the substitution changes the dipole moment along this long axis. The methoxy EDG increases

polarizability by establishing a push-pull mechanism, as lactone and ketone moieties function as EWGs. Contrarily, the chlorine EWGs decrease polarizability in comparison to the unsubstituted ARC. To confirm this push-pull hypothesis, dipole moments were calculated for each species and show that they are correlated with higher molar absorptivities.¹⁸⁹ The highly absorbing ARC-5-OMe and ARC-7-OMe possess dipole moments of 8.40 and 8.60 D while the dipole moments of all chlorine-substituted ARCs are less than 7 D. Attaching a substituent along the same direction as the molecular axis that corresponds to the $S_0 \rightarrow S_1$ transition intensified absorptivity to a greater degree by increasing the effective absorption cross-section. This is why the methoxy substitutions at the C₅ and C₇ positions affected the absorption character most effectively. I note that the methoxy substitution at the C₆ position has a less dramatic effect due to the minor contribution of resonance interference that hinders the effective push-pull mechanism. (SI5.1. Resonance structures)

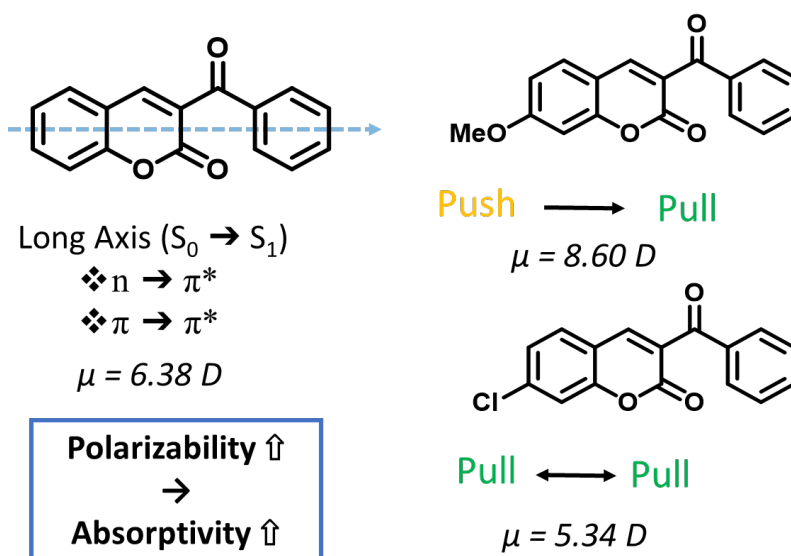


Figure 5.5. Structural depiction of 3-aryl coumarin that corresponds to the light absorption examined within this study. Polarizability along the long molecular axis is responsible for the

desired light absorption, and by increasing the push-pull character of ARC, the dipole moment and resultant polarizability increase the intensity of light absorption.

When these predictions are incorporated into UV-Vis spectra simulated with the peak broadening, ARC with methoxy substitutions at the C₅ and C₇ positions led to $\epsilon_{405\text{nm}}$ of 185 and 286 M⁻¹ cm⁻¹, as opposed to 172 for C₆, 29 M⁻¹ cm⁻¹ for C₈, and 33 M⁻¹ cm⁻¹ for unsubstituted ARC (**Figure 5.3.b**). These results indicate that electron-donating groups at the C₅ and C₇ positions are suitable substitutions and we inferred that double methoxy substitution at both the C₅ and C₇ positions may generate synergistic effects of red-shifting and yield a more strongly absorbing chromophore in the visible. On the other hand, chlorine functional groups at all positions did not red-shift $\lambda_{\text{max},1}$ due to unfavorable orbital energy changes. It also did not increase the molar absorptivity as electron-withdrawing groups such as chlorine reduce the push-pull character. As a result, methoxy substituted ARC was predicted to significantly outperform chlorine-substituted ARC.

Using the insight gained from the single-substitution study, we proposed that 5,7-dimethoxy-3-arylcoumarin (ARC-5,7-2OMe) is an optimal chromophore derivative of 3-arylcoumarin to access the visible light range with appropriate absorption characteristics. ARC-5,7-2OMe is predicted to exhibit a λ_{max} at 338 nm with $\epsilon_{\text{max},1}$ of 18422 M⁻¹ cm⁻¹ and at 322 nm with $\epsilon_{\text{max},2}$ of 13361 M⁻¹ cm⁻¹ (**Table 5.1**). A combination of large $\epsilon_{\text{max},1}$ and $\epsilon_{\text{max},2}$ and red-shifting $\lambda_{\text{max},2}$ to lie near $\lambda_{\text{max},1}$ produced strong visible light absorption of 2371 M⁻¹ cm⁻¹ at 400 nm according to the simulated UV-Vis spectra (**Figure 5.6**). In particular, 5,7-dimethoxy-3-arylcoumarin was computed to respond well to the common wavelengths output by commercial LEDs,¹⁹⁰ exhibiting 1731 M⁻¹ cm⁻¹ for 405 nm, 635 M⁻¹ cm⁻¹ for 420 nm, 48 M⁻¹ cm⁻¹ for 455 nm,

and $15 \text{ M}^{-1} \text{ cm}^{-1}$ for 470 nm (**Figure 5.6**). Such photophysical properties of ARC-5,7-2OMe correspond to my desired molar absorptivity of $1000 \text{ M}^{-1} \text{ cm}^{-1}$ or higher at 405 nm and of $100 \text{ M}^{-1} \text{ cm}^{-1}$ or lower at 450 nm.

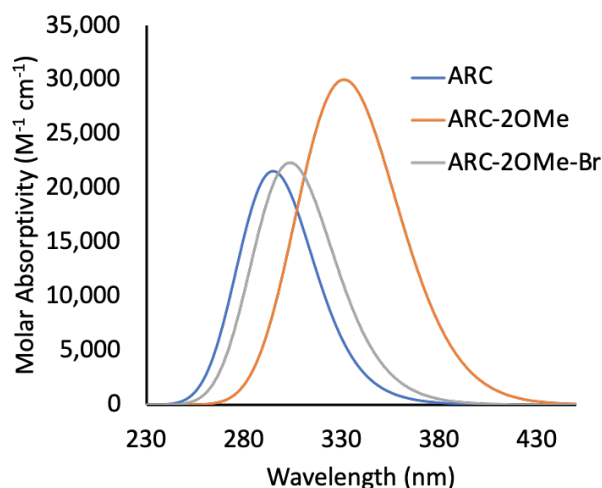


Figure 5.6. Simulated UV-Vis of ARC, ARC-2OMe, and ARC-2OMe-Br. ARC-2OMe improved visible light absorption over the unsubstituted ARC. However, due to synthetic limitations, ARC-2OMe-Br was instead targeted as a potential chromophore for visible DCPI

Table 5.1. Computed photophysical properties of benzophenone and 3-arylcoumarin derivatives including their orbital energies and dipole moments. TD-DFT calculations were conducted on truncated chromophores without ammonium groups at the M06-2X/6-311++g(d,p)/SMD-acetonitrile level of theory with geometries acquired at the M06-2X/6-31+g(d,p)/SMD-acetonitrile level of theory.

	BP	ARC	5-MeO	6-MeO	7-MeO	8-MeO	5-Cl	6-Cl	7-Cl	8-Cl	5,7-2OMe	5,7-2OMe-6-Br
$\lambda_{\max,1}$ (nm)	329	331	332	331	331	331	332	331	331	331	338	332
$\epsilon_{\max,1}$ ($M^{-1} cm^{-1}$)	69	733	2729	2020	4741	632	741	688	1008	563	18422	1506
$\lambda_{\max,2}$ (nm)	250	295	312	321	311	307	295	300	297	292	322	303
$\epsilon_{\max,2}$ ($M^{-1} cm^{-1}$)	19030	21362	17289	6482	30002	1777	21208	15677	27755	18333	13361	21718
n orbital (eV)	-9.19	-9.36	-9.33	-9.36	-9.29	-9.35	-9.42	-9.41	-9.38	-9.41	-9.18	-9.38
π orbital (eV)	-8.26	-8.07	-7.79	-7.57	-7.61	-7.76	-8.24	-8.07	-8.08	-8.23	-7.36	-7.95
π^* orbital (eV)	-1.07	-1.59	-1.59	-1.59	-1.50	-1.56	-1.77	-1.70	-1.68	-1.70	-1.43	-1.62
Dipole (D)	4.94	6.38	8.40	7.49	8.60	7.72	5.92	4.56	5.33	6.89	10.99	8.26

5.3.5 5,7-dimethoxy-6-bromo-3-arylcoumarin

A deeper analysis of the synthesis of the proposed 5,7-dimethoxy-3-arylcoumarin suggested that the dimethoxy substitutions at the C₅ and C₇ positions result in a considerable increase in the electron density at the C₆ position from -0.242 e in ARC to -0.675 in ARC-2OMe. Such density changes may lead to electrophilic aromatic bromination at the C₆ position, producing 5,7-dimethoxy-6-bromo-3-arylcoumarin when attempting to brominate the benzylic methyl group (**Figure 5.2**).¹⁹¹ My speculation was confirmed by NMR studies that we indeed synthesized the brominated chromophore 5,7-dimethoxy-6-bromo-3-arylcoumarin with a benzylic brominated site (**SI5.2. Synthetic details**). Therefore, we re-evaluated the new prospective target (5,7-dimethoxy-6-bromo-3-arylcoumarin) to confirm its potential as a visible DCPI. The presence of a bromine group affected both max absorption and its absorptivity. The bromine atom occupies considerably more space than a hydrogen atom, which led to the slight rotation of both methoxy groups. Therefore, the favorable electron donation to the pi orbital was reduced but not eliminated (**Figure S5.9**), which decreased $\lambda_{\max,2}$ from 322 nm in ARC-5,7-2OMe to 303 nm in ARC-5,7-2OMe-6-Br. Additionally, as bromine is more electronegative than hydrogen (2.8 vs. 2.1), the push-pull character slightly decreased, which led to a lower dipole moment of 10.99 vs 8.26 (**Figure S5.9**). However, we ultimately found that the computationally predicted absorption characteristics of 5,7-dimethoxy-6-bromo-3-arylcoumarin led to sufficient visible light

absorption (**Figure 5.6**) for the DCPI. Therefore, I continued the computational study to confirm that the energetics of the photochemical reaction are feasible. For the calculation of photochemistry energetics, entire chromophore-ammonium structures were simulated that include the photo-releasable amine (DMPT, dimethyl-p-toluidine) without tetraphenyl borate at the M06-2X/6-31+g(d,p)/SMD-ethyl acetate level of theory. Free energies were computed within the bulk reaction approximation used in our previous publications,^{85,98,130,167} where the contributions from the entropies of the solvent-hindered molecular motions including rotation and translation were removed to reflect the highly viscous nature of the resin phase.

Then, I examined several aspects of the photochemical mechanism of ARC-5,7-2OMe-6-Br-DMPT. First, we established that a visible light photon can promote the C-N bond scission. The C-N bond dissociation energies (BDE) of BP, ARC, ARC-5,6-2OMe, and ARC-5,6-2OMe-6-Br were nearly identical (52.4, 52.5, 53.1, and 53.2 kcal/mol, respectively). These bond dissociation energies indicate that photons with wavelengths up to ~540 nm possess sufficient energy to dissociate the C-N bond if none of it is dissipated into other modes. Given that the simulated absorption of ARC-5,7-2OMe-6-Br has a sufficient absorptivity below 500 nm, such a low bond dissociation energy allows the whole absorption spectrum of ARC-5,7-2OMe-Br to be useful. Secondly, we confirmed that an unintended electron transfer reaction between the ground state chromophore-ammonium and tetraphenyl borate does not occur. We calculated that the ground state redox potential ($S_0 E_{A/A^{\bullet-}}$) of BP-DMPT⁺, ARC-DMPT⁺, ARC-5,7-2OMe-DMPT⁺, and ARC-5,7-2OMe-6-Br-DMPT⁺ is -1.81 V, -1.39 V, -1.60 V, and -1.30 V vs SCE in ethyl acetate, while the redox potential of tetraphenylborate anion is reported to range from -0.78 to -0.98 V vs. SCE in various organic solvents.¹⁹² The more negative redox potential of the ground state photoinitiator relative to the tetraphenylborate anion indicates that without

photoexcitation of chromophores, the photo-reductant-generator is stable in the formulation, where we have previously shown that a formulation of BP-DMPT⁺/BPh₄ is stable with and without BPO.¹⁶⁷ Thirdly, the photoexcitation of the chromophore will lead to the desired reactions. Excited-state redox potentials of all four chromophores significantly increased, making them electron acceptors in ET reactions with tetraphenyl borate (**Figure 5.7**). The redox potentials of BP-DMPT⁺, ARC -DMPT⁺, ARC-5,7-2OMe -DMPT⁺, and ARC-5,7-2OMe-6-Br-DMPT⁺ singlet excited states (S_1 E_{A/A•-}) were calculated to be 1.53, 1.92, 1.66, and 1.98V vs SCE, which facilitates electron transfer (ET₁) from tetraphenyl borate with redox potentials of -0.78 to -0.98 V and instigates the resultant reaction cascade of the mechanism discussed above (**Figures 5.1** and **5.7**). If triplet excited states instead of singlet excited states mediate the electron transfer, their reduction potentials (T_1 E_{A/A•-}) are still sufficient (1.10 V for BP, 1.27 V for ARC, 0.90 V for ARC-5,7-2OMe, 1.09 V for ARC-5,7-2OMe-6-Br vs. SCE)

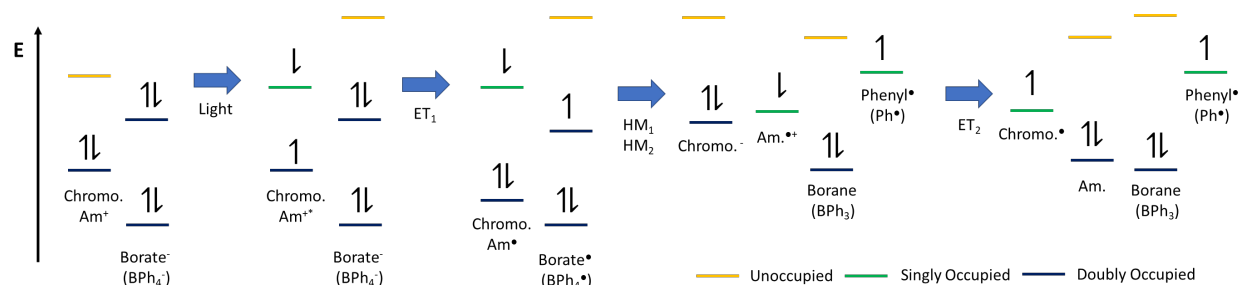


Figure 5.7. Changes in the electron configurations of chromophore-ammonium/BPh₄ leading up to the generation of two radicals and one amine. The positions of the orbitals qualitatively represent energies of the orbitals for all chromophores studied herein

After ET₁, two homolysis reactions ensue (**Figures 5.1** and **5.7**). The homolysis of tetraphenylborate (HM₁) is well known and discussed in my previous publication and many

others.^{144,145,167,193–195} On the other hand, the homolysis (HM₂) of chromophore-DMPT radical is a novel aspect of the new visible DCPI design that enables the photo-release of an amine, where homolysis (HM₂) of the zwitterionic radical leads to two molecular fragments of amine radical cation and chromophore anion that form an ionic complex (**SI5.3. Ionic complexation**). I found that the homolysis for BP-DMPT radical was exergonic with a reaction free energy of -16.8 kcal/mol while ARC-DMPT radical, ARC-5,7-2OMe-DMPT radical, and ARC-5,7-2OMe-6-Br-DMPT radical were found to be exergonic with free energy changes of -7.7, -11.5, and -6.5 kcal/mol, respectively. The exergonicity indicates that C-N homolysis reactions in these four reduced chromophores after ET₁ are spontaneous and rapid; this is supported by the observed irreversibility after reduction in cyclic voltammetry of BP-DMPT/BPh₄.¹⁶⁷

The last reaction of interest is electron transfer from the chromophore anion to the amine radical cation (ET₂) to generate an amine with a restored lone pair that facilitates ground state redox reaction with the peroxide and hence extended dark curing. I calculated ET₂ from BP anion to DMPT radical cation to be 12.6 kcal/mol and the analogous reaction for ARC, ARC-5,7-2OMe, and ARC-5,7-2OMe-6-Br to be 13.2, 12.9, and 14.8 kcal/mol. The energetics of the DCPI mechanism based on the new chromophores are nearly identical to that of the preceding BP-based DCPI, which we interpreted as validation of viable photo-generation of the tertiary amine (**Table 5.2**). Consequently, our systematic study led to 5,7-dimethoxy-6-bromo-3-aryl coumarin that we proposed to be a desirable DCPI structure after computing the absorption wavelength and corresponding molar absorptivity and favorable photochemical energetics. Therefore, I synthesized ARC-5,7-2OMe-6-Br-DMPT/BPh₄ and described its experimental photophysical and photochemical properties that ultimately culminated in the demonstration of dark-curing photopolymerization in the following section.

