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Wavelength-Selective Sequential Polymer Network Formation Controlled with a Two-Color Responsive Initiation System

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Abstract

We report a wavelength-selective polymerization process controlled by visible/UV light, whereby a base is generated for anion-mediated thiol–Michael polymerization reaction upon exposure at one wavelength (400–500 nm), while radicals are subsequently generated for a second stage radical polymerization at a second, independent wavelength (365 nm). Dual wavelength, light controlled sequential polymerization not only provides a relatively soft intermediate polymer that facilitates optimum processing and modification under visible light exposure but also enables a highly cross-linked, rigid final material after the UV-induced second stage radical polymerization. A photobase generator, NPPOC-TMG, and a photo-radical initiator, Irgacure 2959, were selected as the appropriate initiator pair for sequential thiol–Michael polymerization and acrylate homopolymerization. FT-IR and rheological tests were utilized to monitor the dual cure photo-polymerization process, and mechanical performance of the polymer was characterized at each distinct stage by dynamic mechanical analysis (DMA). By demonstrating complete light control in another sequential polymerization system (thiol–Michael and thiol–ene hybrid polymerization), this initiator pair exhibits great potential to regulate many other coupled anion and radical hybrid polymerizations in both a sequential and controllable manner.

Graphical Abstract

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Notes

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Supporting Information

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INTRODUCTION

Owing to distinct advantages such as the high spatiotemporal precision, relatively high reaction rate, and the reduced temperatures that render it compatible with heat-sensitive substrates, photoinduced reactions have been widely used in numerous materials applications. In particular, wavelength-selective radiation methods (using multiple wavelengths of light to control distinct processes) have recently been implemented to investigate and regulate multiple photoreactive processes simultaneously or sequentially to enable more complicated, tunable systems to be developed.¹ These dual-wavelength controlled methods enable manipulation of multiple photo-chemical processes in an orthogonal manner. Owing to their wavelength selectivity and highly controllable reactions, wavelength-selective systems both provide an efficient method to study complex reaction systems in chemical and biological research²⁻⁴ and also have many practical applications, such as in drug delivery⁵ and neuroscience.⁶ In polymer chemistry and material science, a multiple wavelength strategy is capable of regulating the polymer network formation and/or the degradation process^{1,7-10} and, in some other cases, provides external stimuli to achieve the desired, photoinitiated behavior of the programmed materials.¹¹ Del Campo and co-workers formed a polyurethane-based dual photoresist material based on a *p*-dialkylaminonitrobiphenyl caged molecule (cleaves at 520 nm) that was used to initiate polymerization and another methoxynitrobiphenyl-based caged molecule (cleaves at 397 nm) that would degrade the polymer network.⁸ With the help of this dual wavelength control system, sequential polymer formation and degradation were achieved. Scott et al. implemented a two-color irradiation scheme, whereby initiating species and inhibiting species generated at different wavelengths (480 and 365 nm) were used to achieve precise control on polymerization rate and thus facilitate enhanced spatial control over the photopolymerization.⁹ As such, the marriage of a two-wavelength strategy with the desire for customizable, highly tunable polymer behavior leads to demands and capabilities in optical lithography,^{9,12-14} photodegradable materials,^{15,16} and light-responsive elastomers.^{11,17,18}

