Published in final edited form as:

Dent Mater. 2015 September ; 31(9): 1075–1089. doi:10.1016/j.dental.2015.06.005.

Hexaarylbiimidazoles as Visible Light Thiol–Ene Photoinitiators

Dowon Ahn^{#a}, Sameer S. Sathe^{#b}, Brian H. Clarkson^c, and Timothy F. Scott^{a,b,*}

^a Macromolecular Science and Engineering, University of Michigan, Ann Arbor, MI 48109, United States

^b Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, United States

^c Department of Cariology, Restorative Sciences and Endodontics, University of Michigan, Ann Arbor, MI 48109, United States

[#] These authors contributed equally to this work.

Abstract

Objectives—The aim of this study is to determine if hexaarylbiimidazoles (HABIs) are efficient, visible light-active photoinitiators for thiol–ene systems. We hypothesize that, owing to the reactivity of lophyl radicals with thiols and the necessarily high concentration of thiol in thiol–ene formulations, HABIs will effectively initiate thiol–ene polymerization upon visible light irradiation.

Methods—UV-vis absorption spectra of photoinitiator solutions were obtained using UV-vis spectroscopy, while EPR spectroscopy was used to confirm radical species generation upon HABI photolysis. Functional group conversions during photopolymerization were monitored using FTIR spectroscopy, and thermomechanical properties were determined using dynamic mechanical analysis.

Results—The HABI derivatives investigated exhibit less absorptivity than camphorquinone at 469 nm; however, they afford increased sensitivity at this wavelength when compared with bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide. Photolysis of the investigated HABIs affords lophyl radicals. Affixing hydroxyhexyl functional groups to the HABI core significantly improved solubility. Thiol–ene resins formulated with HABI photoinitiators polymerized rapidly upon irradiation with 469 nm. The glass transition temperatures of the thiol–ene resin formulated with a bis(hydroxyhexyl)-functionalized HABI and photopolymerized at room and body temperature were 49.5±0.5°C and 52.2±0.1°C, respectively.

Significance—Although thiol–enes show promise as continuous phases for composite dental restorative materials, they show poor reactivity with the conventional camphorquinone/tertiary

* Corresponding author at: Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, United States. Tel: +1 734 763 3493; fax: +1 734 763 0459. tfscott@umich.edu (T. F. Scott). ahndowon@umich.edu (D. Ahn), sssathe@umich.edu (S. S. Sathe), bricla@umich.edu (B. H. Clarkson)

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

amine photoinitiation system. Conversely, despite their relatively low visible light absorptivity, HABI photoinitiators afford rapid thiol–ene photopolymerization rates. Moreover, minor structural modifications suggest pathways for improved HABI solubility and visible light absorption.

Keywords

Thiol–ene; photoinitiator; HABI; camphorquinone

1. Introduction

Resin formulations primarily composed of dimethacrylate-based monomers, including bisphenol A diglycidyl ether dimethacrylate (bisGMA), triethyleneglycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA), have been commonly utilized as the continuous polymeric phase in composite dental restorative materials for several decades [1, 2]. The long-standing success of these materials is attributable to several factors, including their high modulus and glass transition temperature upon polymerization, and adequate hydrophobicity and concomitant low water sorption. Unfortunately, the radical-mediated polymerization of these dimethacrylates is strongly inhibited by oxygen [3, 4], yielding tacky surfaces owing to incomplete surface polymerization. Additionally, as the molecular weight evolution of these polymerizations proceeds *via* chain-growth [5, 6], large amounts of unreacted, extractable monomer often remain after polymerization has ceased, potentially leading to acute toxicity or sensitization [7, 8]. Moreover, as this chain-growth mechanism yields a low gel point conversion, frustration of the shrinkage accompanying polymerization occurs early in the reaction, resulting in the development of high shrinkage stress levels in the polymerized material [1, 9, 10]. Attempts to mitigate high shrinkage stress, the clinical consequences of which include marginal discoloration and debonding, enamel and dentin crack formation, and secondary caries [9, 11, 12], by limiting the conversion *via* the utilization of resin formulations that vitrify early during their polymerization in turn affords materials with undesirably high residual methacrylate monomer concentrations [13, 14].

In recent years, several polymerization mechanisms have emerged as potential alternatives to the prevalent dimethacrylate polymerization for composite dental restorative materials, including the cation-mediated ring-opening of oxiranes [15, 16], copper(I)-catalyzed azide–alkyne cycloadditions [17], and radical-mediated thiol–ene additions [13, 18–20]. The utilization of thiol–ene polymerizations for dental restorative materials is particularly promising owing to their potential as toxicologically safer alternatives to acrylics [13] and their unique and desirable combination of characteristics relative to other radical polymerization systems [14, 19, 20]. In contrast to the chain-growth mechanism typically associated with (meth)acrylate systems, thiol–ene polymerizations proceed *via* a radical-mediated step-growth mechanism between multifunctional thiol and non-homopolymerizable vinyl monomers [21], where functional groups can coreact on any size monomer, oligomer, or polymer, such that the molecular weight grows geometrically [22]. Here, a thiyl radical adds to a vinyl, which subsequently abstracts a hydrogen from a thiol, generating a thioether moiety and regenerating a thiyl radical (see Fig. 1a). These thiol–ene systems demonstrate nearly all of the advantages of typical radical-mediated polymerizations in that they polymerize rapidly, do not require solvents for processing, are

optically clear, and provide an excellent range of mechanical properties [23]. Additionally, owing to their step-growth polymerization mechanism, thiol–ene polymerizations display delayed gelation [24], form homogeneous polymer networks with very narrow glass transitions [13], and exhibit less shrinkage per mole of double bonds reacted ($12\text{--}15\text{ cm}^3\cdot\text{mol}^{-1}$ for thiol–enes versus $22.5\text{ cm}^3\cdot\text{mol}^{-1}$ for methacrylates) [13, 25], leading to reduced polymerization shrinkage stress [13]. Furthermore, thiol–ene polymerizations demonstrate extraordinary resistance to oxygen inhibition [21], attributable to facile hydrogen abstraction by peroxy radicals from the ubiquitous thiol.

As composite dental restorative materials are typically cured *in situ* via photopolymerization, visible light irradiation is used in preference to ultraviolet light for clinical acceptability, necessitating the incorporation of a visible light-absorbing photoinitiator in the resin formulation. The most commonly employed visible light-active photoinitiator for dimethacrylate-based formulations is camphorquinone (CQ) which, in order to afford sufficient radical-generation activity, is used in combination with a tertiary amine [26]. Thus, CQ is a ‘Type II’ photoinitiator (i.e., H-abstraction) where, upon photoexcitation, it abstracts a hydrogen from the tertiary amine H-donor to yield a reactive, initiating radical centered on the amine and a relatively unreactive camphorquinone-centered radical [27]. As hydrogen abstraction only proceeds while the Type II photoinitiator remains in its excited state, the lifetime of which is often short [28], the radical generation quantum yield for these compounds can be low. In contrast, ‘Type I’ photoinitiators undergo direct homolysis upon irradiation to yield two polymerization-initiating radicals at typically high radical generation efficiencies [28]. Moreover, the necessity for Type II photoinitiators to be formulated with a co-initiator can lead to potentially deleterious consequences such as co-initiator discoloration and toxicity [29].

Although the CQ/tertiary amine photoinitiation system is employed extensively in dimethacrylate dental formulations, it displays poor reactivity in thiol–ene-based resins [30, 31]. Conversely, direct-cleavage-type photoinitiators have been shown to efficiently initiate thiol–ene formulations upon irradiation [13, 22, 31]. Notably, whereas the absorbance peak of CQ is centered at approximately 470 nm [32, 33], only a very few single component photoinitiators, such as benzoyl phosphine oxides [34], titanocenes [35, 36], and benzoyl germanes [29], absorb well into the visible spectral region. Hexaarylbiimidazoles (HABIs), a class of photoinitiators first synthesized by Hayashi and Maeda in 1960 [37], are presented here as promising direct cleavage, visible light-active photoinitiators specifically for thiol–ene systems. Upon irradiation, HABIs undergo homolytic cleavage to yield two lophyl radicals (Fig. 1b) that are unreactive with oxygen and show slow recombination rates [38], attributable to steric hindrance and electron delocalization [39]; indeed, HABI photoinitiators show no initiation activity in (meth)acrylate formulations without the presence of a hydrogen-donating coinitiator [40]. Thiols are commonly used as coiniciators in conjunction with HABIs [40], where hydrogen abstraction by the HABI-derived lophyl radicals yields initiating thiyl radicals (Fig. 1b), suggesting a particular suitability for HABI photoinitiators in thiol–ene formulations. Unfortunately, commercial HABIs often exhibit poor absorption in the visible spectrum, sometimes requiring a photosensitizer, and low solubility in common resins and organic solvents [41, 42]. Here, we examine the hypothesis

that HABIs will effectively initiate thiol–ene polymerization upon visible light irradiation by describing the synthesis of a novel, dihydroxy-functionalized HABI with enhanced solubility and visible light absorptivity, and investigating its utilization as a photoinitiator in thiol–ene formulations, focusing on its influence on the polymerization kinetics and thermomechanical properties of the resultant polymers.