Table 5.2. Computed photochemical properties of benzophenone and 3-aryl coumarin derivatives. DFT and TD-DFT calculations were conducted on chromophore-ammonium species without tetraphenyl borate at the theory of M06-2X/6-31+g(d,p)/SMD-ethyl acetate. The $S_0 E_{A/A^\bullet}$ -of BPh₄ ranges from -0.78 to -0.98 V. Reduction potentials are reported with respect to SCE.

	C-N BDE (kcal/mol)	$S_0 E_0$ (V)	$S_1 E_0$ (V)	$T_1 E_0$ (V)	HM ₂ (kcal/mol)	ET ₂ (kcal/mol)
BP-DMPT	52.4	-1.81	1.53	1.10	-16.8	12.6
ARC-DMPT	52.5	-1.39	1.92	1.27	-7.7	13.2
ARC-2OMe-DMPT	53.1	-1.60	1.66	0.90	-11.5	12.9
ARC-5,7-2OMe-6-Br-DMPT	53.2	-1.30	1.98	1.09	-6.5	14.8

5.3.6 Synthesis of 5,7-dimethoxy-6-bromo-3-aryl coumarin

Based on the proposed synthetic method (**Figure 5.2**), I synthesized ARC-5,7-2OMe-6-Br-DMPT/BPh₄. First, ARC-5,7-2OMe was prepared with a high yield of ~98% from the condensation of ethyl(4-methylbenzoyl)acetate with 2,4-dimethoxy-6-hydroxybenzaldehyde. ARC-5,7-2OMe is then subjected to bromination using 3-bromosuccinimide and benzoyl peroxide. The bromination occurred at the desired tolyl group and the hypothesized C₆ position that is evidenced by the disappearance of the C₆ hydrogen peak at 6.33 ppm (**SI5.2. Synthetic details**). The resultant brominated chromophore was prepared with a 50% yield. With this brominated compound, the addition of DMPT and then sodium tetraphenyl borate gave the target quaternary ammonium borate salt PBG with a 25% yield.

5.3.7 Optical measurement of 5,7-dimethoxy-6-bromo-3-aryl coumarin

I measured an optical spectrum of the synthesized ARC-5,7-2OMe-6-Br-DMPT/BPh₄ and compared it to the spectrum of BP-DMPT/BPh₄ in *N,N*-dimethylformamide. Using a series of spectra, a plot of molar absorptivity ($\text{M}^{-1} \text{cm}^{-1}$) vs. wavelength (nm) was generated for a direct comparison. BP-DMPT/BPh₄ has a maximum absorption of $134 \text{ M}^{-1} \text{cm}^{-1}$ at 342 nm with its tail-end absorption of $80 \text{ M}^{-1} \text{cm}^{-1}$ at the commonly used 365 nm wavelength. In comparison, our new DCPI based on ARC-5,7-2OMe-6-Br-DMPT/BPh₄ has drastically improved light-absorbing characteristics over the useful range of wavelengths including the UV (**Figure 5.8**). The maximum absorption of ARC-5,7-2OMe-6-Br-DMPT/BPh₄ was measured at 371 nm with molar absorptivity of $13066 \text{ M}^{-1} \text{cm}^{-1}$. At the near-UV wavelength of 365 nm, ARC-5,7-2OMe-6-Br-DMPT/BPh₄ has 4 orders of magnitude higher than BP-DMPT/BPh₄ (12924 vs. $80 \text{ M}^{-1} \text{cm}^{-1}$), indicating that this new DCPI will likely initiate more rapidly in UV-initiated photopolymerization and subsequent dark curing assuming a similar efficiency for each photoinitiator.

More importantly, ARC-5,7-2OMe-6-Br-DMPT/BPh₄ has strong visible light absorption; Violet absorption at 405 nm and 420 nm is $5710 \text{ M}^{-1} \text{cm}^{-1}$ and $1620 \text{ M}^{-1} \text{cm}^{-1}$, and blue absorption is much weaker with $50 \text{ M}^{-1} \text{cm}^{-1}$ at 455 nm and $25 \text{ M}^{-1} \text{cm}^{-1}$ at 470 nm, which favorably compares to our desired molar absorptivity of $1000 \text{ M}^{-1} \text{cm}^{-1}$ or higher at 405 nm and of $100 \text{ M}^{-1} \text{cm}^{-1}$ or lower at 450 nm. Interestingly, its UV-Vis spectrum can be deconvoluted into two major peaks that correspond to the computationally predicted $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions (**Figure S5.12**).

I then calculated the effective depth of curing dependent on the wavelength for a given initiator concentration, where 90% transmission is defined to guarantee rapid through cure of a sample. (**SI5.4. Depth of cure**). Due to the extreme molar absorptivity, the effective depth of curing at 365 nm is only $4.6 \mu\text{m}$ with this photoinitiator in UV polymerizations, which will limit various thin-film applications that require deeper depths of cure. However, optically uniform

depths of 10.5 and 36.9 μm were achieved at 405 and 420 nm, which matches the requirements of most thin-film applications (~ 5 to 50 μm). More importantly, the use of 455 and 470 nm light will enable the depth of cure to 1195 and 2389 μm , allowing photopolymer resins more than a millimeter-thick to be uniformly photocured at these wavelengths even before considering the DCPI's latent radical production capability.

In addition to the blue absorption, ARC-5,7-2OMe-6-Br-DMPT/BPh₄ exhibited photobleaching, that increases the depth of curing (**Figure S5.14**).¹⁷² With the increased light dose from 0.6 to 201.5 kJ/m², the maximum absorption of 371 nm gradually disappeared which reduced the violet and blue absorptions and hence the yellow coloration. Concurrently, the deep UV peak at 270 nm gradually increased in response, likely due to the product of Type II-like reactions between photoproducts.¹⁹⁶ Lastly, the UV-Vis spectrum of the complete formulation does not differ from the linear addition of two spectra that respectively contains BPO and ARC-5,7-2OMe-6-Br-DMPT/BPh₄ (**Figure S5.15**). This result indicates that the formulation is stable where BPO and ARC-5,7-2OMe-6-Br-DMPT/BPh₄ do not react with each other without irradiation due to the intentional design of the PBG without the reactive lone pair. With the confirmation of visible light absorption, I investigated its photochemistry leading to reductant-release and polymerization.

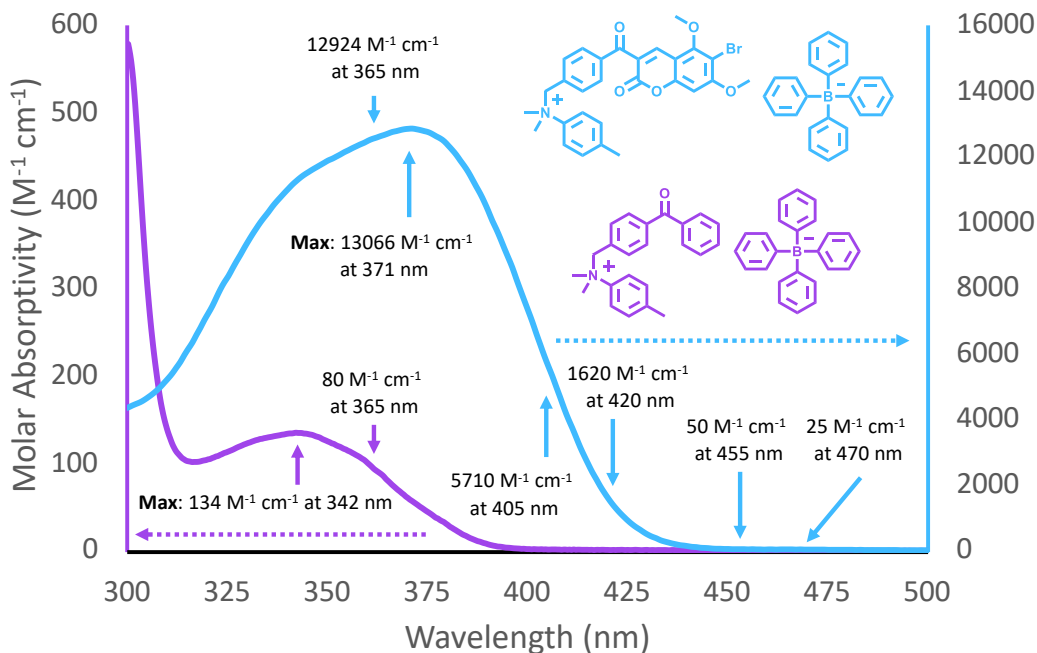


Figure 5.8. Experimentally measured optical spectra of BP-DMPT/BPh₄ and ARC-5,7-OMe-6-Br-DMPT/BPh₄ in *N,N*-dimethylformamide. ARC-based PBG exhibits strong visible light absorption while BP-based PBG is limited to near UV. Two y-axes were used to accommodate the molar absorptivity difference between two DCPI structures. The concentration of BP-PBG is 7.50 mM and that of ARC-PBG is 0.16 mM

5.3.8 Photochemistry of 5,7-dimethoxy-6-bromo-3-arylcoumarin

To probe whether photogeneration of redox initiator DMPT from ARC-5,7-OMe-6-Br-DMPT/BPh₄ is indeed occurring, I studied the evolution of ¹H-NMR peaks specific to ARC-5,7-OMe-6-Br-DMPT and DMPT (**Figure 5.9**) in deuterated DMSO with ethylene carbonate as an internal standard. Following irradiation with a 405 nm LED, the peak associated with the methylene hydrogens of ARC-5,7-OMe-6-Br-DMPT at 5.09 ppm diminishes while three sets of methyl hydrogen peaks of DMPT (N-CH₃ at 2.83 ppm and Ph-CH₃ at 2.19 ppm) emerge,

demonstrating that DMPT is absent before irradiation and is photo-generated from ARC-5,7-OMe-6-Br-DMPT/BPh₄. This signifies this new chromophore's potential to induce dark-curing with BPO within the amine-peroxide redox polymerization framework. Furthermore, we conducted a quantitative NMR to study the dose-dependence of photo-base-release from ARC-5,7-OMe-6-Br-DMPT/BPh₄ by varying irradiation time at a fixed irradiance of 2.0 mW/cm². The PBG degradation and amine generation linearly responded to the increasing time, leading to a pseudo-zero-order reaction kinetics within the low conversion of the reaction (~20%). Under our experimental conditions, ~77% of ARC-5,7-OMe-6-Br-DMPT/BPh₄ degradation yielded DMPT amine generation. Such high efficiency of the new DCPI is similar to that of my previous UV-based BP-DMPT/BPh₄ that was found to be the most photon-efficient photoinitiator.¹⁶⁷ These results directly validate my computational study where the mechanism energetics between BP-DMPT and ARC-5,7-OMe-6-Br-DMPT were essentially identical.

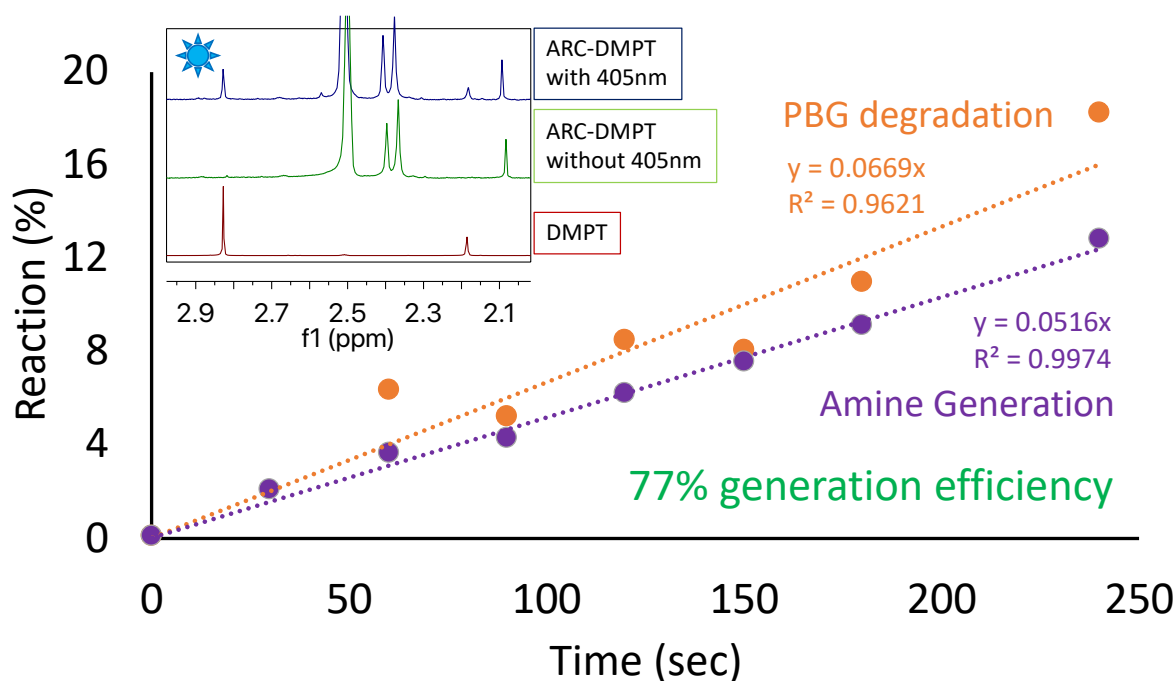


Figure 5.9. NMR evidence of photo base generator from ARC-5,7-OMe-6-Br-DMPT/BPh₄. The peaks of DMPT emerge after irradiation of the PBG, where the efficiency of photo-reductant-generation is 77%. Ethylene carbonate was used as an internal standard for quantitative NMR. The concentration was 14.7 mM in deuterated dimethyl sulfoxide with 2.0mW/cm² 405 nm LED irradiation.

Lastly, I studied photo- and dark-polymerization enabled by the new visible DCPI that was initiated by 365, 405, and 455 nm LEDs in a methacrylate resin of 80 wt% triethylene glycol dimethacryate and 20 wt% α -methylene- γ -butyrolactone, a cyclic analog of methyl methacrylate. As in our previous publication of DCPI, in addition to complete photopolymerization, we used the partial curing protocol where 20% of functional group conversion is achieved by irradiation to observe post-irradiation dark-curing behavior. The control is just the PBG without the BPO oxidant. With 455 nm LED at 50 mW/cm², both DCPI (PBG + BPO) and the control PBG rapidly photopolymerized in the methacrylate resin (**Figure 5.10**). Interestingly, final conversions observed within 10 min of irradiation are noticeably different. The DCPI sample reached 75% conversion while the PBG-only sample reached 65%. Such a difference is commonly attributed to increased chain mobility enabled by exothermicity of polymerization where faster rates of polymerization lead to a larger exothermicity that surpasses the sample's ability to dissipate the released heat.¹⁹⁷ However, I found that the temperature evolution is insignificant (< 3 °C) and does not differ between the two samples, which likely has a minimal effect on chain mobility in glassy polymers.¹⁹⁸ We hypothesize that the final conversion difference is likely due to the difference of excess free volume generated from the delayed shrinkage with respect to conversion.^{197,199} The faster polymerization rates can “freeze” the developing polymer in a kinetically trapped position that is further away from the thermodynamic equilibration, creating excess free volume that allows higher vitrification-limited conversion to be achieved.