Here, we intended to incorporate the concept of wavelength-selective photolysis to regulate sequential interpenetrating polymer networks (IPNs).^{2,19} IPNs contain two (or more) distinct polymer networks, which are held together by their mutual entanglements within the same polymerization system. Distinct from a simultaneous IPN, in which the two polymer networks form at the same time, a sequential IPN is one in which a first stage network is constructed, and then at a later stage, swollen unreacted moieties are reacted to form a secondary cross-linking system. As compared to conventional networks formed in a single polymerization, sequential IPNs provide advantages in forming intermediate polymers that are stable and storable for extended periods. Further, the ultimate network properties are readily tuned and patterned for a variety of different applications. To reduce or avoid the interference of two distinct stages, sequential polymerization generally involves distinct initiation systems, which use different initiator species to generate different reactive intermediates that initiate each polymerization stage with combinations, such as anion/radical or cation/radical used. For example, Oxman and co-workers introduced the controlled, sequential free radical/cationic hybrid photopolymerization in acrylate and epoxide based systems and also investigated the initiation mechanism of a corresponding three-component initiator systems.²⁰ González and co-workers developed a two-stage thermoset process based on a thermal aza-Michael reaction and radical photopolymerization dual curing of a nonstoichiometric amine-acrylate formulation.²¹ In addition, sequential network formation has also been achieved with many different types of polymerization methods, such as thiol-Michael/acrylate hybrid networks construction,²² epoxy/acrylate curable resins,^{20,23} thiol-acrylate/thiol-acetoacetate thermosets,²⁴ and thiol-ene/epoxy-based polymers.²⁵⁻²⁸

These pioneering works broadly explored the methodology needed to construct two-stage polymers and demonstrated their potential application in shape memory materials, holographic materials, impression and imprint materials, microarrays, adhesives, etc. However, typical sequential polymerizations usually utilize either a single photo trigger (at a certain wavelength) or a combined thermal/photo trigger to control the network formation. Systems completely controlled by irradiation have been seldom reported. Here, we report a novel initiation system to initiate sequential thiol-Michael and radical homopolymerization with different wavelengths, whereby a photobase first cleaves to initiate the anion-mediated thiol-Michael polymerization reaction at one wavelength (400–500 nm), while radicals are generated for the second-stage polymerization at a second wavelength (365 nm). The thiol-Michael “click” reaction is a robust reaction that rapidly achieves quantitative reaction yields in the absence of any solvents²⁹⁻³¹ and, thus, has been widely exploited in many areas such as dendrimer synthesis³² as well as polymer network formation and modification³³⁻³⁵ and in biomaterial fabrication.^{29,36} The typical photo thiol-Michael reaction initiator species, namely photobase generators, have also made great progress over the past decade, and different photosensitive chemical groups, such as nitrophenylpropyl,³⁷⁻³⁹ coumarin,^{40,41} thioxanthone,^{42,43} phenylglyoxylic acid,⁴⁴ and tetraphenylborate,^{45,46} have been employed in photobase design and synthesis. NPPOC-TMG (2-(2-nitrophenyl)-propyloxycarbonyl/tetramethylguanidine) was used here to initiate the initial photo thiol-Michael stage in our dual cure system due to its high quantum yield, high light sensitivity/absorption, insignificant radical-based side reactions, and facile synthesis. Because of the difference

between the absorption of the photobase generator and the radical initiator (Figure 1), different light sources were used to achieve selective, sequential initiator cleavage and thus initiate the thiol–Michael polymerization and acrylate homopolymerization in an orthogonal, noninterfering fashion.

As shown in Scheme 1, in a nonstoichiometric thiol–acrylate system with excess acrylate, the first stage of the thiol–Michael polymerization is initiated by exposure of photobase catalyst to visible light (400–500 nm) which results in the formation of a loosely cross-linked network. For the second-stage reaction, UV exposure of the radical initiator induces subsequent radical homopolymerization of the remaining excess acrylate moieties, which results in the formation of a final highly cross-linked material with both a high stiffness and high glass transition temperature. The different propagation intermediates (i.e., the anion for thiol–Michael stage and radicals for the homopolymerization stage) enable distinct two-stage network formation, and photopatterning is possible at either or both polymerization stages. Real-time FT-IR, rheological characterization, and dynamic mechanical analysis (DMA) were performed at each stage of the reaction to investigate the polymerization kinetics and network performance of this wavelength-selective dual cure polymerization.