2. Materials and methods

2.1. Materials

The monomers bisphenol A bis(2-hydroxy-3-methacryloxypropyl) ether (bisGMA, Esstech Inc., Essington, PA, USA) and triethylene glycol dimethacrylate (TEGDMA, Esstech) were formulated as a mixture consisting of 70 wt% bisGMA and 30 wt% TEGDMA and used as a model dimethacrylate-based resin. The monomers pentaerythritol tetra-3-mercaptopropionate (PETMP, Evans Chemetics, Teaneck, NJ, USA) and 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO, Sigma-Aldrich, St. Louis, MO, USA) were similarly formulated as a mixture, such that the thiol (i.e., mercapto) and ene (i.e., allyl) functional groups were present at a 1:1 stoichiometric ratio, and used as a model thiol–ene resin. Prior to thiol and ene component mixing, 0.01 wt% tris(*N*-nitroso-*N*-phenylhydroxylamino)aluminum (Q1301, Wako Chemicals, Richmond, VA, USA) was added to the PETMP as a radical polymerization inhibitor to preclude premature thiol–ene polymerization. Camphorquinone (CQ, Esstech), ethyl 4-dimethylaminobenzoate (EDAB, Esstech), bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819, BASF, Florham Park, NJ, USA), 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole (*o*-Cl-HABI, TCI America, Portland, OR, USA), and 2,2'-bis(2-chloro-4-hexan-1-ol-phenoxy)-4,4',5,5'-tetraphenyl-1,2'-biimidazole (*p*-HOH-HABI) were used as visible light-active photoinitiating systems. CQ was used in conjunction with EDAB as a co-initiator (1 wt% CQ:0.5 wt% EDAB). Irgacure 819, *o*-Cl-HABI, and *p*-HOH-HABI were used at the concentrations as indicated in the text. All commercial monomers and photoinitiators were used without further purification, the synthesis of *p*-HOH-HABI is described in reference [43], and the structures of all materials used are shown in Fig. 2.

The solubility of the HABI photoinitiators was determined by addition of a photoinitiator to a liquid monomer or organic solvent (by weight ratio) and heating the combined materials in an oven (50–60°C) while mixing. Samples were then kept at room temperature for 30 minutes and, if no recrystallization occurred, the photoinitiator loading was recorded as soluble. Photoinitiator concentration increments of 5 wt% were employed in this study. Thus, for example, the solubility of *o*-Cl-HABI in dimethylformamide (DMF) is <20 wt%, which means that its solubility in DMF is above 15 wt% but below 20 wt%.

2.2. Methods

2.2.1. Light sources and intensity measurement—Blue light was provided by an LED-based dental lamp (G-Light, GC America) equipped with a longpass filter (435 nm cut-on wavelength) yielding a single emittance curve peak centered at 469 nm (full width at half maximum (FWHM) 29 nm), while violet light was provided by a collimated, LED-based illumination source (Thorlabs M405L2-C) with an emittance centered at 405 nm

(FWHM 13 nm), used in combination with a current-adjustable LED driver (Thorlabs LEDD1B) for intensity control. UV light was provided by a high pressure mercury vapor lamp (EXFO Acticure 4000) equipped with a filter to isolate the 365 nm spectral line (FWHM 10 nm). Irradiation intensities were measured with an International Light IL1400A radiometer equipped with a broadband silicon detector (model SEL033), a 10× attenuation neutral density filter (model QNDS1), and a quartz diffuser (model W).

2.2.2. UV-vis Spectrophotometry—UV-visible spectrophotometry was performed on 1 wt% samples of photoinitiator in toluene using an Agilent Technologies Cary 60 UV-Vis spectrophotometer. Spectra were collected from 200 to 800 nm on solutions using a 1 mm pathlength quartz cuvette both in the dark and under irradiation once the radical concentration reached equilibrium. HABI photodissociation and subsequent recombination was examined by monitoring 554 nm and 598 nm for *o*-Cl-HABI and *p*-HOH-HABI, respectively, the wavelengths where the visible light absorbance by the generated lophyl radicals was greatest (i.e., λ_{max}), while the sample solutions in the cuvette were irradiated with 405 nm for 9.5 minutes to ensure radical concentration equilibration, then for a further 10 minutes after the light was turned off.

2.2.3. EPR Spectroscopy—Electron paramagnetic resonance (EPR) spectroscopy was performed on 1 wt% samples of HABI photoinitiators in toluene using a Bruker EMX spectrometer. A TE₁₀₂ cavity (ER4102ST, Bruker), 100 kHz modulation frequency, and 1 G_{pp} modulation amplitude were used for all experiments. Optical access within the cavity was afforded by a 10 mm × 23 mm grid providing 50% light transmittance to the sample. All sample solutions were held in a 3.2 mm inner diameter quartz EPR sample tube which was inserted into the spectrometer cavity for analysis. The sample solutions were irradiated *in situ* with 405 nm light at 10 mW·cm⁻² and spectra were collected once the radical concentration reached steady state. All experiments were performed at room temperature.

2.2.4. FTIR Spectroscopy—Resin formulations were introduced between glass microscope slides separated by spacers (250 μm thick for bisGMA/TEGDMA and 50 μm thick for PETMP/TATATO) to maintain constant sample thickness during polymerization. Each sample was placed in a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a horizontal transmission accessory, as described elsewhere [44], and spectra were collected from 2000 to 7000 cm⁻¹ at a rate of 3 every 2 seconds. The functional group conversion upon irradiation was determined by monitoring the disappearance of the peak area centred at 2571 cm⁻¹ corresponding to the thiol group stretch, 3083 cm⁻¹ corresponding to the allylic vinyl group stretch, and 6164 cm⁻¹ corresponding to the methacrylate group stretch. The respective sample thicknesses for methacrylate and thiol-ene formulations were selected to ensure that the functional group peaks remained within the linear regime of the instrument detector while affording good signal to noise and maintaining optically thin and isothermal polymerization conditions. All experiments were performed in triplicate, and the photoinitiator concentrations and irradiation intensities were as indicated in the figure captions.

2.2.5. Dynamic Mechanical Analysis—Cross-linked polymer films were prepared from bisGMA/TEGDMA formulations containing 1 wt% CQ/0.5 wt% EDAB and from PETMP/TATATO formulations containing 1 wt% *p*-HOH-HABI which were polymerized between glass microscope slides separated by 250 μm thick spacers for 20 minutes at either 23°C (room temperature) or 37°C (body temperature) under 469 nm irradiation at 10 $\text{mW}\cdot\text{cm}^{-2}$. Samples of approximately 15 mm $\times$ 5 mm $\times$ 0.25 mm were cut from the cured films and mounted in a TA Instruments Q800 dynamic mechanical analyzer equipped with a film tension clamp. Experiments were performed at a strain and frequency of 0.1% and 1 Hz, respectively, scanning the temperature from -20°C to 200°C twice at $1^{\circ}\text{C}\cdot\text{min}^{-1}$, and the elastic moduli (E') and $\tan \delta$ curves were recorded; the repeated temperature scan was used to determine the influence of dark polymerization at temperatures greater than the glass transition temperature (T_g). The T_g was assigned as the temperature at the $\tan \delta$ curve peak.