A steady-state analysis of the photopolymerization kinetics based on **Figure 5.10** indicated that the rates of polymerization during irradiation are 0.24 s^{-1} for the PBG without peroxide and 0.50 s^{-1} for full DCPI composed of the PBG and peroxide, the difference of which must originate from the presence of ground state redox initiation between amine and peroxide during irradiation. This yields initiator efficiencies (Φ) for the respective photoinitiators of 0.65 and 2.82 as calculated from the free radical photopolymerization kinetic equation (**SI5.5. Kinetic property calculation**).²⁰⁰ The ARC-based PBG activated with a 455 nm LED is more efficient than the previous BP-based PBG activated with a 365 nm LED ($\Phi_{\text{ARC-455nm}} = 0.65$ vs. $\Phi_{\text{BP-365nm}} = 0.43$). This is likely due to a greater redox potential of the ARC-based PBG in comparison to the BP-based PBG (1.98 V for ARC-PBG vs. 1.54 V for BP-PBG vs. SCE assuming excitations into their lowest energy singlet excited states). The larger redox potential difference with respect to that of the tetraphenyl borate results in a larger thermodynamic driving force that often leads to faster electron transfer kinetics. This also implies that the photochemical mechanism is operative with the singlet excited states, facilitated by the proximity of chromophore-ammonium and tetraphenyl borate via an ionic attraction. We support the implication with the redox potential of the first triplet excited state ARC-based PBG at 1.09 V that is very comparable to that of the first triplet excited state BP-based PBG at 1.10 V. vs. SCE, whose difference is too small to significantly affect electron transfer kinetics. On the other hand, we found the initiator efficiency of DCPI to be larger than 1, whose theoretical maximum value is 1 by definition.²⁰⁰ This anomaly is created by the additional radicals generated from the redox reactions initiated by photo-released amine reductants, which occurs concurrently with photolysis during irradiation. The higher efficiency relative to our previous report is primarily due to our use of a higher concentration of the formulated peroxide in this study (1.82 wt% here vs. 0.5 wt% in our previous study). The ability to modulate

photopolymerization rates with concentration changes of visible-light-transparent peroxide is exceptionally useful, as this provides the ability to increase photopolymerization rates while maintaining the relatively low overall optical density for depth of curing. Otherwise, with conventional photoinitiators, increasing photoinitiator concentrations to increase photopolymerization rates would reduce the depth of cure due to the internal filter effect.

More importantly, when irradiation was ceased at the respective 20% conversions, DCPI and the control PBG exhibited different post-irradiation behaviors (**Figure 5.10**). The conversion with the control photoinitiator plateaued essentially immediately following irradiation, which indicates the rapid bi-radical termination behavior expected of all conventional photoinitiators in the low-conversion regime where relatively high mobility persists. Contrarily, DCPI continued its polymerization to 55% within 25 min post-irradiation. A steady-state analysis of dark-polymerization between 21% and 25% resulted in a polymerization rate of 0.16 s^{-1} , which approximately corresponds to the difference between the PBG and DCPI observed in our photopolymerization experiments. These additional initiating radicals did not require photons and initiated radical polymerization with an initiator efficiency of 0.3. The efficiencies for the photopolymerization of the PBG and the dark-curing of the DCPI do not add to the efficiency found for the photopolymerization of the DCPI because termination-dependent initiator efficiency is not an additive property. I also demonstrated similar dark curing behavior with 365 nm and 405 nm LEDs while the absence of irradiation resulted in the lack of polymerization over 1 h (**Figures S5.15 and S5.16**).

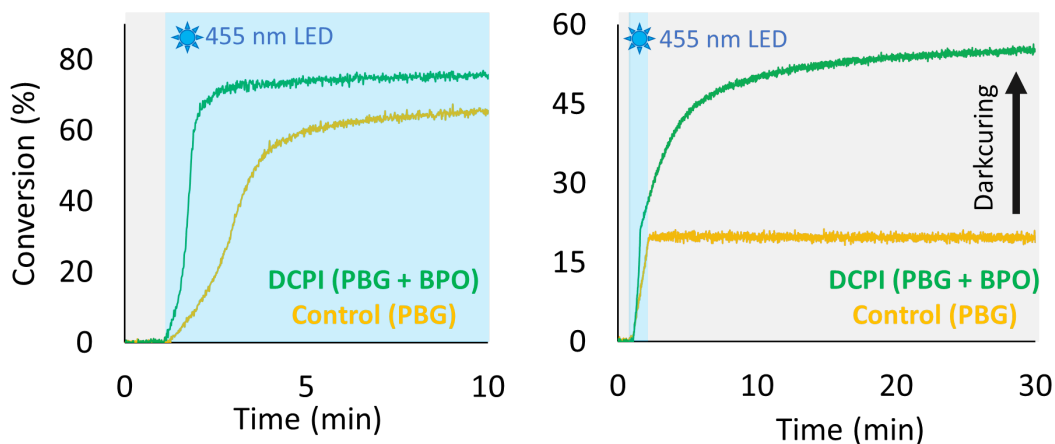


Figure 5.10. Methacrylate photopolymerization and dark curing with dark-curing photoinitiator and control photoinitiator. The control formulation only contains PBG (ARC-5,7-OMe-6-Br-DMPT/BPh₄) that generates amine and radicals during irradiation, excluding the dark-curing potential due to the lack of BPO peroxide. The dark curing photoinitiator formulation contains PBG and BPO that enables an extended conversion post-irradiation. The experimental conditions include the initiator of 0.6 wt% ARC-PBG and 1.8 wt% BPO; the resin of 80 wt% TEGDMA and 20 wt% MBL; and 50 mW/cm² 455 nm LED.

5.4 Conclusion

In this manuscript, I extensively used computational quantum chemical methods, namely time-independent and -dependent density functional theories, to search for a novel dark-curing photoinitiator with a chromophore that offers significant and well-characterized visible light absorption. The theoretical insight into the photochemical mechanism drawn from our previous UV-absorbing dark-curing photoinitiator guided the approach taken here. I identified a 3-aryl coumarin chromophore that proved to be a superior scaffold in photon-absorption by a factor of ~ 10 when compared to the benzophenone chromophore used for the UV-absorption. I then functionalized 3-aryl coumarin at several positions with either methoxy- or chlorine-groups to red-shift the absorption into the visible light range. Overall, methoxy groups, particularly at the C₅

and C₇ positions, allowed moderate visible light absorption while chlorine groups universally failed to increase the absorption wavelength. I found that the bathochromic shift from methoxy substitutions at certain positions is primarily due to increased molar absorptivity instead of maximum absorption changes. Such high molar absorptivity resulted from increased polarizability that originated from the push-pull character through the long axis of the molecule, evidenced by ground state dipole moments. Based on the findings of the substitution study, we determined that 5,7-dimethoxy-3-arylcoumain would be a promising visible light PBG chromophore with an optimal absorption characteristic, which we confirmed using a simulated UV-Vis spectrum. However, due to a synthetic limitation, 5,7-dimethoxy-6-bromo-3-arylcoumarine with slightly poorer absorption was instead targeted. I then computed the energetics of the proposed photochemical mechanism, which showed that 5,7-dimethoxy-6-bromo-3-arylcoumarin-based dark-curing photoinitiator will perform as efficiently as the benzophenone-based predecessor. After its synthesis, 5,7-dimethoxy-6-bromo-3-arylcoumarin-DMPT/BPh₄ was optically examined to possess molar absorptivities of 5710 M⁻¹ cm⁻¹ at 405 nm and 1620 M⁻¹ cm⁻¹ at 420 nm with weaker blue absorption with 50 M⁻¹ cm⁻¹ at 455 nm and 25 M⁻¹ cm⁻¹ at 470 nm. In addition to visible light absorption, we found it to photo-bleach, which reduces the internal filter effect and increases the depth of curing. Using an NMR, we confirmed that the DMPT amine is indeed generated from 5,7-dimethoxy-6-bromo-3-arylcoumarin-DMPT/BPh₄ with 77% efficiency. Lastly, I demonstrated its dark-curing capability with 365, 405, and 455 nm in a methacrylate resin. Based on a steady-state analysis, we found the initiator efficiency of 5,7-dimethoxy-6-bromo-3-arylcoumarin-DMPT/BPh₄ without peroxide is 0.65 while its initiator efficiency with benzoyl peroxide increased to 2.82 due to additional radicals produced by redox initiation that does not require light-activation. More importantly, we demonstrated an extensive dark-curing that tripled

the initial conversion achieved with brief light exposure. The new dark-curing photoinitiator with visible absorption will improve many pre-existing applications and enable new applications that conventional visible light photoinitiators could not achieve due to non-ideal photocuring conditions, making radical photopolymerization an even more useful technology.

5.5 Supporting information

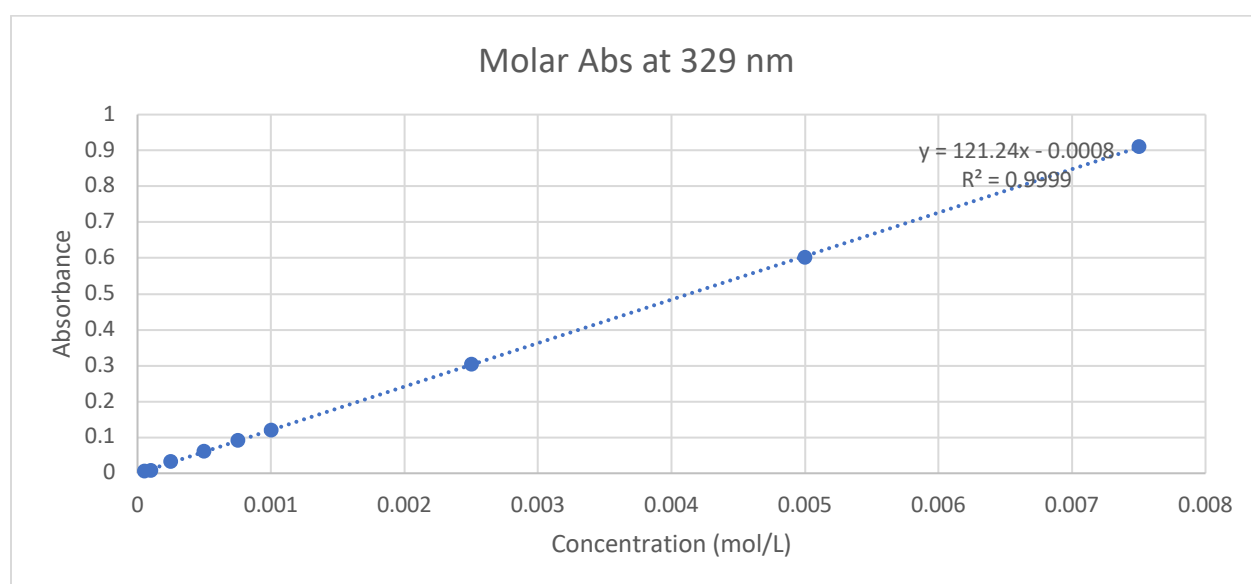


Figure S5.1. Molar absorptivity of BP-based DCPI at 329 nm in DMF

SI5.1. Resonance structures.

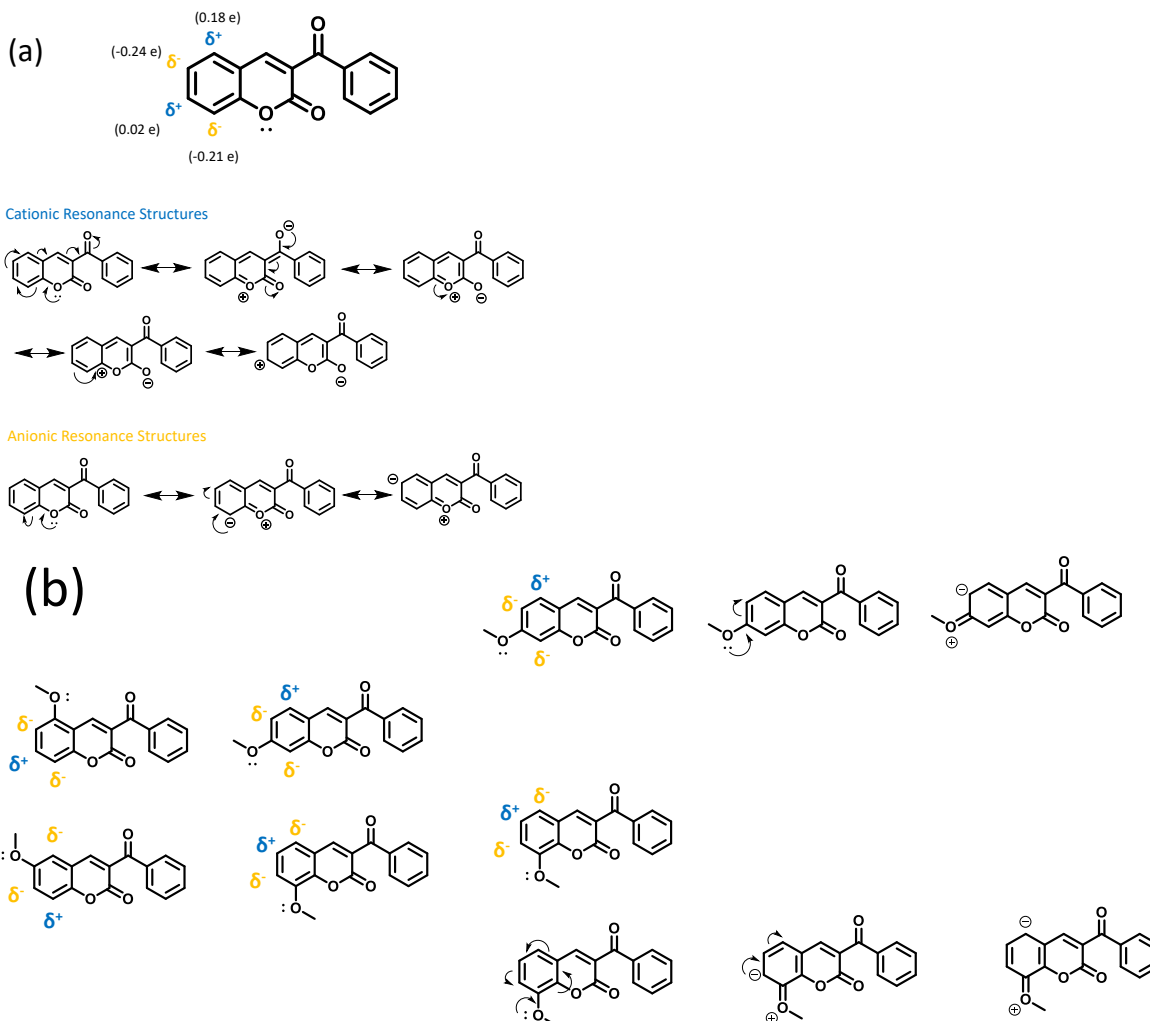


Figure S5.2. (a) Electron densities and resonance structures of ARC that were derived from long pair electron movements. Cationic and anionic locations in the resonance structures allow visualization of electron-rich and -poor sites of ARC, which are confirmed by electron density calculations. (b) Electron-rich and -poor sites of methoxy-substituted ARC and their examples of electron movements. Note that 5 and 7 functionalization resulted in the natural pattern of resonance with ARC while 6 and 8 functionalization affect electron densities in the opposite way reducing the overall resonance.