3. Results

3.1. HABI Absorbance and Photolysis

The UV-vis absorption spectra presented in Fig. 3 show the absorption by solutions of (a) *o*-Cl-HABI and (b) *p*-HOH-HABI both in the dark and under 405 nm irradiation, and the absorbance and molar absorptivity of the four photoinitiating systems examined in this study at three wavelengths tabulated in Table 1. Both HABIs display extended absorption tails well into the visible spectral region; however, whereas *o*-Cl-HABI displays higher absorbance at shorter wavelengths, the absorbance tail of *p*-HOH-HABI extends further into the visible and hence affords higher absorbance in the blue region of the spectrum (i.e., 469 nm). In contrast, CQ exhibits good absorptivity at 469 nm but absorbs poorly at 405 nm and 365 nm. Finally, Irgacure 819 demonstrates negligible absorbance at 469 nm but relatively strong absorbance at 405 nm and 365 nm.

The solubilities of *o*-Cl-HABI and *p*-HOH-HABI in the triallyl monomer TATATO and two common, polar organic solvents are tabulated in Table 2. Although *o*-Cl-HABI is reasonably soluble in the solvents examined, it exhibits limited solubility in the allylic monomer. Conversely, *p*-HOH-HABI is freely soluble in the monomer and both solvents.

During irradiation, these HABI photoinitiator solutions turn indigo, absorbing strongly throughout the visible spectrum with absorbance peaks at 554 and 598 nm for *o*-Cl-HABI and *p*-HOH-HABI, respectively. EPR spectra (Fig. 3a and 3b, inset) indicate an absence of radicals in the as-formulated HABI solutions but confirm significant radical formation upon irradiation, establishing the indigo color generation as attributable to HABI-derived lophyl radical formation (see Fig. 1b) [38, 45]. As shown in Fig. 4, the photo-generated lophyl radicals are uncommonly stable in the absence of hydrogen abstraction source where the HABI photolysis is completely reversible and lophyl radical recombination proceeds over several minutes. Conversely, when formulated in a thiol–ene resin, the indigo color otherwise generated upon irradiation is completely eliminated as the lophyl radicals rapidly abstract hydrogens from the prevalent thiol functional groups.

3.2. Photopolymerization Kinetics – Influence of Photoinitiator

BisGMA/TEGDMA formulations were prepared with four different photoinitiation systems – CQ/EDAB, Irgacure 819, *o*-Cl-HABI and *p*-HOH-HABI – at 1 wt% and their photopolymerization kinetics were examined using FTIR spectroscopy (see Fig. 5). The photopolymerization of these dimethacrylate-based resins was initiated upon exposure to blue light at 469 nm, a wavelength commonly emitted by contemporary LED dental curing units [46, 47], and matching the CQ visible absorbance peak [32, 33], and at several irradiation intensities. Increased incident irradiation intensities afforded correspondingly faster methacrylate polymerization rates and, after the 4 minute irradiation period, raised methacrylate conversions (Fig. 5a). A short polymerization induction period upon irradiation was observed for all CQ/EDAB-containing methacrylate formulations, monotonically decreasing from 12 seconds to 2 seconds with raised intensity from 1 mW·cm⁻² to 20 mW·cm⁻². Conversely, methacrylate polymerization only proceeded upon irradiation of the bisGMA/TEGDMA formulated with Irgacure 819 at the highest intensity (i.e., 20 mW·cm⁻²) after a 1.5 minute induction period (see Fig. 5b), and the resultant polymerization rate was markedly slower than that for the CQ/EDAB-formulated system under 1 mW·cm⁻² irradiation. The bisGMA/TEGDMA formulation containing HABI photoinitiators did not exhibit observable polymerization under any of the applied irradiation conditions.

PETMP/TATATO formulations were similarly prepared with each photoinitiator at 1 wt% and their photopolymerization kinetics when exposed to 469 nm light were examined using FTIR spectroscopy (Fig. 6). All of the examined formulations displayed increased thiol–ene polymerization rates as the incident irradiation intensity was raised. Moreover, although the resins were formulated with an initial 1:1 thiol to allyl functional group stoichiometry, allyl consumption consistently proceeded faster than that of thiol; this allyl and thiol conversion deviation increased throughout the polymerization. Additionally, no distinct polymerization induction period was observed for any system even at the lowest irradiation intensity. The photopolymerization rates for CQ/EDAB- and Irgacure 819-containing formulations were similar, both yielding allyl and thiol conversions of 50% and 44%, respectively, after 4 minutes of irradiation at an intensity of 20 mW·cm⁻² (Fig. 6a and 6b). In contrast, the HABI-containing thiol–ene formulations displayed markedly faster photopolymerization rates than either the CQ/EDAB- or Irgacure 819-containing formulations, with the *p*-HOH-HABI affording approximately twice the polymerization rate of the *o*-Cl-HABI system. After 4 minutes of irradiation at 20 mW·cm⁻², the *o*-Cl-HABI-containing formulation yielded allyl and thiol conversions of 76.4±0.8% and 70.7±0.9%, respectively (Fig. 6c), while the *p*-HOH-HABI-containing formulation yielded allyl and thiol conversions of 81.3±0.8% and 74.5±0.3%, respectively (Fig. 6d). Furthermore, whereas the maximum polymerization rate (R_{p_max}) for the Irgacure 819-containing formulation occurs at the onset of polymerization, R_{p_max} occurs at 21.0±0.6% and 41.8±0.4% for the CQ/EDAB- and both HABI-containing formulations, respectively, irrespective of the incident irradiation intensity (Fig. 6c and 6d).

To ascertain the ultimate conversions of both bisGMA/TEGDMA and PETMP/TATATO upon vitrification for isothermal photopolymerizations at room temperature, the conversion

trajectories of resins formulated with 1 wt% photoinitiator were monitored during irradiation with 469 nm light at $10 \text{ mW}\cdot\text{cm}^{-2}$ for extended periods, as presented in Fig. 7. Photopolymerization of the methacrylate-based resin formulated with CQ/EDAB proceeded rapidly and vitrified at $61.9\pm1.1\%$ conversion while, under the same irradiation conditions, the Irgacure 819-containing methacrylate formulation exhibited a long, ~12 minute induction period prior to polymerization and did not approach vitrification after over 19 minutes of irradiation, having attained only 33% conversion (single run) after the elapsed irradiation time (Fig. 7a). Notably, neither HABI-containing methacrylate formulation demonstrated any observable photopolymerization, even over this extended irradiation. In contrast, photopolymerization proceeded upon irradiation with no observable induction period for all examined PETMP/TATATO formulations (Fig. 7b). Although the conversion for the CQ/EDAB- and Irgacure 819-containing formulations was still increasing after 20 minutes of irradiation, the *p*-HOH-HABI-containing thiol–ene formulation had vitrified with allyl and thiol conversions of $83.7\pm1.2\%$ and $76.1\pm0.7\%$, respectively, while the *o*-Cl-HABI-containing thiol–ene resin had slightly lower allyl and thiol conversions of $82.6\pm0.1\%$ and $74.5\pm0.3\%$, respectively, after 20 minutes irradiation.

3.3. Photopolymerization Kinetics – Influence of Irradiation Wavelength

As contemporary dental lamps can emit a variety of wavelengths [47–49], the influence of the incident irradiation wavelength on photopolymerization kinetics was examined by subjecting the methacrylate systems to three different irradiation wavelengths, including 469 nm (blue), 405 nm (violet), and 365 nm (near UV), at an intensity of $1 \text{ mW}\cdot\text{cm}^{-2}$. For the CQ/EDAB-containing bisGMA/TEGDMA formulation, the induction time increased and photopolymerization rate decreased for progressively shorter incident irradiation wavelengths, whereas the Irgacure 819-containing methacrylate resin did not polymerize after 4 minutes of 469 nm irradiation but exhibited very similar induction times and polymerization rates under 405 and 365 nm irradiation (Fig. 8a and 8b). Again, no conversion was observed for either HABI-containing methacrylate resin.

Equivalent experiments examining the irradiation wavelength on PETMP/TATATO photopolymerization were also performed. For the CQ/EDAB-containing thiol–ene formulation, the photopolymerization rate was very low, yielding conversions of <3% after 4 minutes irradiation, irrespective of wavelength. In contrast, although the Irgacure 819-containing resin also polymerized very slowly under 469 nm irradiation, 405 nm and 365 nm irradiation both afforded rapid thiol–ene photopolymerization with that photoinitiator at near-identical rates throughout the 4 minute irradiation period. HABI-containing PETMP/TATATO resins similarly exhibited very low photopolymerization rates under these reaction conditions at 469 nm irradiation; however, thiol–ene polymerization proceeded rapidly under 405 nm and even more rapidly under 365 nm irradiation for both HABI photoinitiators. Notably, the thiol–ene resin formulated with *o*-Cl-HABI polymerized more rapidly than that formulated with *p*-HOH-HABI at both 405 and 365 nm. Nevertheless, the *p*-HOH-HABI-containing thiol–ene resin achieved allyl and thiol conversions of $81.9\pm0.5\%$ and $74.4\pm0.9\%$ after 4 minutes irradiation at 365 nm, slightly higher than the equivalent *o*-Cl-HABI system that attained allyl and thiol conversions of $79.6\pm0.4\%$ and $71.7\pm0.2\%$, respectively, under the same irradiation conditions.