SI5.2. Synthetic details

The quaternary ammonium salt based visible photobase generator was synthesized starting from 3-ketocoumarin which was prepared in reasonably high yield (~98%) by the condensation of Ethyl (4-methylbenzoyl)acetate with β -ketoester, 2,4-Dimethoxy-6-hydroxybenzaldehyde. 3-ketocoumarin derivative (**1**) was then subjected to bromination of methyl group at 80°C using N-bromosuccinimide and benzyl peroxide (BPO) as radical initiator in chlorobenzene as solvent. ^1H -NMR showed the disappearance of peak at 6.33 ppm confirming the bromination at benzylic position (**2**) (susceptible to radical halogenation) and no benzyl bromides (**3**). Although NBS is well documented as a free radical brominating reagent for allylic and benzylic hydrogens, the bromination at benzylic position can be attributed to the most activated and susceptible position for radical halogenation. Though such system is found to be highly para-selective with respect to the most activating substituent, in instances where the para position is blocked, bromination occurs ortho to the most activating substituent. (Reference: *J. Org. Chem.* 1995, 60, 5328-5331; *Synth. Commun.* 1998, 28, 2087-2095) After electrophilic aromatic bromination (**2**), the obtained product was then subjected again to undergo radical mediated reaction, further resulted in the desired benzyl brominated product in reasonably good yield (~50%) which was confirmed by HRMS. Compound **3** was further treated with Dimethyl-p-toluidine (DMPT) in toluene/DCM solvent mixture to result quaternary ammonium bromide salt which was further reacted with sodium tetraphenyl borate to give the desired quaternary ammonium borate salt as visible photobase (**5**).

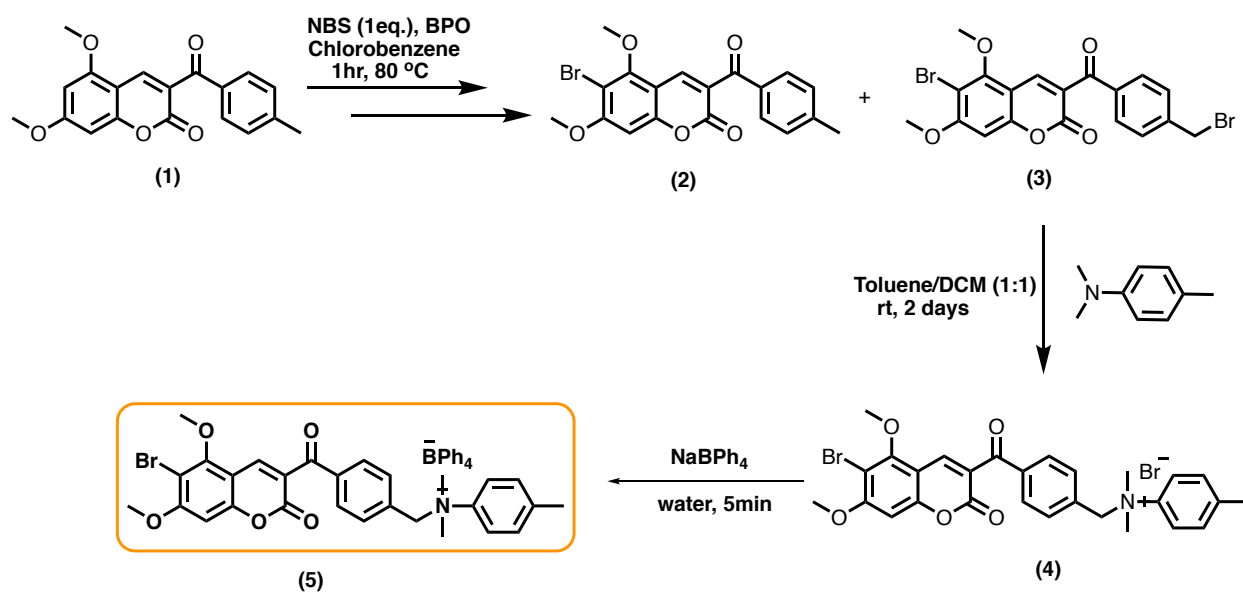


Figure S5.3. Synthesis of quaternary ammonium borate salt based visible photobase.

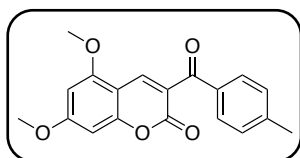
NMR Spectroscopy

^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker 400MHz NMR spectrometer. The δ scale was referenced to deuterated solvents, indicated in the respective measurement. HRMS analysis was carried out on a Waters Synapt G2 HDMS Q-TOF Mass Spectrometer.

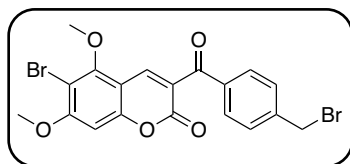
Materials 2,4-Dimethoxy-6-hydroxybenzaldehyde, Ethyl (4-methylbenzoyl)acetate, N-bromosuccinimide (NBS), Benzoyl peroxide (BPO), anhydrous Toluene, and dichloromethane were purchased from Sigma Aldrich. Chlorobenzene, 4-Dimethylaminotoluene (DMPT), and Sodium Tetraphenylborate were purchased from Alfa Aesar. NBS was purified by recrystallization from water, BPO was purified by dissolving in dichloromethane and recrystallizing from methanol. All amines were purchased in the highest purity available and other chemicals were of reagent grade and used without further purification.

Methods.

Synthesis of quaternary ammonium borate salt

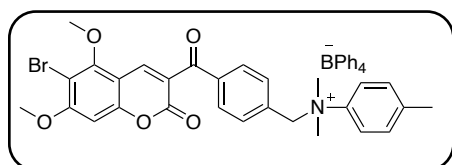


To the solution of 1g (5.4 mmol) of 2,4-Dimethoxy-6-hydroxybenzaldehyde and 1.13 g (5.4 mmol) of Ethyl (4-methylbenzoyl)acetate in 40 mL of ethanol was added 0.5 mL of piperidine and kept to reflux for 2 hr. After refluxing, the reaction mixture was cooled, and the product was obtained by filtering and washing with cold ethanol. The white solid hence obtained was dried under vacuum. Yield: 98%; ^1H NMR (CDCl_3 , δ ppm): 8.45 (s, 1H), 7.78 (dd, 2H), 7.30 (dd, 2H), 6.49 (dd, 1H), 6.33 (dd, 1H), 3.92(s, 6H), 2.45(s, 3H).



1.5g (4.6 mmol) of **1** was dissolved in Chlorobenzene or chloroform at 70°C , followed by the addition of 0.9 g (5mmol) of N-Bromosuccinimide and 0.11g (0.45 mmol) of benzoyl peroxide and kept stirring at 70°C for 1 hr. After 1 hr, the reaction mixture was cooled, and organic solvent was evaporated. The yellow solid hence obtained was re-dissolved in dichloromethane and the organic layer was then washed with NaHCO_3 followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get yellow solid. ^1H NMR (CDCl_3 , δ ppm): 8.42 (s, 1H), 7.76 (dd, 2H), 7.30 (dd, 2H), 6.40 (s, 1H),

4.06 (s, 3H), 3.99 (s, 3H), 2.44 (s, 3H). 1 g (2.4 mmol) of **2** was dissolved in Chlorobenzene at 80°C, followed by the addition of 0.88 g (4.9 mmol) of N-Bromosuccinimide and 0.06g (0.24 mmol) of benzoyl peroxide and kept stirring at 80°C for 4 hr. After 4 hr, the reaction mixture was cooled, and organic solvent was evaporated. The yellow solid hence obtained was re-dissolved in dichloromethane and the organic layer was then washed with NaHCO₃ followed by washing with brine and water. The combined organic layer was then dried over Na₂SO₄ and concentrated at reduced pressure to get yellow solid.



To the solution of 1.5 g (3.7 mmol) of **3** in anhydrous toluene and dichloromethane (1:1) was added 0.55 g (4.1 mmol) of Dimethyl-p-toluidine at room temperature under nitrogen atmosphere. After the completion of the addition, the reaction mixture was then stirred for 2 days at room temperature. After 24 hrs of completion, yellow precipitate was observed. After 2 days, the reaction mixture was centrifuged to obtain the yellow precipitate. The yellow precipitate was washed thrice with toluene followed by washing with hexane and then kept for drying in vacuum oven at 70 °C for 15 min. The yellow solid hence obtained was the desired compound.

To the solution of 0.9 g (1.6 mmol) of **4** in water was added a solution of 0.62 g (1.8 mmol) of sodium tetraphenyl borate in water dropwise at room temperature. The yellow turbidity was observed. The reaction was stirred for 5 min and then subjected to evaporation to obtain yellow solid. The yellow solid was washed with water and dried. The obtained solid was dissolved in acetonitrile and precipitated out in diethyl ether which resulted in pale yellow/yellow solid. The solid hence obtained is subjected to dry under vacuum resulting in the desired compound. ¹H NMR (CDCl₃, d ppm): 8.41 (s, 1H), 7.76 (dd, 2H), 7.52 (dd, 2H), 7.44 (dd, 2H), 7.29(m, 8H), 7.16(dd, 2H), 7.02 (m, 8H), 6.86 (m, 4H), 6.67 (s, 1H), 4.89 (s, 2H), 4.08 (s, 3H), 4.02 (s, 3H), 3.52 (s, 6H), 2.43 (s, 3H).

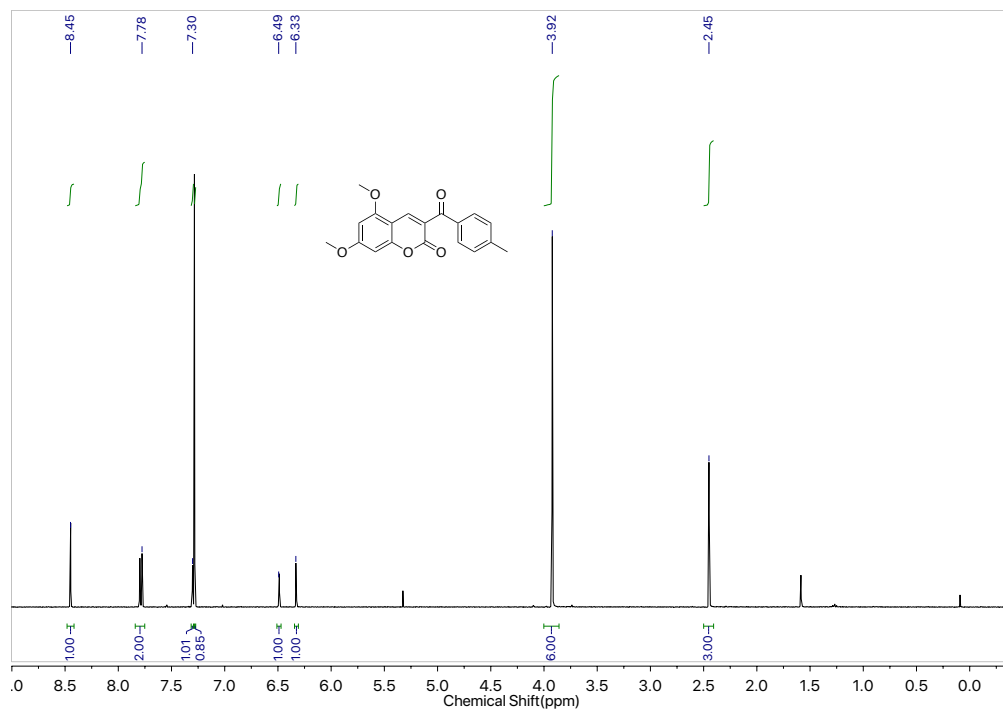


Figure S5.4. ¹H NMR of 1.

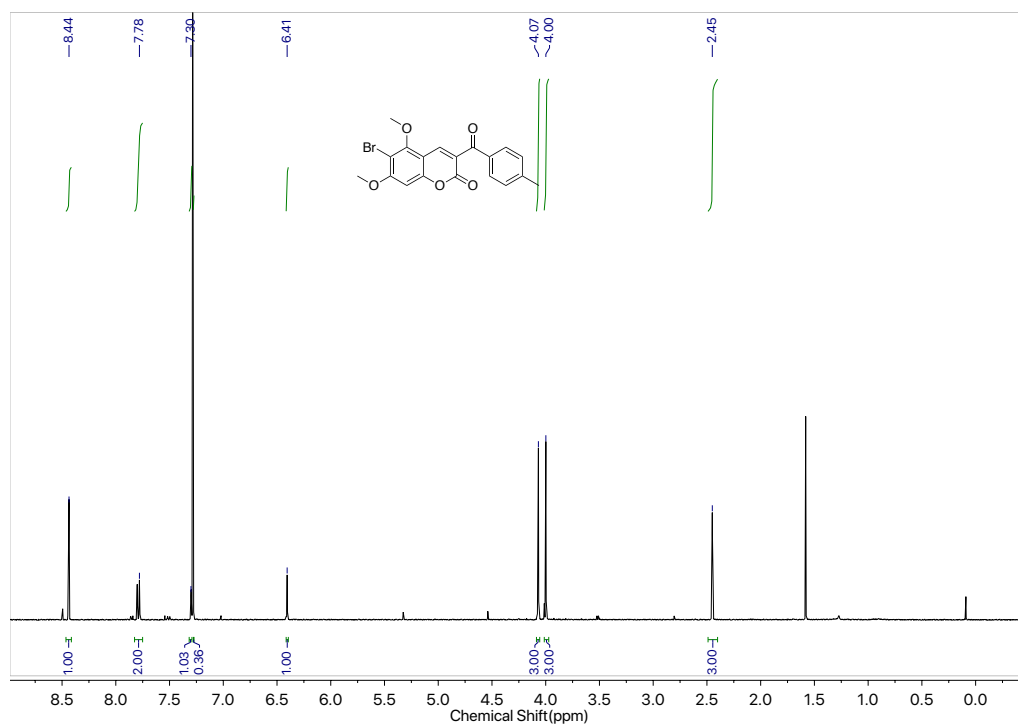


Figure S5.5. ¹H NMR 2.

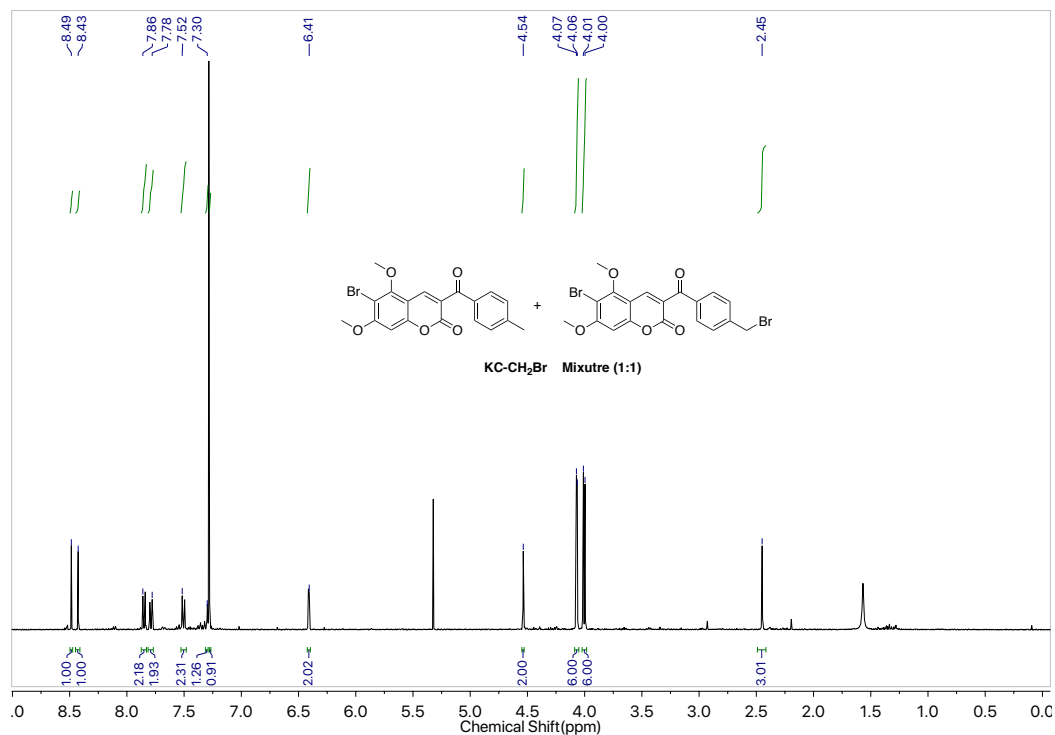


Figure S5.6. ¹H NMR 3.

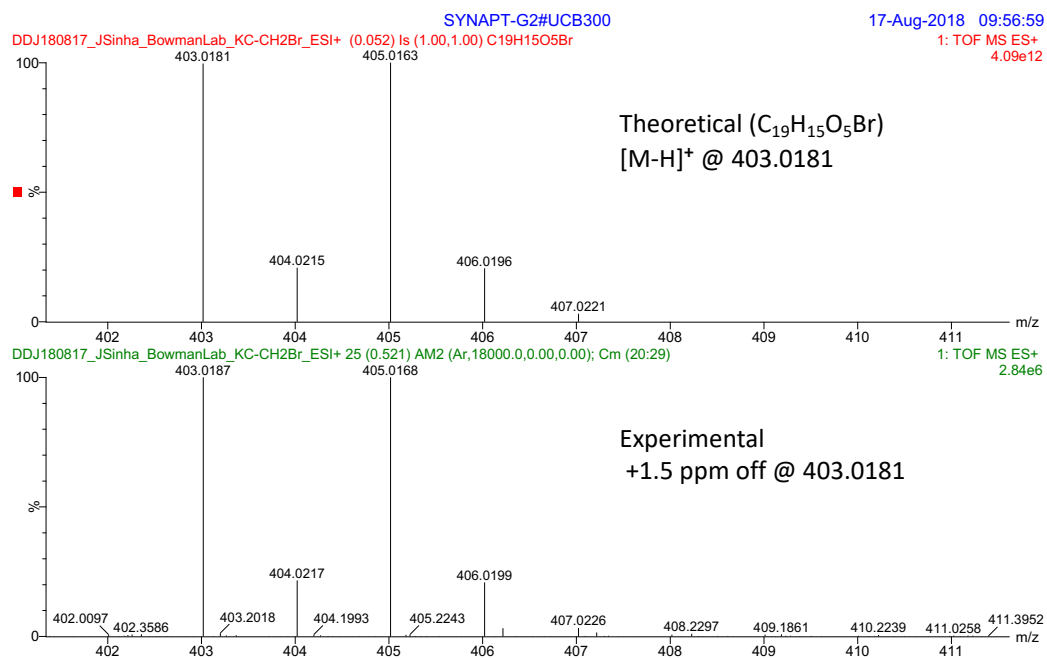
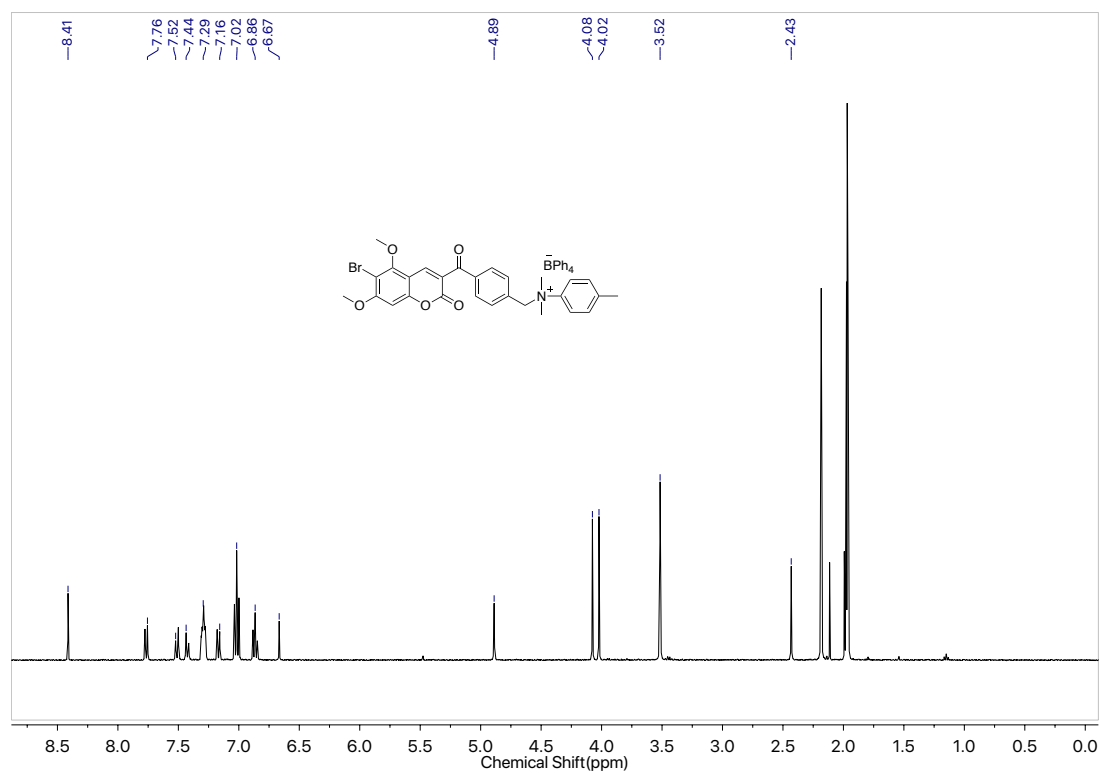


Figure S5.7. HRMS of 3.**Figure S5.8.** ¹H NMR 5.

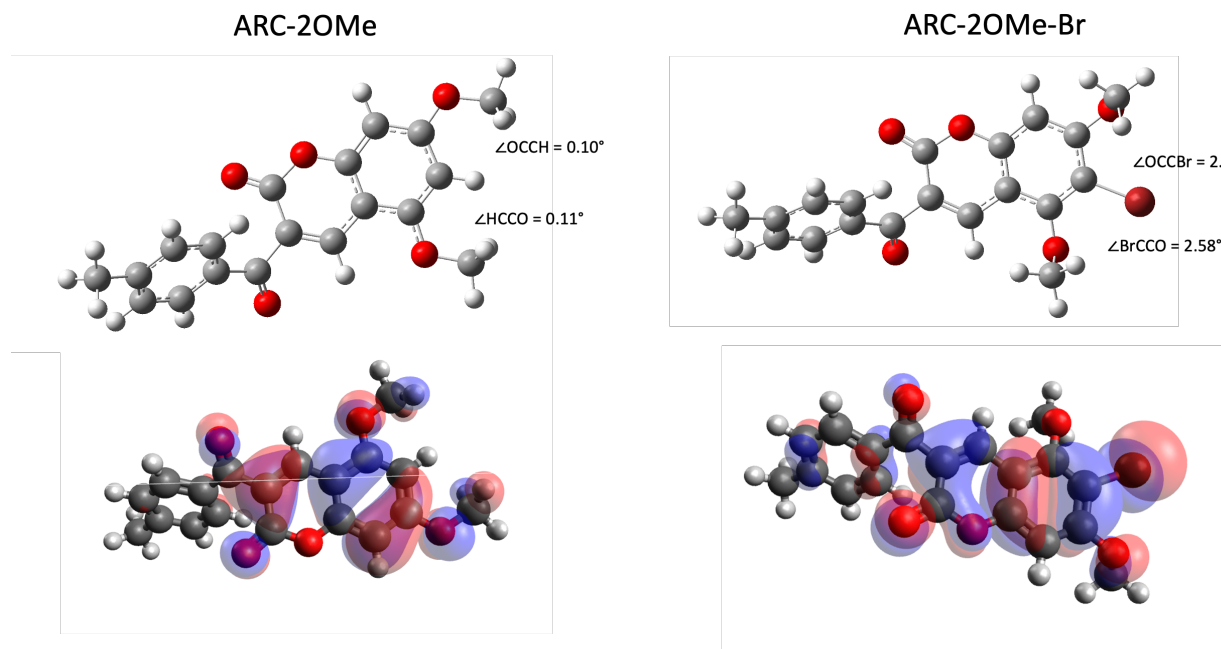


Figure S5.9. The effect of 6-bromo substitution upon ARC-2OMe. The dihedral angles between the methoxy substituents and the aromatic ring increased, which reduced the electron-donating effect of methoxy substituents. Also, the electron withdrawing bromine has a strong overlap with the pi orbital.

SI5.3. Ionic Complexation

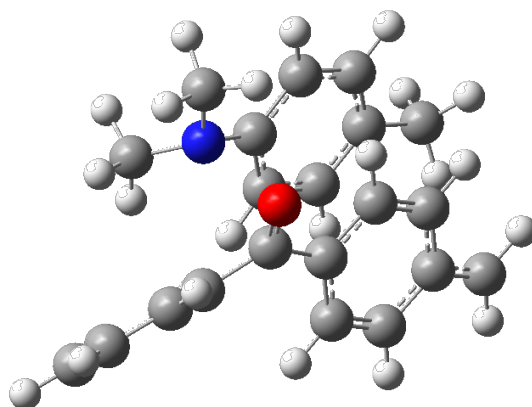
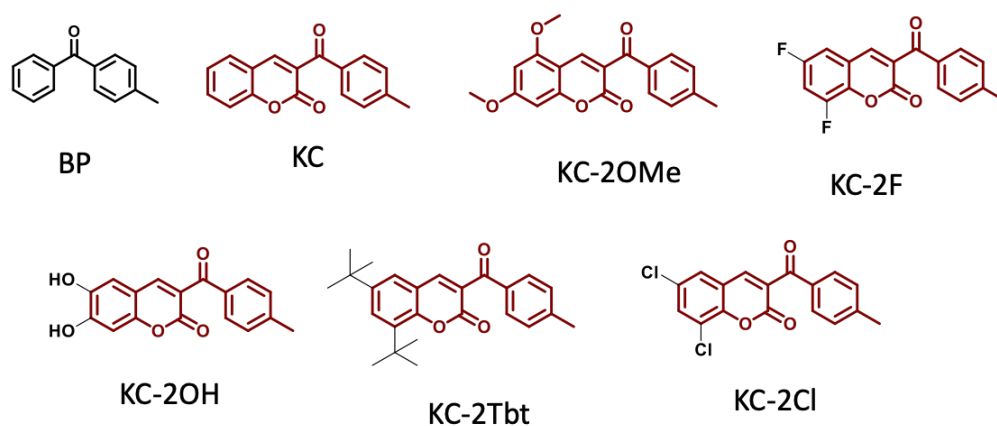


Figure S5.10. Complexation of BP anion and DMPT ARC via an electrostatic attraction.

Table S5.1. Energetics of HM_2 and ET_2 in 4 PBGs with ionic complexation (IC) and without ionic complexation (NIC). Without the incorporation of ionic complexation as part of the mechanism, the reaction mechanism is not feasible at room temperature.

	BP	ARC	ARC-2OMe	ARC-2OMe-Br
HM_2 (IC)	-16.8	-7.7	-11.5	-6.4
ET_2 (IC)	12.6	13.2	12.9	14.8
HM_2 (NIC)	39.6	48.2	45.6	50.3
ET_2 (NIC)	-43.8	-42.7	-44.2	-41.9



	BP	KC	KC-2OMe	KC-2F	KC-2OH	KC-2Tbt	KC-2Cl
lambdaMax1 (nm)	328.94	330.63	338.15	331.33	333.16	330.59	331.37
Absorptivity1 (f)	0.002	0.02	0.46	0.01	0.19	0.03	0.01
eta1 (L mol ⁻¹ cm ⁻¹)	68.83076945	732.8453	18422.35	498.0109	7692.851	1012.217	534.4507
lambdaMax2 (nm)	249.73	294.68	321.63	296.00	320.48	304.87	299.03
Absorptivity2 (f)	0.47	0.53	0.33	0.32	0.34	0.30	0.29
eta2 (L mol ⁻¹ cm ⁻¹)	19029.68332	21361.83	13361.27	13085.94	13636.59	12102.07	11721.48

Figure S5.11. Various ARC derivatives that are generated from available precursors

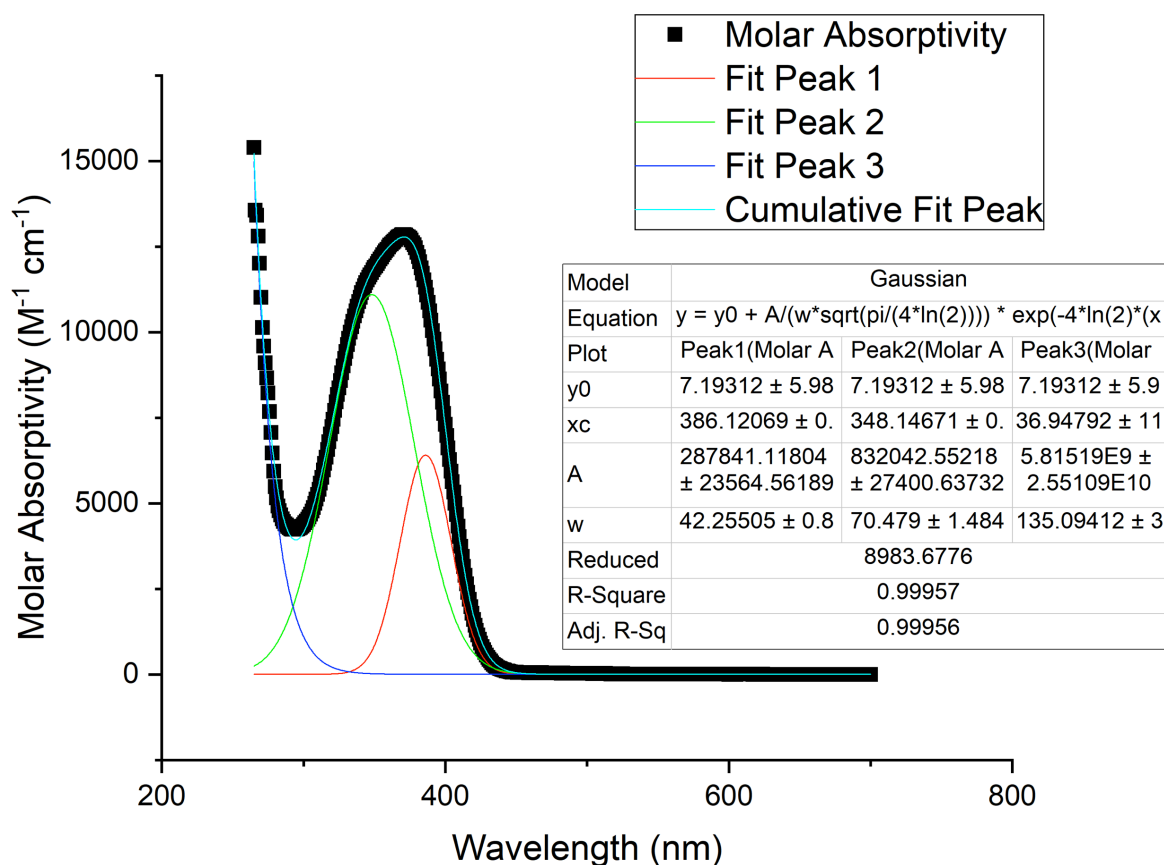


Figure S5.12. Deconvolution of first and second absorptions the computationally predicted $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions

SI5.4. Depth of cure

According to Beer-Lambert, $A = \epsilon cl$ where ϵ is molar absorptivity, c is molar concentration of photochemical species, l is path length.

The UV-Vis spectra (**Figure 8**) indicate that visible DCPI absorb light at 365 nm with $\epsilon = 12924 \text{ M}^{-1} \text{ cm}^{-1}$, at 405 nm with $5710 \text{ M}^{-1} \text{ cm}^{-1}$, at 420 nm with $1620 \text{ M}^{-1} \text{ cm}^{-1}$, at 455 nm with $50 \text{ M}^{-1} \text{ cm}^{-1}$, and at 470 nm $25 \text{ M}^{-1} \text{ cm}^{-1}$. The molar concentration (c) in our experiments was 0.00766 mol/L .

The optically thin film requires transmission (T) to be 90% at least where the Beer-Lambert equation can be reorganized into $A = -\log T$. Therefore, A is 0.045757.

The path lengths (l) were calculated to be 4.6, 10.5, 36.9, 1194.7, and 2389.4 micrometers for respective wavelengths of 365, 405, 420, 455, and 470 nm. At 365 nm, the depth cure would be near impossible due to a high molar absorptivity resulting in very strong light attenuation at the surface level. However, the higher wavelength (455 and 470 nm) is able to penetrate millimeters of the samples with 90% intensity retention, allowing a deep curing.