3.4. Viscoelastic Properties of Cured Films

The viscoelastic properties of photopolymerized bisGMA/TEGDMA and PETMP/TATATO films were examined using DMA (see Fig. 10, summary of results tabulated in Table 3). The bisGMA/TEGDMA samples attained methacrylate conversions of $60.3 \pm 0.8\%$ and $68.6 \pm 0.7\%$ when photopolymerized at 23°C and 37°C , respectively; however, after the first temperature ramp in the DMA, the methacrylate conversions increased to $85.3 \pm 0.5\%$ and $87.3 \pm 0.4\%$ for the samples initially photopolymerized at 23°C and 37°C , respectively. The TATATO/PETMP samples attained allyl and thiol conversions of $85.4 \pm 0.6\%$ and $77.5 \pm 0.5\%$, respectively, when photopolymerized at 23°C , and allyl and thiol conversions of $86.1 \pm 0.5\%$ and $81.4 \pm 0.5\%$, respectively, when photopolymerized at 37°C . After the first DMA temperature ramp, the allyl and thiol conversions increased to $99.1 \pm 0.2\%$ and $93.7 \pm 0.3\%$, respectively, for the TATATO/PETMP samples initially photopolymerized at 23°C , while the allyl and thiol conversions increased to $99.6 \pm 0.1\%$ and $94.3 \pm 0.2\%$, respectively, for the samples initially photopolymerized at 37°C . The FWHM of the second DMA temperature ramp $\tan \delta$ curve peaks for the bisGMA/TEGDMA samples initially photopolymerized at 23°C and 37°C (Fig. 10b) were $75.2 \pm 0.5^\circ\text{C}$ and $76.7 \pm 0.5^\circ\text{C}$, respectively. Conversely, the FWHM of the second DMA temperature ramp $\tan \delta$ curve peaks for the PETMP/TATATO samples initially photopolymerized at 23°C and 37°C (Fig. 10d) were $15.9 \pm 0.1^\circ\text{C}$ and $15.5 \pm 0.1^\circ\text{C}$, respectively.

4. Discussion

Composite dental restorative materials are typically photopolymerized *in situ* using visible, blue light, a wavelength range that ensures clinical acceptability. Consequently, CQ, in conjunction with a coinitiator such as a tertiary amine, is the predominant radical-generating photoinitiator for dimethacrylate-based dental resins owing to its well-known blue light absorbance peak, attributable to the $n \rightarrow \pi^*$ transition of the dicarbonyl group [50, 51]. Importantly, the absorbance by a photoinitiator at the incident irradiation wavelength must be sufficient to ensure rapid polymerization rates, but not excessive which would limit polymerization depth and thus necessitate multiple, incremental restorative layers to fully address the defect. Thus, the success of CQ as a dental resin photoinitiator is attributable to its moderate absorbance at 469 nm (Table 1) which offers an excellent compromise between polymerization rate and cure depth. The ubiquity of CQ has resulted in most conventional halogen- and LED-based dental lamps emitting across a wavelength range tailored to match the CQ visible absorbance peak [46, 52]. Thus, compatibility of novel photoinitiators with these legacy dental lamps would promote the rapid clinical adoption of alternate, non-dimethacrylate-based dental resins that are not readily photopolymerized by CQ/coinitiator systems.

HABI photoinitiators are yellow, indicating that they absorb at least somewhat in the blue region of the spectrum (see Fig. 3). Although the HABI derivatives examined here exhibit lower absorptivity than CQ at 469 nm, a common dental lamp peak emission wavelength, they do afford higher sensitivity than Irgacure 819 (a commercially-available, benzoyl phosphine oxide-based, visible light-active, Type I photoinitiator) at this wavelength (see Table 1). Notably, as lower absorptivity results in increased irradiation penetration,

utilization of the HABI derivatives examined here should be anticipated to afford improved polymerization depth relative to CQ-formulated resins. Some recently-marketed dental lamps also emit in the violet region of the spectrum (405 nm) [48, 52], a wavelength range where Irgacure 819 and both HABI derivatives exhibit significantly increased sensitivity relative to their absorbance at 469 nm. Of course, photopolymerization initiation rates are not exclusively determined by the photoinitiator absorptivity at the incident irradiation wavelength; rather, the initiating radical quantum yield must be accounted for when determining a photoinitiator's overall efficiency. Although HABI photolysis is very efficient, with quantum yields approaching 2 (i.e., approximately two lophyl radicals generated for each absorbed photon) [40, 53], the resultant lophyl radicals are uncommonly stable and do not initiate vinyl polymerizations in the absence of a hydrogen donating thiol coinitiator [40]. Importantly, the stability of the generated lophyl radicals results in sluggish recombination rates (Fig. 4), where recombination proceeds over several minutes. Thiol-ene formulations, where thiol and vinyl functional groups are present in a 1:1 stoichiometric ratio, inherently provide high thiol concentrations for hydrogen abstraction by lophyl radicals. Thus, the generation of long-lived lophyl radicals in thiol-rich formulations should provide sufficient time for hydrogen abstraction from thiol to proceed prior to significant lophyl radical recombination, yielding highly efficient photoinitiation by HABIs in thiol-ene formulations.

Commercially-available HABI photoinitiators such as *o*-Cl-HABI generally exhibit very low blue light absorbance (Fig. 3 and Table 1) and poor solubility in common resins (Table 2). Fortunately, the facile synthetic accessibility of HABIs enables their ready modification to induce particular properties. For example, the solubility of these typically solid materials has been dramatically increased by affixing alkyl substituents [41, 42], and the lophyl radical recombination rate has been decreased, with a corresponding bathochromic shift in its absorption spectrum, by incorporating extended π -conjugated moieties [54]. In the present study, HABI solubility was increased by affixing flexible, hydroxyhexyl pendant groups to each triphenylimidazolyl moiety. As tabulated in Table 2, this HABI functionalization greatly increased solubility of the resultant HABI, where *p*-HOH-HABI (i.e., the bis(hydroxyhexyl)-functionalized compound) is consistently more soluble in an allyl monomer and polar organic solvents than the unfunctionalized *o*-Cl-HABI. The hydroxyhexyl HABI functionalization was also accompanied by enhanced absorptivity at 469 nm compared with *o*-Cl-HABI (Table 1), suggesting a potentially increased photopolymerization rate for *p*-HOH-HABI-containing thiol-ene formulations under conventional dental lamp irradiation.

To establish a benchmark against which thiol-ene photopolymerizations could be compared, the photopolymerization kinetics of methacrylate-based bisGMA/TEGDMA resins formulated with four different photoinitiation systems were examined under several irradiation intensities (Fig. 5). As the CQ visible absorption peak occurs at approximately 470 nm [32, 33], the rapid photopolymerization observed for the methacrylate-based resin formulated with CQ/EDAB upon 469 nm irradiation is expected. As the commercially-sourced monomers were used as received, the short polymerization induction periods for this system are attributable to radical polymerization inhibitors and dissolved oxygen in the

resin. Prior to the onset of polymerization, radicals generated upon irradiation rapidly react with adventitious radical inhibitors and oxygen; however polymerization proceeds immediately upon complete consumption of the inhibiting species. Raised irradiation intensities increase radical generation rates, consuming inhibiting species more quickly and hence reducing the polymerization induction time (Fig. 5a). Moreover, the increased radical generation rates at raised intensities afford correspondingly increased polymerization rates (Fig. 5a). In contrast, as Irgacure 819 exhibits very low absorptivity at 469 nm, the radical generation rate upon irradiation at 469 nm of methacrylate formulations containing this photoinitiator is so low that the consumption of the inhibiting species proceeds over the course of minutes even under a high irradiation intensity. Notably, although *o*-Cl-HABI and *p*-HOH-HABI offer raised absorptivities at 469 nm compared with Irgacure 819, no polymerization was observed at all for bisGMA/TEGDMA resins formulated with these HABI photoinitiators, indicating that the lophyl radicals are inactive towards methacrylate groups [40].

To determine the relative efficiency of HABI compounds to initiate thiol–ene polymerization upon blue light irradiation, the photopolymerization kinetics of PETMP/TATATO resins formulated with four different photoinitiator systems were similarly examined under several blue light irradiation intensities (Fig. 6). Interestingly, no polymerization induction period was observed for any system even at low irradiation intensity and correspondingly slow polymerization rates, despite the inclusion of a potent free radical inhibitor (i.e., Q1301) in the resin formulations. This notable absence of induction period may be attributable to the well-known resistance of radical-mediated thiol–ene reaction to oxygen inhibition [13]. Additionally, whereas all PETMP/TATATO resins examined were formulated in a 1:1 thiol to allyl stoichiometric ratio, the unequal monomer consumption rates, where allyl conversion was consistently higher than thiol conversion (see Figs. 6, 7b, and 9), is attributable to a small amount of allylic homopolymerization [13].

With the exception of the CQ/EDAB-containing formulation, the relative thiol–ene photopolymerization rates proceed according to the absorptivities at 469 nm for the respective photoinitiators, where the *p*-HOH-HABI-containing formulation reacts most rapidly while blue light initiated photopolymerization of the Irgacure 819-containing formulation proceeds slowest (Fig. 6). In contrast, despite relatively strong absorbance at 469 nm, the photopolymerization of CQ/EDAB-containing formulations proceeds no more rapidly than Irgacure 819-containing formulations upon blue light irradiation, confirming the poor compatibility of CQ/tertiary amine photoinitiator/coinitiator systems, used ubiquitously in conventional methacrylate-based dental resins, for thiol–ene photopolymerization.

The curves of allyl and thiol conversion versus time for the photopolymerization of both HABI-containing thiol–ene formulations followed distinctive ‘S’-shaped trajectories at all examined irradiation intensities (Figs. 6c and 6d). Similar conversion trajectories are typically associated with polymerization autoacceleration by the gel effect [55], where the termination reaction rate rapidly drops as radical diffusion is restricted, impeding bimolecular radical-radical reactions and leading to a rise in radical concentration and concomitant increase in polymerization rate. However, as the polymerization rates are observed to increase prior to gelation, attaining their maxima near the gel point conversion

(calculated using Flory-Stockmayer theory [56, 57] as 40.8% conversion for an ideal tetrathiol/triallyl step-growth reaction), and similar conversion trajectories are not observed for the Type I initiation provided by Irgacure 819, autoacceleration does not account for the observed characteristic conversion trajectories afforded by HABI photoinitiators in thiol-ene resins. Furthermore, for ideal free radical polymerizations where termination is exclusively bimolecular, the polymerization rate (R_p) is anticipated to scale with the square root of the initiation rate (R_i) [22], which for photopolymerizations is proportional to the incident irradiation intensity. The conversion versus time data obtained at different intensities (i.e., Fig. 6), scaled by R_i to an exponent, are shown in Fig. 11. As indicated by Fig. 11a, the classical square root dependence of R_p on R_i (i.e., $R_p \sim R_i^{0.5}$) fails to accurately describe the experimental data; rather the data are well fit by an R_i scaling exponent of 0.84, suggesting concurrent bimolecular and unimolecular termination mechanism in these polymerizations, as has been observed in other thiol-ene systems [22]. As the irradiation intensity emitted at the light guide tip of conventional dental lamps often approaches or even exceeds $1 \text{ W}\cdot\text{cm}^{-2}$ [47, 52], high R_i scaling exponents can provide more rapid polymerization rates of dental restoratives in clinical settings.

As seen in Fig. 7, the CQ/EDAB-containing bisGMA/TEGDMA formulation vitrifies at a relatively low conversion such that a significant amount of unreacted monomer could potentially leach out if this material were in an oral environment. In contrast, the *p*-HOH-HABI-containing PETMP/TATATO formulation, which of the thiol-ene samples reaches the highest conversion contains significantly less unreacted functional groups post-polymerization, and hence it is anticipated to contain significantly less low molecular weight, extractable material.

BisGMA/TEGDMA formulations containing CQ/EDAB and Irgacure 819, photopolymerized slowly using a light intensity of $1 \text{ mW}\cdot\text{cm}^{-2}$ and a photoinitiator concentration of 0.1 wt%, mitigating both the temperature rise owing to the exothermic polymerization and lessening light intensity gradients through the sample thicknesses at shorter wavelengths, respectively, demonstrate opposing R_p trends for progressively shorter incident irradiation wavelengths (see Fig. 8). Here, the CQ/EDAB-containing formulation polymerizes fastest under 469 nm irradiation but exhibits negligible polymerization under 365 nm, whereas the Irgacure 819-containing formulation exhibits negligible polymerization under 469 nm irradiation but polymerizes rapidly under both 405 and 365 nm. These trends are readily explained by considering the absorptivities of the two photoinitiators at the relevant wavelengths (Table 1). Thus, as CQ exhibits good absorptivity at 469 nm and progressively lower absorptivity at 405 and 365 nm, the R_i for the CQ/EDAB-containing formulation will be reduced at these shorter wavelengths which is reflected in the relative R_p s. Similarly, Irgacure 819 exhibits very low absorptivity at 469 nm but good absorptivity at 405 and 365 nm, reflected in the relative polymerization rates of the Irgacure 819-containing formulations. Notably, irradiation of the HABI-containing methacrylate formulations again did not afford any observable polymerization, even at shorter wavelengths where both HABIs offer good absorptivity (Table 1), confirming lophyl radical inactivity towards methacrylate functional groups.

This relation between R_p and photoinitiator absorptivity is likewise applicable to the photopolymerization of PETMP/TATATO formulations under various incident irradiation wavelengths (Fig. 9). For the Irgacure 819-containing thiol–ene formulation, the negligible R_p under 469 nm but rapid photopolymerization at shorter wavelengths is a consequence of the relative absorptivity of this photoinitiator at the relevant wavelengths. Interestingly, the relatively more rapid thiol–ene polymerization of the *o*-Cl-HABI-containing formulation versus the *p*-HOH-HABI-containing formulation under 405 nm irradiation, again a consequence of the relative absorptivities of the two photoinitiators at this wavelength, would afford reduced cure time in a clinical setting where the dental lamp used emits violet light. However, unlike the commonplace blue light emitted by conventional dental lamps, 405 nm has yet to see widespread clinical use and thus the raised R_p for *o*-Cl-HABI at this wavelength is less relevant than the higher relative R_p for *p*-HOH-HABI under blue light irradiation. The very low R_p s afforded by irradiation of CQ/EDAB-containing PETMP/TATATO formulations again illustrates the poor compatibility of this photoinitiator system for thiol–ene photopolymerizations.

As composite dental restorative materials are polymerized *in situ* at defect sites, vitrification of the continuous resin phase as the polymerization proceeds is essential to approximate tooth mechanical properties and fully recover the utility of this hard tissue. To determine the capacity of *p*-HOH-HABI to act as a thiol–ene photoinitiator and yield cross-linked, vitrified polymers, DMA was performed on the model *p*-HOH-HABI-containing thiol–ene and, for comparison, CQ/EDAB-containing dimethacrylate formulations. In the absence of polymerization during a DMA temperature ramp experiment, the $\tan \delta$ curve peak preceding the rubbery plateau is assigned as the T_g . The two distinct $\tan \delta$ peaks and corresponding storage modulus reductions displayed by the dimethacrylate films photopolymerized at both room and body temperature (Fig. 10a) could be the result of either radicals, generated during irradiation but trapped in the vitrified matrix, gaining sufficient mobility during the temperature ramp to induce dark polymerization, or could result from a phase separated film. Notably, the significant methacrylate conversion increase observed after the first DMA experiments and the single thermal transition revealed upon second DMA temperature ramps (Fig. 10b) discounted phase separation and confirmed the two transitions as attributable to polymerization mediated by trapped radicals; nevertheless, although this dark polymerization prevents accurate assessment of the T_g in these methacrylate-based materials, they are vitrified at room temperature with storage moduli in excess of 2 GPa (Table 3).