Table S5.2. Pathlength (l) allowing 90% transmission of initial intensity dependent on wavelength at 0.00766 mol/L of concentration (c) used in our kinetic study.

Wavelength (nm)	c ($\text{M}^{-1} \text{cm}^{-1}$)	l (cm)	l (micrometer)
365	12924	0.00046	4.6
405	5710	0.00105	10.5
420	1620	0.00369	36.9
455	50	0.11947	1194.7
470	25	0.23894	2389.4

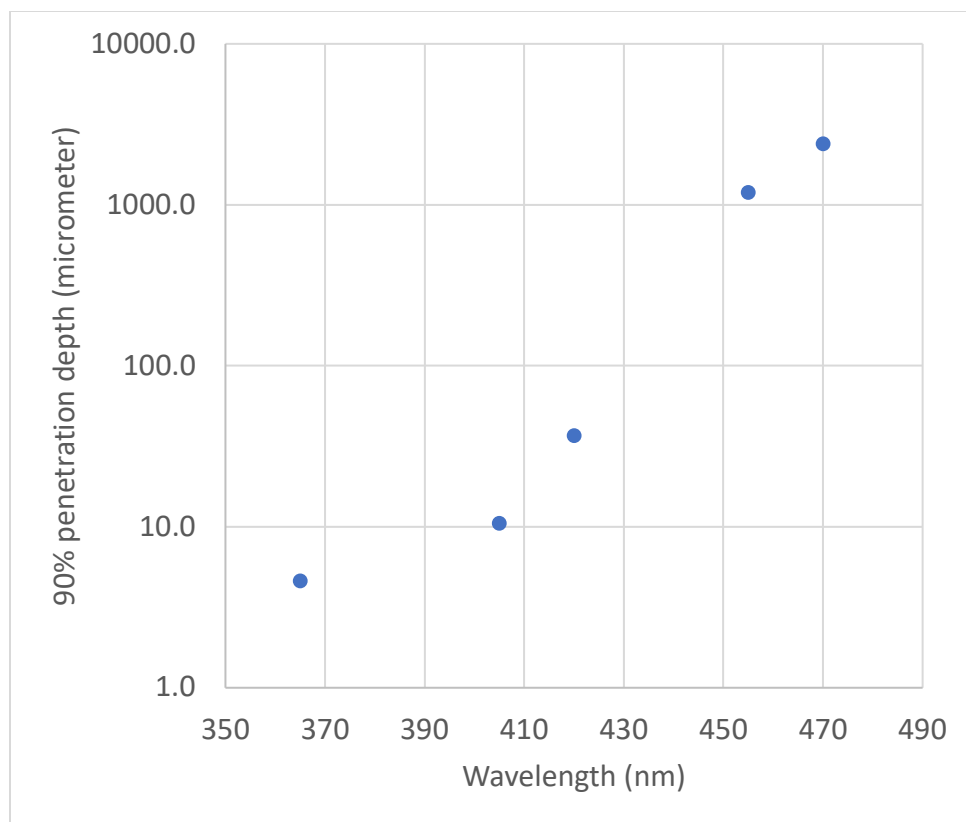


Figure S5.13. Logarithmic relationship between wavelength and 90% penetration depth based on Beer-Lambert law

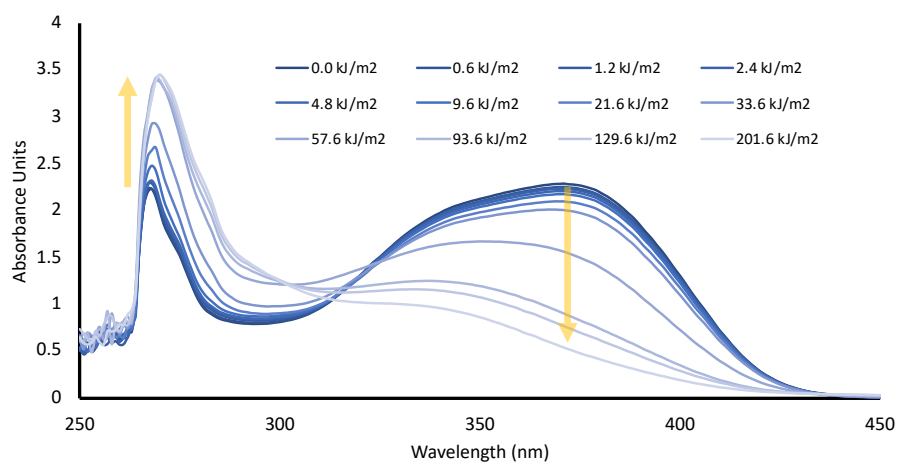


Figure S5.14. Photobleaching experiment of increasing doses. 1mW/cm² is used from 0.6 kJ/m² to 9.6 kJ/m², 10 mW/ cm² is from 21.6 kJ/m² to 57.6 kJ/m², 30mW/cm² is used from 93.6 to 201.6 kJ/m². The concentration was 0.16mM in DMF.

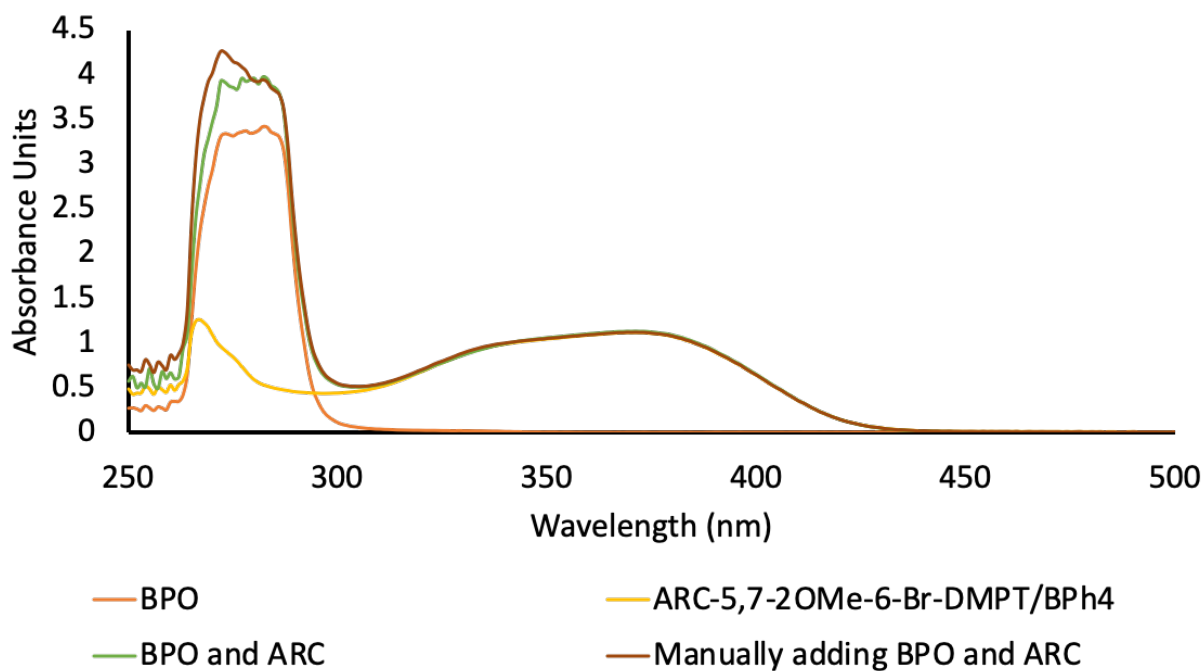


Figure S5.15. UV-Vis Spectra of DCPI components. BPO and PBG do not react with each other without irradiation.

SI5.5. Kinetic property calculations

Based on a steady-state analysis, the rate of methacrylate free radical polymerization (R_p) can be expressed as¹⁶¹

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](\epsilon I_0 \Phi [I] 1000)^{1/2}} \quad \text{Eq. 1}$$

Whereas k_p is propagation kinetic constant, k_t is termination kinetic constant. The molar concentration of monomer is represented by $[M]$, the initiator molar absorption by ϵ , light

intensity by I_0 , initiator efficiency by Φ , and the initiator concentration by $[I]$. Therefore, the initiator efficiency can be calculated by reorganizing **Eq. 1**

$$\Phi = \frac{k_t R_p^2}{1000 \epsilon I_0 [I] ([M] k_p)^2} \quad \text{Eq 2}$$

Based on **Figure 5.10**, R_p for each system was calculated based on the time that it took the reaction proceed from 5% to 10% conversion. $\frac{k_p}{k_t^{1/2}}$ for TEGDMA was obtained from the previous literature, where k_p is $516 \text{ M}^{-1}\text{s}^{-1}$ and k_t is $5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.¹⁶¹ From **Figure 5.8**, the molar absorption for the ARC-PBG at 455 nm is $\epsilon = 11500 \text{ L/m}^2/\text{mol}$. Initiator concentration $[I]$ is 0.00766 mol/L . Light intensity I_0 is $500 \text{ W/m}^2 = 1.9 \times 10^{-6} \text{ M}^*\text{m/s}$

Hence, Φ for DCPI can be determined as

$$\Phi = \frac{k_t R_p^2}{1000 \epsilon I_0 [I] ([M] k_p)^2} = \frac{5 \times 10^5 \times 0.50^2}{1000 \times 11500 \times 1.9 \times 10^{-6} \times 0.00766 \times (1 \times 516)^2} = 2.82$$

A similar calculation were done for PBG.

Table S5.3. Rate of polymerization and initiator efficiency of photoinitiators

	PBG	DCPI
$R_p \text{ (s}^{-1}\text{)}$	0.24	0.50
Φ	0.65	2.82

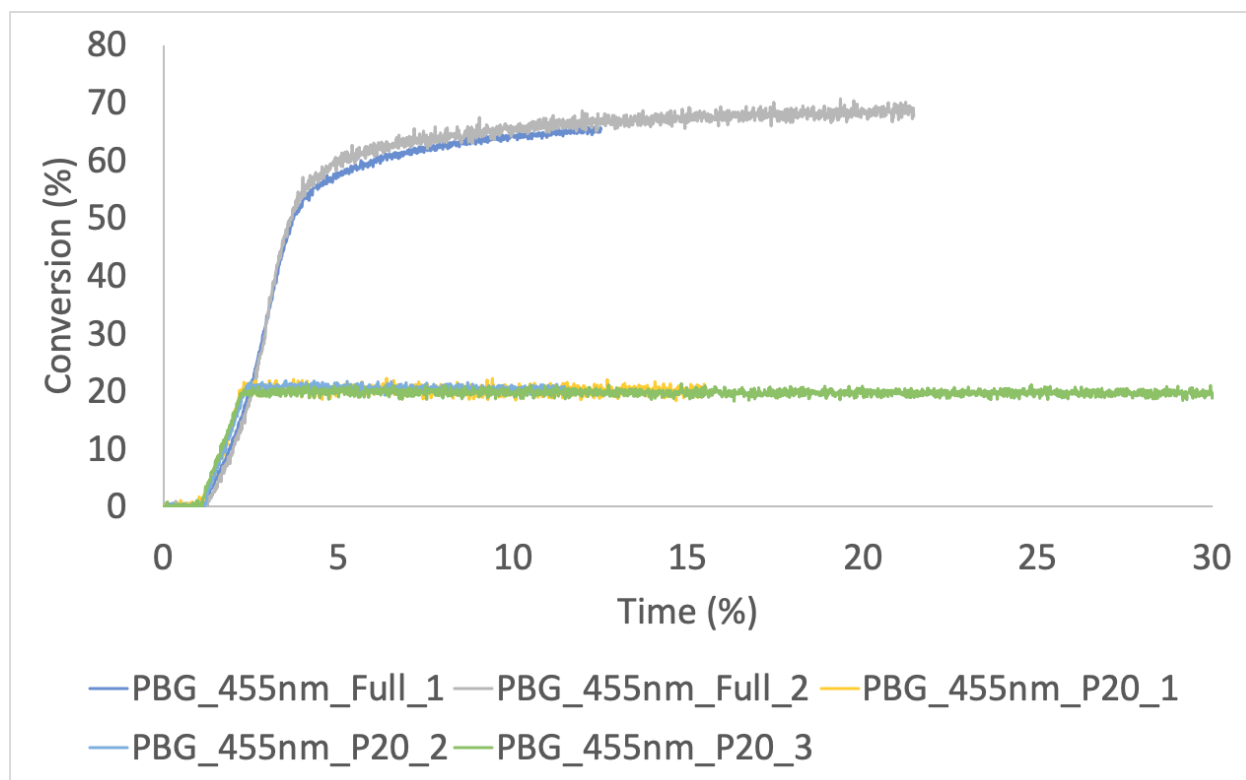


Figure S5.13. Polymerization profiles of ARC-5,7-2OMe-6-Br under full and 20% partial cure.

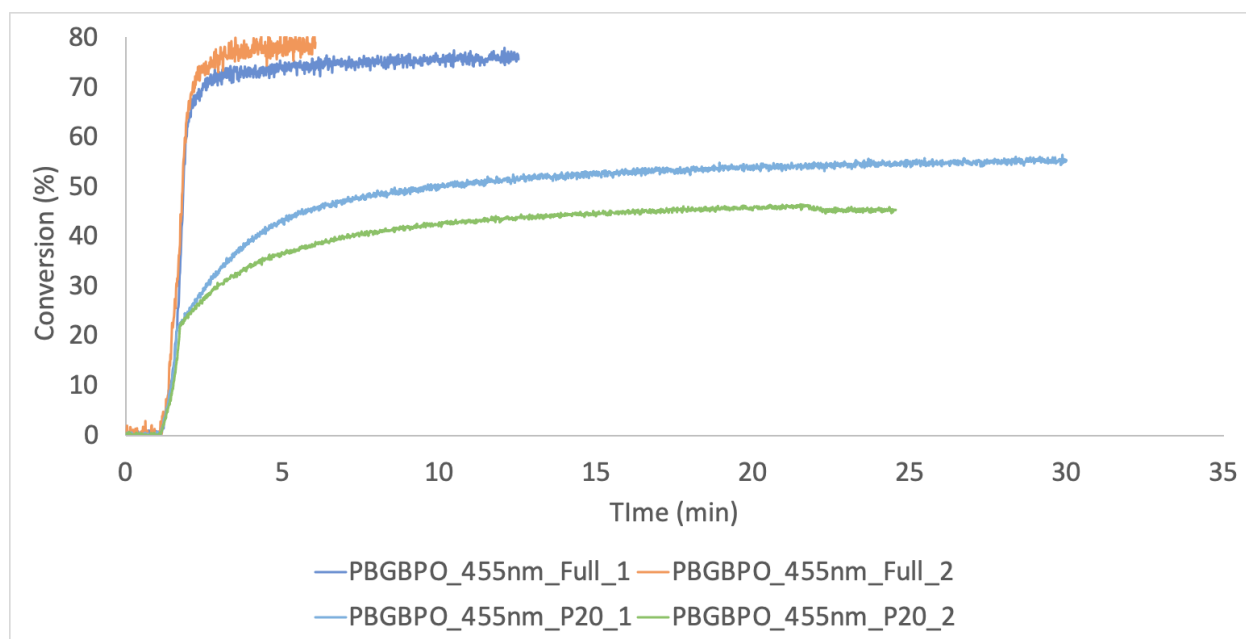


Figure S5.13. Polymerization profiles of ARC-5,7-2OMe-6-Br with BPO under full and 20% partial cure.