In contrast to the methacrylate-based materials, the single $\tan \delta$ curve peaks exhibited by the thiol–ene films photopolymerized at room and body temperature upon a first DMA temperature ramp (Fig. 10c) indicates that the temperature at the $\tan \delta$ peak for these samples closely reflected the T_g . Thus, the T_g s for these samples of approximately 50°C, in conjunction with storage moduli in excess of 2 GPa at room temperature, demonstrates that *p*-HOH-HABI is capable of photoinitiating thiol–ene formulations to afford vitrified polymeric matrices. Interestingly, a small increase in storage modulus towards the end of the glass transition, but prior to the rubbery plateau, is observed during the first temperature ramp of both thiol–ene samples. Given the raised allyl and thiol conversion after the first

DMA temperature ramp and the absence of similar storage moduli increases during the second temperature ramp, we again attribute the observed storage moduli increases to dark polymerization. The notably narrower $\tan \delta$ curve peak FWHMs, obtained from the second DMA temperature ramp experiments, for the thiol–ene films as compared to the dimethacrylate films demonstrates the homogeneity of cross-linked thiol–ene networks (Fig. 10b and 10d), a consequence of their step-growth polymerization mechanism [13]. Finally, although the monomer conversion is raised, a significant decrease in the room temperature storage modulus for the thiol–ene films is observed after the polymer networks have been subject to the first temperature ramp (Fig. 10c and 10d, Table 3); indeed, the storage moduli of the thiol–ene films are lower than those of the methacrylate-based materials, and a similar storage modulus drop is observed for the bisGMA/TEGDMA sample polymerized at body temperature after its first temperature ramp (Fig. 10a and 10b, Table 3). Similar results have been previously observed in cross-linked epoxy/amine polymer networks, where the modulus passed through a maximum value with increasing fractional chemical conversion [58]. This counterintuitive effect was attributed to ‘self-antiplasticization’, where the unreacted functional groups can decrease the T_g but increase the modulus of certain glassy, polymeric networks [58]. Consequently, this suggests a path to yield thiol–ene polymer networks with increased moduli by employing rigid, high functionality monomers that vitrify at low conversions, thus enhancing the antiplasticization effect; however, the associated leachability of low molecular weight species from such materials limits the potential utility of this approach.

5. Conclusion

Upon irradiation with UV or short wavelength visible light, HABI compounds generate lophyl radicals that are inactive towards methacrylate groups but are capable of abstracting thiol hydrogens to afford thiyl radicals. Unlike the conventional CQ/tertiary amine photoinitiator system, HABI compounds were shown to be efficient as visible- and UV-active initiators for thiol–ene photopolymerizations owing to the aforementioned thiol hydrogen abstraction mechanism. To address the shortcomings of *o*-Cl-HABI, a commercially-available HABI photoinitiator with limited solubility and low visible light absorptivity, a novel, bis(hydroxyhexyl)-functionalized HABI was successfully synthesized and demonstrated improved solubility in monomer and organic solvents, in addition to raised blue light absorbance, resulting in increased thiol–ene photopolymerization rates upon blue light irradiation. Notably, both examined HABI compounds exhibited good absorptivity and afforded rapid thiol–ene polymerization rates upon 405 nm irradiation, demonstrating their compatibility with emergent violet LED dental light sources.

The potential for *p*-HOH-HABI to act as photoinitiator of a glass-forming, thiol–ene based dental restorative was demonstrated using a model thiol–ene formulation. Extended blue light irradiation of the resin formulation yielded vitrified, cross-linked polymer matrices that were significantly more homogeneous than methacrylate based polymer networks photopolymerized under equivalent irradiation conditions. The observed disparity in network homogeneity was attributed to the different polymerization mechanisms for the two examined systems.

Acknowledgements

The authors gratefully acknowledge the support for this work by the NIH grant 1U01DE023771-01 from the National Institute of Dental and Craniofacial Research. TFS gratefully acknowledges support from the 3M Nontenured Faculty Award.

References

1. Peutzfeldt A. Resin composites in dentistry: The monomer systems. *Eur J Oral Sci.* 1997; 105:97–116. [PubMed: 9151062]
2. Ferracane JL. Resin composite-State of the art. *Dental Materials.* 2011; 27:29–38. [PubMed: 21093034]
3. Rueggeberg FA, Margeson DH. The effect of oxygen inhibition on an unfilled/filled composite system. *Journal of dental research.* 1990; 69:1652–8. [PubMed: 2212209]
4. Gauthier MA, Stangel I, Ellis TH, Zhu XX. Oxygen inhibition in dental resins. *Journal of Dental Research.* 2005; 84:725–9. [PubMed: 16040730]
5. Cramer NB, Stansbury JW, Bowman CN. Recent advances and developments in composite dental restorative materials. *Journal of Dental Research.* 2011; 90:402–16. [PubMed: 20924063]
6. Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G. Progress in dimethacrylate-based dental composite technology and curing efficiency. *Dental Materials.* 2013; 29:139–56. [PubMed: 23199807]
7. Schweikl H, Schmalz G. Triethylene glycol dimethacrylate induces large deletions in the hprt gene of V79 cells. *Mutation Research - Genetic Toxicology and Environmental Mutagenesis.* 1999; 438:71–8. [PubMed: 9858690]
8. Darmani H, Al-Hiyasat AS. The effects of BIS-GMA and TEG-DMA on female mouse fertility. *Dental Materials.* 2006; 22:353–8. [PubMed: 16038970]
9. Davidson CL, Feilzer AJ. Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *Journal of Dentistry.* 1997; 25:435–40. [PubMed: 9604575]
10. Lu H, Stansbury JW, Bowman CN. Towards the elucidation of shrinkage stress development and relaxation in dental composites. *Dental Materials.* 2004; 20:979–86. [PubMed: 15501327]
11. Winkler MM, Katona TR, Paydar NH. Finite element stress analysis of three filling techniques for Class V light-cured composite restorations. *Journal of Dental Research.* 1996; 75:1477–83. [PubMed: 8876599]
12. Braga RR, Ballester RY, Ferracane JL. Factors involved in the development of polymerization shrinkage stress in resin-composites: A systematic review. *Dental Materials.* 2005; 21:962–70. [PubMed: 16085301]
13. Lu H, Carioscia JA, Stansbury JW, Bowman CN. Investigations of step-growth thiol-ene polymerizations for novel dental restoratives. *Dental Materials.* 2005; 21:1129–36. [PubMed: 16046231]
14. Cramer NB, Couch CL, Schreck KM, Boulden JE, Wydra R, Stansbury JW, et al. Properties of methacrylate-thiol-ene formulations as dental restorative materials. *Dental Materials.* 2010; 26:799–806. [PubMed: 20553973]
15. Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. *Dental Materials.* 2005; 21:68–74. [PubMed: 15681004]
16. Palin WM, Fleming GJP, Nathwani H, Burke FJT, Randall RC. In vitro cuspal deflection and microleakage of maxillary premolars restored with novel low-shrink dental composites. *Dental Materials.* 2005; 21:324–35. [PubMed: 15766579]
17. Gong T, Adzima BJ, Baker NH, Bowman CN. Photopolymerization Reactions Using the Photoinitiated Copper (I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) Reaction. *Advanced Materials.* 2013; 25:2024–8. [PubMed: 23401189]
18. Carioscia JA, Lu H, Stanbury JW, Bowman CN. Thiol-ene oligomers as dental restorative materials. *Dental Materials.* 2005; 21:1137–43. [PubMed: 16046232]