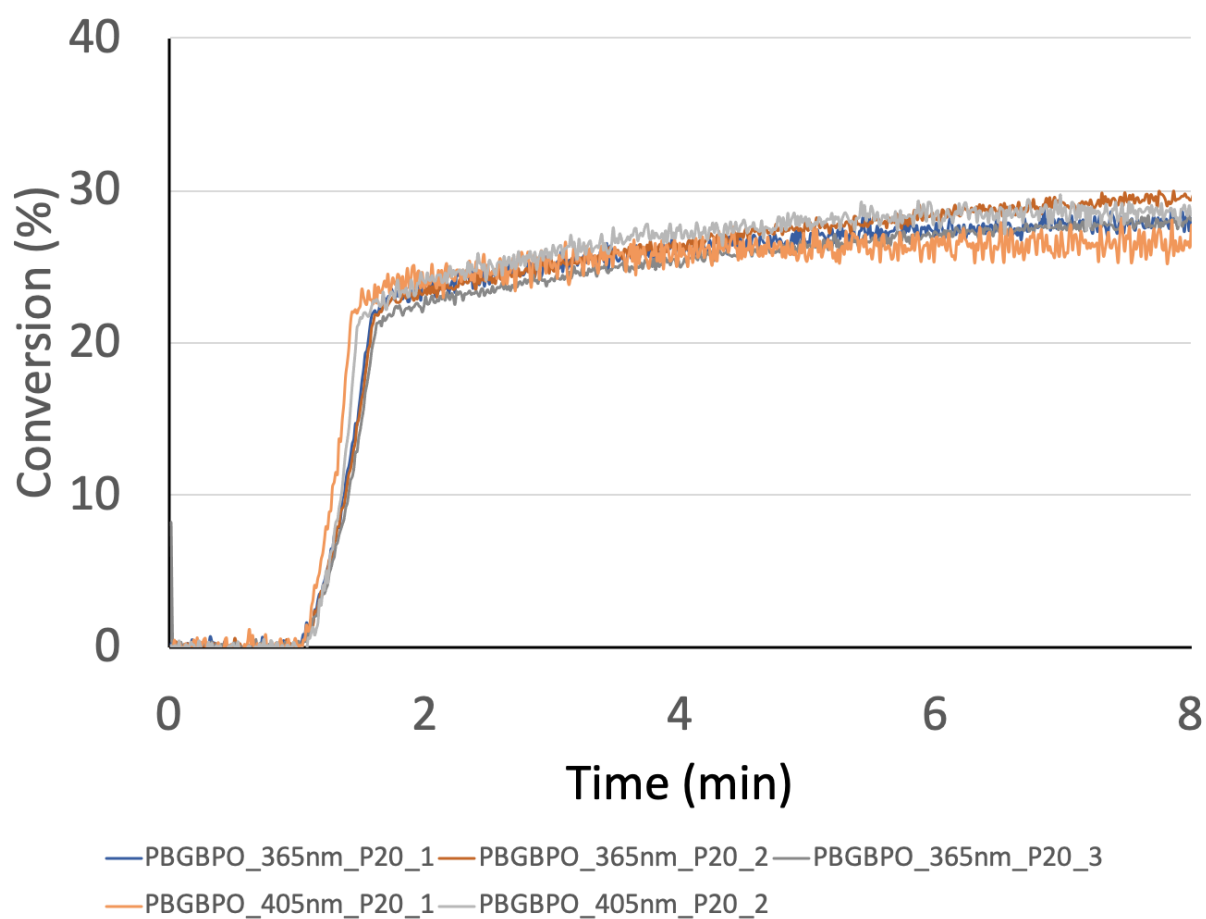


Figure S5.15. Polymerization profiles of ARC-5,7-2OMe-6-Br with BPO under full and 20% partial cure with a 365 nm LED and a 405 nm LED

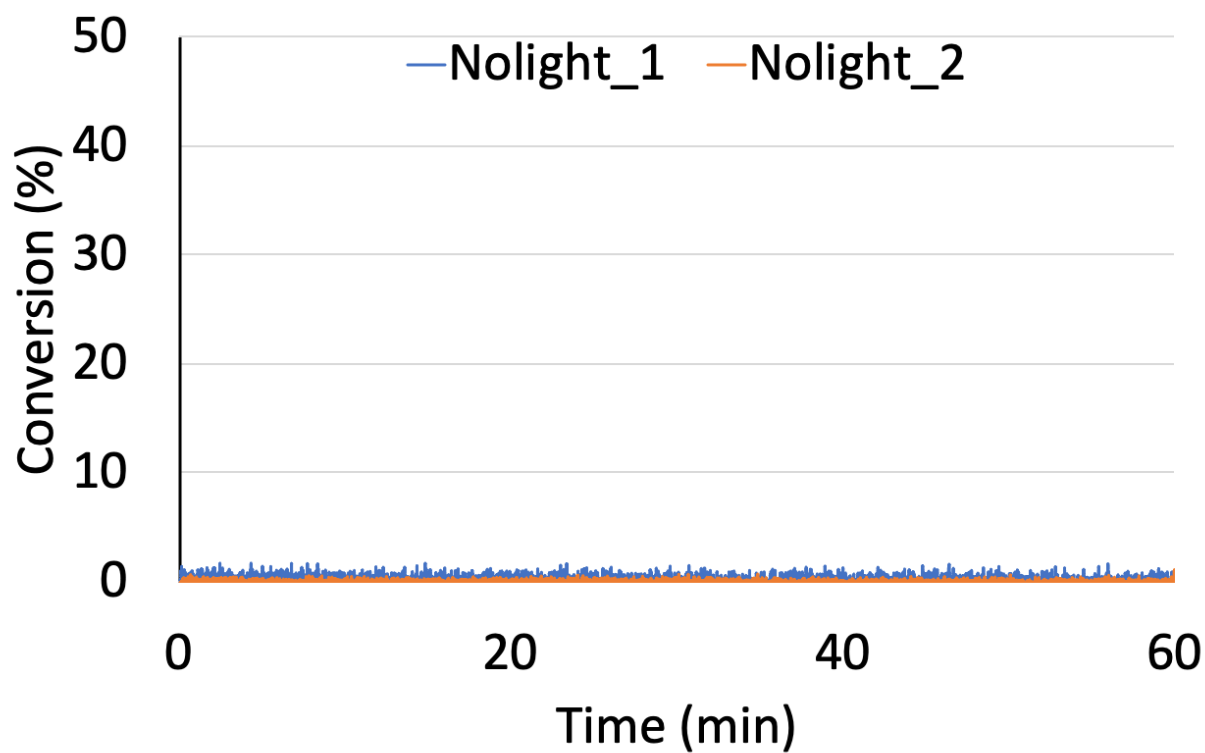


Figure S5.16. Polymerization profiles of ARC-5,7-2OMe-6-Br with BPO in the absence of light

Chapter 6: Conclusions and future work

6.1 Conclusions

Radical-mediated photopolymerization is a disruptive technology that will only increase in the value of its applications over the next several decades due to the increasing use of polymer products and the increasing environmental restrictions on manufacturing. In order for radical photopolymerization to be more universally applicable, however, the decoupling of light dose from conversion is needed for applications that involve various non-ideal photocuring conditions, including irregular 3D-surfaces and non-uniform light exposure as well as strongly light-attenuating resins and thick film situations. In my doctoral studies, I developed new types of radical photoinitiation systems that continue conversion even after the light source is removed. I used a bottom-up approach to rationally design such dark-curing photoinitiation using both computational and experimental methods. I first elucidated the mechanistic details of the amine-peroxide redox polymerization (APRP) in **Chapters 2 and 3** to optimize the initiation reactions between photo-released amine and peroxide that are responsible for the latent dark-curing. Based on this new understanding of the redox initiation, I developed dark-curing photoinitiators with two chromophores that can efficiently absorb respective UV and visible spectra of electromagnetic radiation and demonstrated various capabilities that other conventional photoinitiators do not possess, which I described in **Chapters 4 and 5**. I assert that these new initiators based on redox- and photo-activation set a new standard in the field of radical initiation by improving pre-existing applications or enabling new applications.

In **Chapter 2**, I presented the results of an extensive computational and experimental investigation of the mechanism of the widely used amine-peroxide redox polymerization process. I used quantum chemistry to compute the initiation kinetics of a common redox pair, *N,N*-dimethylaniline and benzoyl peroxide, which allowed me to determine the radical generation mechanisms and that homolysis is the rate-determining step, in disagreement with the prevailing conclusions in this field. Using my new detailed understanding of the detailed mechanism and its associated energetics, including those of the intermediates, I derived a kinetic equation that I then used to correlate computational and experimental kinetic results with $R^2=0.80$ among structurally dissimilar amines. My results also elucidate that primary and secondary amines do not promote redox polymerization because they proceed through a more favorable alternative proton transfer mechanism that does not generate initiating radicals. To discover more effective amines for redox polymerization, I examined different types of tertiary amines and found that aromatic amines with resonant electron-donation and minimal steric hindrance outperformed other nucleophilic amines and non-nucleophilic basic amines, where conjugation between the electron-deficient half-empty p-orbitals of nitrogen and the π -space of their phenyl rings in their amine radical cation intermediate states effectively lowers the rate-determining HM barrier. Finally, I conducted a small-scale computational and experimental screening effort on various *para*- and *N*-substitutions on such aromatic amines to identify *N*-(4-methoxyphenyl)pyrrolidine (MPP) as an initiator that exhibits unprecedented reactivity for redox polymerization relative to other “state-of-the-art” amines. This demonstration of applying quantum chemical methods to predict the reactivity of amines in APRP unlocks an array of opportunities to efficiently search the vast chemical space of amines to discover novel amines with desirable properties for redox polymerization. For example, the discovery of amines with high reactivity may allow rapid *in situ* polymerization that can be

utilized to promote chemically-induced additive manufacturing or spray-coating of large structures in the automotive and aerospace industries. Additionally, amines that possess fast initiation kinetics, such as MPP, can be used at low concentrations, which may facilitate important biomedical materials applications for developing polymers with low toxicity, better aesthetics, and superior mechanical properties, or simply accelerates current manufacturing applications. This study provides a valuable fundamental framework to practitioners to guide the discovery and optimization of initiating systems for their specific applications, as well as providing a framework for other researchers to investigate similar polymerization processes and inner-sphere electron transfer involving organic compounds.

In **Chapter 3**, I have presented an extensive computational investigation of 15 peroxide oxidants to initiate amine-peroxide redox polymerization through a mechanism I previously reported to accurately predict experimental APRP rates. I found that acyl groups not only increase the electrophilicity of peroxides to enhance the S_N2 reaction but also stabilize anion and radical intermediates generated from the parent peroxides. As such, functionalization of acyl groups either through addition of *para*-EWG's (to increase peroxy electrophilicity) or through addition of phenyl rings (to improve resonance stabilization) is imperative for improved redox efficiency. On the other hand, alkyl peroxides may have a low homolysis barrier due to their tertiary carbons stabilizing radical intermediates, yet their reduced electrophilicity at the peroxy bond increases the S_N2 barrier and lowers alkyl peroxides' overall reactivity. While peroxycarbonate structures appeared promising in terms of their predicted initiation kinetics resulting from their higher electrophilicity and stronger resonance, their low thermal stability currently discourages their practical use for accelerated APRP. Inorganic peroxides such as peroxydisulfate and hydrogen peroxide are predicted to perform poorly in APRP initiation of bulk resins. Phthaloyl peroxide,

which appeared to be the most promising candidate from my analysis, does not proceed through the APRP mechanism of an inner-sphere electron transfer, but instead proceeds through an outer-sphere ET to produce non-initiating radicals. However, the ability to switch between different ET mechanisms based on the amine-peroxide pair is nonetheless novel and provides an additional route to modulate the polymerization characteristics as well as chemical and mechanistic insight into novel amine-peroxide redox chemistry; this discovery could enable an entirely new class of redox initiators that leverage outer-sphere ET. Ultimately, I find that benzoyl peroxide remains the gold standard due to its rapid APRP performance and high thermal stability. Furthermore, I demonstrated an APRP direct-writing system leveraging an optimized redox pair, where automated mixing of two resins on a movable platform enabled printing of a spiral polymer. This amine-peroxide direct-writing technology has the potential to be the preeminent form of 3D printing where high filler concentrations and low toxicity is imperative.

In **Chapter 4**, I reported a radical dark-curing photoinitiator (BP-DMPT/BPh₄ + BPO) that defies the conventional RPP paradigm that light dosage must correlate to conversion by enabling substantial dark-phase polymerization activated by light. I used quantum chemical modeling to elucidate a foundational mechanistic understanding of light-phase photochemistry and dark-phase redox-chemistry and then exploited this understanding to design a new photoinitiator that also satisfies the practical constraints imposed by its potential applications. With a computationally predicted successful rational design, I then demonstrated that the dark-curing photoinitiator achieved an additional 25-60% monomer conversion in the dark after light exposure was ceased at 20% conversion, far exceeding the marginal 1-3% dark conversion observed for a conventional photoinitiator (type II control). My computational study and electrochemical and spectroscopic experiments elucidated the origin of high photopolymerization and dark-curing efficiency of the

photoinitiator while a steady-state kinetic analysis suggested that it may be the most photon-efficient photoinitiator to date. This photoinitiator with such high photon efficiency results in four or more initiating radicals per photon while conventional photoinitiators make one or two viable radicals. The resulting dark-cured polymers exhibit properties similar to, or in some cases superior to, polymers obtained by conventional photo-curing. The potential enhancement of polymer properties is not achieved by any other photoinitiators under typical photopolymer conditions. This new class of photoinitiators represents a new and higher standard in energy-efficient photopolymerization, while enabling both the improvement of existing photopolymerization applications and new applications that were previously unattainable because conventional photoinitiators are limited by their inability to cure in depth or with light attenuation. The dark-curing ability automatically corrects initially under-cured regions within a specimen by raising the conversion levels of all regions that received different light exposures. This homogenizes the polymer properties and increases the reliability of photocuring processes. As a result, the dark-curing photoinitiator, which can be readily substituted for conventional photoinitiators in pre-existing formulations, minimizes potential user errors and facilitates higher throughput, higher energy-efficiency, more reliable polymer parts, and lower cost production of superior polymers with lower internal stress.

In **Chapter 5**, I described my extensive use of computational methods, namely time-independent and dependent density functional theories, to search for another dark-curing photoinitiator with a new chromophore that can absorb visible light, which exploited the theoretical insight on the photochemical mechanism from my previous computationally guided UV-absorbing dark-curing photoinitiator studies. I identified 3-acylcoumarine chromophore to be a superior scaffold in photon-absorption by a factor of 10 when compared to benzophenone

chromophore used for the UV-absorption. I then functionalized 3-arylcoumarine at several positions with either methoxy- or chlorine-groups to red-shift the absorption into visible light range. Overall, methoxy groups, particularly at the C₅ and C₇ positions, allowed moderate visible light absorption while chlorine groups universally failed to increase the absorption wavelength. I found that the bathochromic shift from methoxy substitutions at certain positions are primarily due to increased molar absorptivity instead of changes in the maximum absorption. Such high molar absorptivity resulted from increased polarizability that originated from the push-pull character through the long axis of the molecule, evidenced by ground state dipole moments. Based on the findings of the substitution study, I determined that 5,7-dimethoxy-3-arylcourmain would be the desired chromophore with an optimal absorption characteristic, which I confirmed by a simulated UV-Vis spectrum. However, due to the synthetic limitation, 5,7-dimethoxy-6-bromo-3-arylcoumarine with slightly poorer absorption was instead targeted. I then computed the energetics of the proposed photochemical mechanism, which showed that 5,7-dimethoxy-6-bromo-3-arylcoumarin-based dark-curing photoinitiator will perform as efficiently as the benzophenone-based predecessor. After its synthesis, 5,7-dimethoxy-6-bromo-3-arylcoumarine-DMPT/BPh₄ was optically examined to possess molar absorptivities of 5710 M⁻¹ cm⁻¹ at 405 nm and 1620 M⁻¹ cm⁻¹ at 420 nm with weaker blue absorption with 50 M⁻¹ cm⁻¹ at 455 nm and 25 M⁻¹ cm⁻¹ at 470 nm. In addition to visible light absorption, it was found to photo-bleach, which would contribute to an increased depth of curing by reducing the inner filtering effect. Using an NMR, I confirmed that the DMPT amine is indeed generated from 5,7-dimethoxy-6-bromo-3-arylcoumarine-DMPT/BPh₄ and with 77% efficiency. Lastly, I demonstrated its dark-curing capability with 365, 405, and 455 nm light in a methacrylate resin. Based on a steady state analysis, we found the initiator efficiency of 5,7-dimethoxy-6-bromo-3-arylcoumarine-DMPT/BPh₄

without peroxide is 0.65 while its initiator efficiency with benzoyl peroxide increased to 2.82 due to added radicals from redox initiation that does not require light-activation. More importantly, I demonstrated an extensive dark-curing that tripled the initial conversion achieved with a brief light exposure. The new dark-curing photoinitiator with visible absorption will improve many pre-existing applications and enable new applications that conventional visible light photoinitiators do not achieve under non-ideal photocuring conditions, making radical photopolymerization an even more useful technology.