19. Cramer NB, Couch CL, Schreck KM, Carioscia JA, Boulden JE, Stansbury JW, et al. Investigation of thiol-ene and thiol-ene-methacrylate based resins as dental restorative materials. *Dental Materials*. 2010; 26:21–8. [PubMed: 19781757]
20. Reinelt S, Tabatabai M, Moszner N, Fischer UK, Utterodt A, Ritter H. Synthesis and Photopolymerization of Thiol-Modified Triazine-Based Monomers and Oligomers for the Use in Thiol-Ene-Based Dental Composites. *Macromolecular Chemistry and Physics*. 2014; 215:1415–25.
21. Hoyle CE, Lee TY, Roper T. Thiol-enes: Chemistry of the past with promise for the future. *Journal of Polymer Science, Part A: Polymer Chemistry*. 2004; 42:5301–38.
22. Scott TF, Kloxin CJ, Draughon RB, Bowman CN. Nonclassical dependence of polymerization rate on initiation rate observed in thiol-ene photopolymerizations. *Macromolecules*. 2008; 41:2987–9.
23. Hoyle CE, Lowe AB, Bowman CN. Thiol-click chemistry: A multifaceted toolbox for small molecule and polymer synthesis. *Chemical Society Reviews*. 2010; 39:1355–87. [PubMed: 20309491]
24. Chiou BS, Khan SA. Real-time FTIR and in situ rheological studies on the UV curing kinetics of thiol-ene polymers. *Macromolecules*. 1997; 30:7322–8.
25. Patel MP, Braden M, Davy KWM. Polymerization shrinkage of methacrylate esters. *Biomaterials*. 1987; 8:53–6. [PubMed: 3828447]
26. Cook WD. Photopolymerization kinetics of dimethacrylates using the camphorquinone/amine initiator system. *Polymer*. 1992; 33:600–9.
27. Jakubiak J, Allonas X, Fouassier JP, Sionkowska A, Andrzejewska E, Linden LA, et al. Camphorquinone-amines photoinitiating systems for the initiation of free radical polymerization. *Polymer*. 2003; 44:5219–26.
28. Fouassier J-, P.; Lalevée, J. Photoinitiators for Polymer Synthesis: Scope, Reactivity, and Efficiency. Wiley-VCH; Weinheim: 2012.
29. Moszner N, Fischer UK, Ganster B, Liska R, Rheinberger V. Benzoyl germanium derivatives as novel visible light photoinitiators for dental materials. *Dental Materials*. 2008; 24:901–7. [PubMed: 18155290]
30. Senyurt AF, Hoyle CE. Three component ketocoumarin, amine, maleimide photoinitiator II. *European Polymer Journal*. 2006; 42:3133–9.
31. Uygun M, Tasdelen MA, Yagci Y. Influence of type of initiation on thiol-ene “click” Chemistry. *Macromolecular Chemistry and Physics*. 2010; 211:103–10.
32. Chen YC, Ferracane JL, Prahl SA. Quantum yield of conversion of the photoinitiator camphorquinone. *Dental Materials*. 2007; 23:655–64. [PubMed: 16859741]
33. Scott TF, Kowalski BA, Sullivan AC, Bowman CN, McLeod RR. Two-color single-photon photoinitiation and photoinhibition for subdiffraction photolithography. *Science*. 2009; 324:913–7. [PubMed: 19359546]
34. Kolczak U, Rist G, Dietliker K, Wirz J. Reaction mechanism of monoacyl- and bisacylphosphine oxide photoinitiators studied by P-31-, C-13-, and H-1-CIDNP and ESR. *Journal of the American Chemical Society*. 1996; 118:6477–89.
35. Davidenko N, Garcia O, Sastre R. The efficiency of titanocene as photoinitiator in the polymerization of dental formulations. *J Biomater Sci-Polym Ed*. 2003; 14:733–46. [PubMed: 12903740]
36. Kitano H, Ramachandran K, Bowden NB, Scranton AB. Unexpected visible-light-induced free radical photopolymerization at low light intensity and high viscosity using a titanocene photoinitiator. *Journal of Applied Polymer Science*. 2013; 128:611–8.
37. Hayashi T, Maeda K. Preparation of a New Phototropic Substance. *Bulletin of the Chemical Society of Japan*. 1960; 33:565–6.
38. Berdzinski S, Horst J, Straßburg P, Strehmel V. Recombination of lophyl radicals in pyrrolidinium-based ionic liquids. *ChemPhysChem*. 2013; 14:1899–908. [PubMed: 23649608]
39. Kawano M, Sano T, Abe J, Ohashi Y. The First in Situ Direct Observation of the Light-Induced Radical Pair from a Hexaarylbiimidazolyl Derivative by X-ray Crystallography. *Journal of the American Chemical Society*. 1999; 121:8106–7.

40. Berdzinski S, Strehmel N, Lindauer H, Strehmel V, Strehmel B. Extended mechanistic aspects on photoinitiated polymerization of 1,6-hexanediol diacrylate by hexaarylbiimidazoles and heterocyclic mercapto compounds. *Photochem Photobiol Sci*. 2014; 13:789–98. [PubMed: 24671230]
41. Shi YT, Yin J, Kaji M, Yori H. Photopolymerization of acrylate derivatives initiated by hexaarylbiimidazole with ether groups. *Polym Int*. 2006; 55:330–9.
42. Shi Y, Yin J, Kaji M, Yori H. Synthesis of a Novel Hexaarylbiimidazole With Ether Groups and Characterization of Its Photoinitiation Properties for Acrylate Derivatives. *Polymer Engineering and Science*. 2006; 46:474–9.
43. Sathe SS, Ahn D, Scott TF. Re-examining the photomediated dissociation and recombination kinetics of hexaarylbiimidazoles. *Industrial and Engineering Chemistry Research*. 2015 doi: 10.1021/ie504230c.
44. Lovell LG, Berchtold KA, Elliott JE, Lu H, Bowman CN. Understanding the kinetics and network formation of dimethacrylate dental resins. *Polym Adv Technol*. 2001; 12:335–45.
45. Caspar JV, Khudyakov IV, Turro NJ, Weed GC. ESR study of lophyl free radicals in dry films. *Macromolecules*. 1995; 28:636–41.
46. Neumann MG, Miranda WG Jr, Schmitt CC, Rueggeberg FA, Correa IC. Molar extinction coefficients and the photon absorption efficiency of dental photoinitiators and light curing units. *Journal of Dentistry*. 2005; 33:525–32. [PubMed: 15935273]
47. Price RBT, Felix CA, Andreou P. Knoop hardness of ten resin composites irradiated with high-power LED and quartz-tungsten-halogen lights. *Biomaterials*. 2005; 26:2631–41. [PubMed: 15585266]
48. Kameyama A, Kato J, Yoshinari M, Kotoku Y, Akashi G, Hirai Y. Ultimate micro-tensile strength of dental adhesives cured at different light source. *J Photopolym Sci Technol*. 2008; 21:31–5.
49. Vandewalle KS, Roberts HW, Andrus JL, Dunn WJ. Effect of light dispersion of LED curing lights on resin composite polymerization. *Journal of Esthetic and Restorative Dentistry*. 2005; 17:244–54. [PubMed: 16231495]
50. Tsai L, Charney E. The triplet states of α -dicarbonyls. Camphorquinone. *Journal of Physical Chemistry*. 1969; 73:2462–3. [PubMed: 5798198]
51. Teshima W, Nomura Y, Tanaka N, Urabe H, Okazaki M, Nahara Y. ESR study of camphorquinone/amine photoinitiator systems using blue light-emitting diodes. *Biomaterials*. 2003; 24:2097–103. [PubMed: 12628830]
52. Brandt WC, Schneider LFJ, Frollini E, Correr-Sobrinho L, Sinhoreti MAC. Effect of different photo-initiators and light curing units on degree of conversion of composites. *Brazilian oral research*. 2010; 24:263–70. [PubMed: 20877961]
53. Zhu QQ, Fink M, Seitz F, Schneider S, Schnabel W. On the photolysis of bis[2-(*o*-chlorophenyl)-4,5-diphenylimidazole] sensitized by 2-isopropylthioxanthone or Michler's ketone. *J Photochem Photobiol A-Chem*. 1991; 59:255–63.
54. Kikuchi A, Iyoda T, Abe J. Electronic structure of light-induced lophyl radical derived from a novel hexaarylbiimidazole with pi-conjugated chromophore. *Chemical Communications*. 2002:1484–5. [PubMed: 12189855]
55. Soh SK, Sundberg DC. Diffusion-Controlled Vinyl Polymerization. I. The Gel Effect. *J Polym Sci Pol Chem*. 1982; 20:1299–313.
56. Flory PJ. Molecular size distribution in three dimensional polymers. I. Gelation. *Journal of the American Chemical Society*. 1941; 63:3083–90.
57. Stockmayer WH. Theory of molecular size distribution and gel formation in branched-chain polymers. *J Chem Phys*. 1943; 11:45–55.
58. Venditti RA, Gillham JK, Jean YC, Lou Y. Free Volume After Cure vs. Fractional Conversion for a High-Tg Epoxy/Amine Thermosetting System. *Journal of Applied Polymer Science*. 1995; 56:1207–20.

Highlights

- A novel, bis(hydroxyhexyl)-functionalized hexaarylbiimidazole (HABI) compound was examined as an efficient visible- and UV-light-active initiator for thiol–ene photopolymerization.
- Affixing hydroxyhexyl functional groups to the HABI core significantly improved solubility of resultant photoinitiator compound compared with the parent material.
- Compared with conventional photoinitiators, HABIs exhibited improved sensitivity as visible light photoinitiators for thiol–ene resin formulations.

Fig. 1.

(a) The radical-mediated thiol-ene polymerization mechanism proceeds *via* alternating propagation and chain transfer events, where a thiyl radical initially propagates to a vinyl group, yielding a thioether and carbon-centered radical reaction product. This radical subsequently abstracts a hydrogen from a thiol, regenerating a thiyl radical. (b) Upon irradiation, the inter-imidazole HABI bond undergoes homolytic cleavage, generating two relatively stable, long-lived phenyl radicals which then abstract a hydrogen from thiol to produce thiyl radicals.

Fig. 2.

Materials used: (a) bisGMA ($512.6 \text{ g}\cdot\text{mol}^{-1}$), (b) TEGDMA ($286.3 \text{ g}\cdot\text{mol}^{-1}$), (c) PETMP ($488.6 \text{ g}\cdot\text{mol}^{-1}$), (d) TATATO ($249.3 \text{ g}\cdot\text{mol}^{-1}$), (e) CQ ($166.2 \text{ g}\cdot\text{mol}^{-1}$), (f) EDAB ($193.2 \text{ g}\cdot\text{mol}^{-1}$), (g) Irgacure 819 ($418.5 \text{ g}\cdot\text{mol}^{-1}$), (h) *o*-Cl-HABI ($609.6 \text{ g}\cdot\text{mol}^{-1}$), and (i) *p*-HOH-HABI ($891.9 \text{ g}\cdot\text{mol}^{-1}$).

Fig. 3. UV-vis absorbance spectra and EPR spectra (inset) for (a) *o*-Cl-HABI and (b) *p*-HOH-HABI prior to (solid line) and during (dashed line) irradiation with 405 nm at 10 mW·cm⁻².

Fig. 4. Absorbance at λ_{max} versus time for *o*-Cl-HABI (solid line) and *p*-HOH-HABI (dashed line), irradiated with 405 nm at $1 \text{ mW}\cdot\text{cm}^{-2}$ from 0.5 – 10 minutes.

Fig. 5.

Conversion versus time for the photopolymerization of bisGMA/TEGDMA irradiated with 469 nm light at intensities of 1 (black, squares), 3 (red, circles), 10 (blue, triangles), and 20 (green, diamonds) $\text{mW}\cdot\text{cm}^{-2}$ and formulated with 1 wt% (a) CQ/EDAB and (b) Irgacure 819. No photopolymerization was observed for bisGMA/TEGDMA formulations containing 1 wt% *o*-Cl-HABI or *p*-HOH-HABI under these irradiation conditions.

Fig. 6.

Conversion versus time for the photopolymerization of PETMP/TATATO irradiated with 469 nm light at intensities of 1 (black, squares), 3 (red, circles), 10 (blue, triangles), and 20 (green, diamonds) $\text{mW}\cdot\text{cm}^{-2}$ and formulated with 1 wt% (a) CQ/EDAB, (b) Irgacure 819, (c) *o*-Cl-HABI, and (d) *p*-HOH-HABI. Vinyl conversions are indicated by solid lines, whereas thiol conversions are indicated by dashed lines.

Fig. 7.

Conversion versus time for the photopolymerization of (a) bisGMA/TEGDMA, and (b) PETMP/TATATO, formulated with 1 wt% CQ/EDAB (black, squares), Irigacure 819 (red, circles), *o*-Cl-HABI (blue, triangles), and *p*-HOH-HABI (green, diamonds) and irradiated with 469 nm light at $10 \text{ mW} \cdot \text{cm}^{-2}$. Vinyl conversions are indicated by solid lines, whereas thiol conversions are indicated by dashed lines.

Fig. 8.

Conversion versus time for the photopolymerization of bisGMA/TEGDMA irradiated at $1 \text{ mW} \cdot \text{cm}^{-2}$ with 469 (black, squares), 405 (red, circles), and 365 (blue, triangles) nm light and formulated with 0.1 wt% (a) CQ/EDAB and (b) Irgacure 819. No photopolymerization was observed for bisGMA/TEGDMA formulations containing 0.1 wt% *o*-Cl-HABI or *p*-HOH-HABI under these irradiation conditions.

Fig. 9.

Conversion versus time for the photopolymerization of PETMP/TATATO irradiated at 1 mW·cm⁻² with 469 (black, squares), 405 (red, circles), and 365 (blue, triangles) nm light and formulated with 0.1 wt% (a) CQ/EDAB, (b) Irgacure 819, (c) *o*-Cl-HABI, and (d) *p*-HOH-HABI. Vinyl conversions are indicated by solid lines, whereas thiol conversions are indicated by dashed lines.

Fig. 10.

Storage modulus (E' , solid lines) and $\tan \delta$ (dashed lines) versus temperature for photopolymerized films, irradiated for 20 minutes at 10 $\text{mW}\cdot\text{cm}^{-2}$ with 469 nm and at 23 $^{\circ}\text{C}$ (black, squares) or 37 $^{\circ}\text{C}$ (red, circles), of (a) bisGMA/TEGDMA formulated with 1 wt% CQ/0.5 wt% EDAB ((b) second temperature ramp), and (c) PETMP/TATATO formulated with 1 wt% *p*-HOH-HABI ((d) second temperature ramp).

Fig. 11.

Conversion versus time, scaled assuming that (a) $R_p \sim R_i^{0.50}$, and (b) $R_p \sim R_i^{0.84}$, for the photopolymerization of PETMP/TATATO formulated with 1 wt% *p*-HOH-HABI and irradiated with 469 nm light at intensities of 1 (black, squares), 3 (red, circles), 10 (blue, triangles), and 20 (green, diamonds) mW·cm⁻². Vinyl conversions are indicated by solid lines, whereas thiol conversions are indicated by dashed lines.

Table 1

Absorbance of 1 wt% photoinitiator in toluene solutions and molar absorptivities at various wavelengths.

Photoinitiator	$\lambda = 469 \text{ nm}$		$\lambda = 405 \text{ nm}$		$\lambda = 365 \text{ nm}$	
	Absorbance	Molar absorptivity ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	Absorbance	Molar absorptivity ($\text{M}^{-1}\cdot\text{cm}^{-1}$)	Absorbance	Molar absorptivity ($\text{M}^{-1}\cdot\text{cm}^{-1}$)
CQ/Amine	0.268	51.4	0.035	6.80	0.011	2.05
Irgacure 819	0.003	1.39	1.44	696	2.07	1002
<i>o</i> -Cl-HABI	0.007	5.69	0.287	219	0.494	376
<i>p</i> -HOH-HABI	0.014	14.7	0.096	99.0	0.390	401

Table 2

Solubility of HABI photoinitiators in monomer and polar organic solvents

Photoinitiator	Solvent		
	TATATO	Dimethylformamide	Tetrahydrofuran
<i>o</i> -Cl-HABI	<0.2 wt% *	<20 wt%	<40 wt%
<i>p</i> -HOH-HABI	<35 wt%	<40 wt%	<65 wt%

* Owing to the low solubility of *o*-Cl-HABI in TATATO, increments of 0.1 wt% were used for this solute/solvent combination, such that the solubility of *o*-Cl-HABI in TATATO is above 0.1 wt% but below 0.2 wt%.

Table 3

Summary of photopolymerized film viscoelastic properties.

Resin formulation	Room temperature photopolymerization			Body temperature photopolymerization		
	E' at 23°C (GPa)	E' at 200°C (MPa)	Temperature at tan δ peak(s) (°C)	E' at 23°C (GPa)	E' at 200°C (MPa)	Temperature at tan δ peak(s) (°C)
BisGMA/TEGDMA, 1 st ramp	2.1±0.1	57.7±1.0	41.0, 138.1±2.0	3.6±0.1	80.4±1.0	68.5, 145.2±2.5
BisGMA/TEGDMA, 2 nd ramp	2.7±0.1	57.1±1.0	146.2±2.5	2.9±0.1	68.5±1.0	148.6±2.0
PETMP/TATATO, 1 st ramp	2.1±0.03	37.2±2.1	49.5±0.5	2.3±0.1	31.3±1.1	52.2±0.1
PETMP/TATATO, 2 nd ramp	1.7±0.1	35.0±0.2	82.0±0.2	1.7±0.1	35.0±0.1	81.0±0.1