6.2. Future Directions

Throughout my doctoral studies, I used both computational and experimental methods to develop new initiators and demonstrate their unprecedented capabilities. My future direction of this project will involve development of a photoinitiator that can not only dark-cure but also shadow-cure. Such photoinitiators would not be limited by the footprint of light exposure and would continue to cure in unexposed areas, which will revolutionize many polymer applications that involve light-attenuating and 3D-surface specimens. Unexposed areas may be formed in either vertical or horizontal directions due to various non-ideal photocuring conditions. The vertical shadow curing will extend my dark-curing photoinitiator and achieve polymerization in areas where light attenuation is too severe to allow any light exposure. More interestingly, the horizontal shadow curing will enable conversions in the photo-masked area, which has been a long-term aspiration of many photopolymerization practitioners (**Figure 6.1 (a)**). I hypothesized that the same latent redox initiation used in my dark-curing photoinitiator can realize an athermal shadow curing process, where irradiation of photo-base-generators releases amines that can

activate a base-amplifier that undergoes a self-catalytic generation of additional amines (**Figure 6.1 (b)**).

The concept of base-amplifiers (BA) was conceived in 2000.²⁰¹ Arimitsu et al. utilized the 9-fluorenylmethoxycarbonyl (Fmoc) group that is commonly used as a protecting group for amino groups in peptide synthesis. The Fmoc group is degraded by an amine (e.g. piperidine) to release amino groups of the peptides. Instead of amino acids, Arimitsu et al. protected piperidine with the Fmoc group, in which addition of catalytic piperidine degraded base-amplifiers to release additional base molecules, establishing autocatalytic decomposition of the base-amplifier or autocatalytic generation of the amine species. The authors used this system in a base-catalyzed polymerization to increase reaction rates. If base-amplifiers were to be used for radical shadow curing within the amine-peroxide redox polymerization framework, they would have to be completely redesigned, as this autocatalysis was activated by a relatively strong amine and included heat and polar solvents in their reaction conditions. APRP utilizes weakly basic tertiary amines, which may not activate the Fmoc group at room temperature. Therefore, the challenges of enabling shadow-curing are: 1) base amplification of tertiary amine and 2) autocatalysis by a weak base. I have conducted a preliminary work on the development of base-amplifier for shadow-curing and reported the results in **Appendix 7.1**.

Ultimately, the shadow curing photoinitiating system will consist of a photo-base-generator, a base-amplifier, and an oxidant initiator, which leverages my development of both UV- and visible- dark-curing photoinitiators (**Figure 6.1. (c)**). Irradiation will activate a photo-base-generator that releases an amine. This amine either can react with a peroxide to produce initiating radicals or activate a base amplifier to release another amine, which establishes auto-catalysis and amplifies the population of amines. These new amines again may react with peroxide or base-

amplifiers. As amines do not undergo termination processes, they diffuse out of the area initially irradiated. Due to increasing chemical potential from increasing amine concentration, the diffusion to an unexposed area where amines don't exist will be spontaneous and rapid. Such self-propagating reaction diffusion-processes can be dramatically more rapid and efficient than physical diffusion processes, as the former has directionality while the latter is only based on random-walk Brownian motions. I believe that the utilization of both computational and experimental methods is desirable for realizing this goal, as not only do base-amplifying structures need to be designed but also reactions between three components need to be considered. However, when such a shadow curing photoinitiator is developed, it will revolutionize many industrial and medical polymer applications.

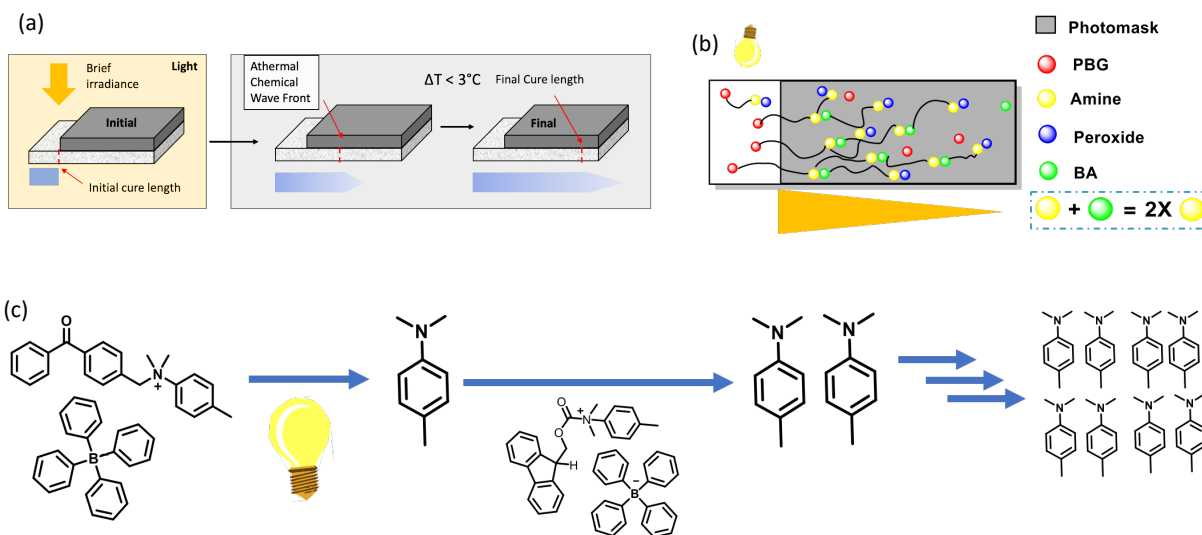


Figure 6.1. (a) Shadow curing demonstration with respect to local conversion. Brief irradiation would cure the exposed areas and activate the shadow curing mechanism, which would form temperature-independent chemical front to cure the un-exposed areas. (b) Schematic of reactive diffusion to enable athermal shadow curing process. When a photo-base-generator (PBG) generate an amine, this amine can react with a base-amplifier (BA) to produce two amines

or react with a peroxide to give initiating radicals. Although these amines diffuse omnidirectionally via Brownian motion, increasing local amine concentration via auto-catalytic reactions will direct their collective motion into un-exposed areas of low amine concentration as reactive diffusion. (c) Molecular depiction of autocatalytic chemistry that enables shadow curing. Upon irradiation, a PBG generates an amine that reacts with a BA to produce two amines. This process can repeat to produce a high concentration of amines that can direct their motion towards un-exposed areas and react with peroxides.

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Appendix

7.1 Preliminary work on the development of base-amplifiers for shadow curing

My preliminary work regarding the development of base-amplifier for shadow-curing is to elucidate the energetics of the mechanism. The potential BA scaffolds included 9-fluorenylmethyl,²⁰¹ malonate,²⁰² phenylsulfonylethyl,²⁰³ nitropentanyl,²⁰⁴ and oxidized thioxanthanyl carbamates.²⁰⁵ All base-amplifiers share an analogous mechanism, where a catalytic amine deprotonates a BA. The anionic BA rearranges electrons that leads to elimination and subsequent decarboxylation. Lastly, anionic amine deprotonates ammonium to establish two amines (**Figure 7.1**). I computed the energetics of a model chemistry using FMOC and hexylamine. Deprotonation and decarboxylation were endergonic while elimination and protonation were exergonic (**Figure 7.2**). Deprotonation is endergonic (22.4 kcal/mol) due to the generation of ionic species in non-polar solvent (ethyl acetate). If an analogous reaction occurs in a polar solvent (DMSO), the thermodynamics is more favorable (5.8 kcal/mol). The elimination step is promoted by aromatization that stabilizes the reaction by nearly 60 kcal/mol (**Figure 7.3**). Decarboxylation was found to be the rate-determining step in the mechanism with the model chemistry with an extremely unfavorable endergonicity of 68.4 kcal/mol. This is likely why Arimitsu et al. needed to heat the reaction to 100 °C.²⁰⁶ However, despite the extreme endergonicity, this reaction is irreversible because CO₂ can exit the reacting system as vapor. When using aniline instead of cyclohexyl amine, the rate-determining decarboxylation became more favorable by 26.3 kcal/mol, yielding 42.1 kcal/mol while all other reactions became less favorable to a similar degree (**Figure 7.4**). This mechanistic study directed my efforts on designing scaffolds with low deprotonation and decarboxylation barriers.

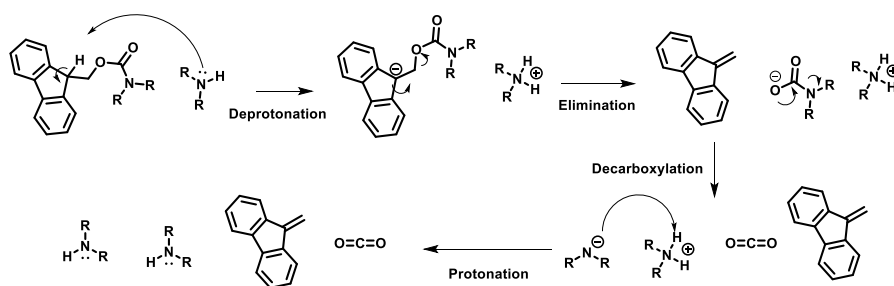


Figure 7.1 Base-amplifying mechanism using the base-labile 9-fluorenylmethoxycarbonyl protecting group through deprotonation, elimination, decarboxylation, and protonation steps. The mechanism begins with a sufficiently basic amine deprotonating the benzylic proton of the base-amplifier (Deprotonation). Then, the lone pair electron rearrange themselves to form an aromatic compound with anionic benzoyloxy leaving group (Elimination). The leaving group removes carbon dioxide to generate a de-protonated anionic amine that acquires a proton from the previous amine to give two amines.

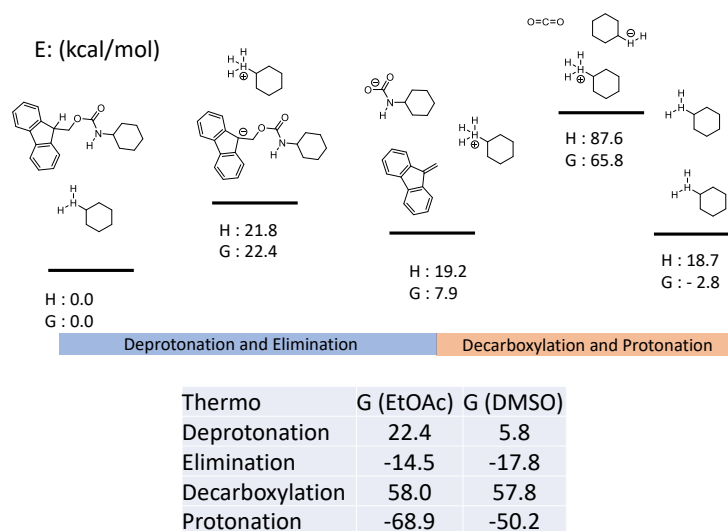


Figure 7.2 Computed energetics of a model chemistry using FMOC and cyclohexylamine simulated in either ethyl acetate (EtOAc) and dimethyl sulfoxide (DMSO). Deprotonation of the FMOC group resulted into two ionic species that are relatively unstable in EtOAc and more stable in DMSO. Elimination of the leaving group has a favorable thermodynamics due to the

aromatization in both solvents. Decarboxylation has a very unfavorable thermodynamics due to the loss of resonance in the leaving group but proceeds as the carbon dioxide product can leave the reaction system. Lastly, protonating the anionic amine quenches ionic charges and stabilizes the products of two amines. Deprotonation and decarboxylation are high-barrier reactions that should be the focus of the future study.

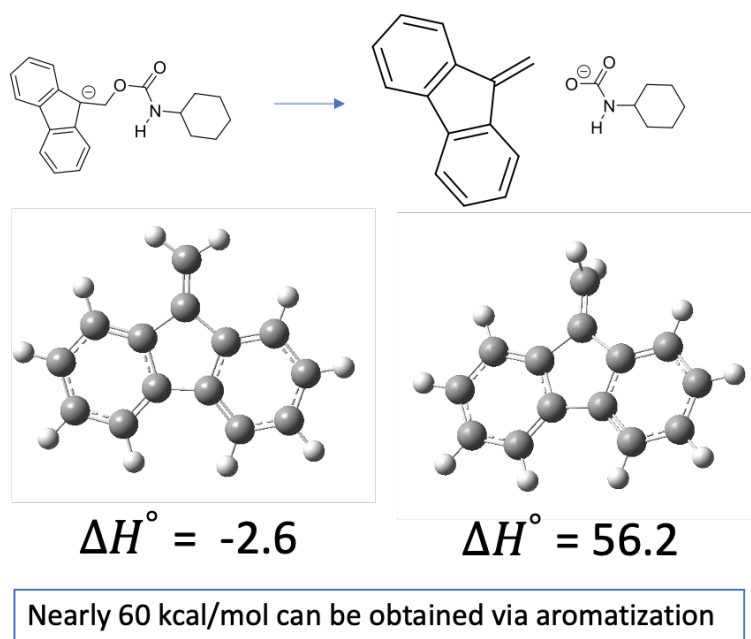


Figure 7.3. Aromatization as the driving force for base amplification. In FMOC, aromatization during the elimination step provides stabilization of ~ 60 kcal/mol. Therefore, incorporation of aromatization as part of the mechanism should be sought after.

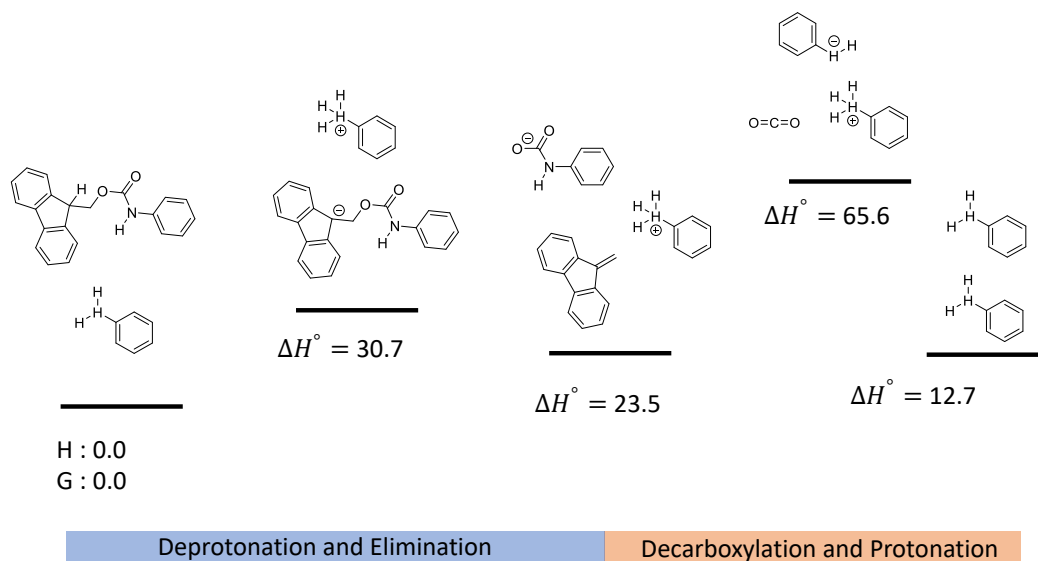


Figure 7.4 Computed energetics of a model chemistry using Fmoc and aniline. Deprotonation and decarboxylation are still high-barrier reactions, although decarboxylation is more favorable with aniline than with cyclohexylamine. Due to the low basicity of aniline, the deprotonation is less thermodynamically favored.