MATERIALS AND METHODS

Materials

Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was purchased from Bruno Bock. Trimethylolpropane triacrylate (TMPTA), benzophenone (BP), triallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (TTT), tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate (TCDDA), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959), camphorquinone (CQ), triethylamine (TEA), ethyl 4-(dimethylamino)benzoate (EDAB), isopropyl-thioxanthone (ITX), butyl 3-mercaptopropionate, and butyl acrylate were purchased from Sigma-Aldrich without further purification.

NPPOC-TMG Synthesis—2-(2-Nitrophenyl)propyl chloroformate (3 mmol, 1.174 g) in 10 mL of CH₂Cl₂ was added dropwise to a stirred solution of TMG (5 mmol, 630 μ L) in 50 mL of CH₂Cl₂. The reaction was stirred at ambient temperature for 8 h. The mixture was washed with brine (30 mL $\times$ 3) and dried with anhydrous Na₂SO₄. The crude product was purified by chromatography (MeOH:DCM = 1:10) to give a pure product (0.975 g, 76%) as a light yellow solid.

Resin Preparation—The light controlled polymerization films were prepared by casting in glass molds. Resins were mixed in certain ratios (1:1, 1:1.5, 1:2) of thiol to acrylate based on functional groups. The first stage photopolymers were cured in the presence of 2 wt % NPPOC-TMG with 400–500 nm of the irradiance intensity of 20 mW/cm², and the second stage polymerizations were performed with 2 wt % Irgacure 2959 in the presence of 20 mW/cm² UV light irradiation (365 nm). Spacers (250 μ m) were inserted on the sides of the glass slide. The resins were usually irradiated for 3–10 min, followed by annealing in a preheated oven at 80 °C for 24 h.

Synthesized Compounds Characterization—NMR spectra were performed on a Bruker Avance-III 400 NMR spectrometer in d-chloroform at room temperature. The synthesis of the photo base (Figures S1 and S2) and small molecule reaction model (Figure S4) were assessed with NMR.

Real-Time Fourier Transform Infrared (FT-IR) Spectroscopy—Polymerization kinetics were analyzed using a Fourier transform infrared spectroscopy (FTIR) instrument (Nicolet 8700) to monitor the real-time functional group conversions in transmission mode. Irradiation was performed using a mercury lamp (Acticure 4000) with 365 or 400–500 nm bandgap filters. The conversions of the thiol and vinyl functional groups were determined by monitoring the disappearance of the corresponding IR peaks. The thiol and acrylate monomer mixtures were placed between NaCl plates, and the thiol peak was monitored in the absorption range between 2500 and 2600 cm^{-1} while the acrylate peak was monitored in the range between 780 and 820 cm^{-1} .

Rheological Measurements—All rheology experiments were conducted using a TA Instruments ARES rheometer. Samples were prepared on 8 mm parallel geometry plates for dynamic testing. A dynamic time sweep test was performed using a strain of 30% and a frequency of 10 Hz for the first photo stage and a strain of 0.5% and a frequency of 0.2 Hz for the second stage photopolymerization, with data points being collected once every second. The evolutions of the modulus for both first and second stage were studied.

Dynamic Mechanical Analysis (DMA)—Mechanical properties of the polymers films, such as the glass transition temperature (T_g), rubbery modulus, and $\tan \delta$, were measured with a DMA Q800 (TA Instruments). Specimens were measured in multifrequency strain mode by applying a sinusoidal stress of 1 Hz frequency with the temperature ramping at 3 $^{\circ}\text{C min}^{-1}$. The T_g was determined as the maximum of the $\tan \delta$ profile. The rubbery moduli were measured in the rubbery region at $T_g + 30$ $^{\circ}\text{C}$. DMA resins were prepared by injecting between two glass sides with 0.45 mm thickness spacers irradiating with Acticure 4000 light source with 365 or 400–500 nm bandpass filter. T_g half-widths were taken as the widths of the $\tan \delta$ peaks at half-maximum values. DMA experiments were thermally cycled and replicated two times, and the representative curves are presented as the second heating cycle.

RESULTS AND DISCUSSION

Polymerization Kinetics

The anion-mediated thiol–Michael reaction and the radical-mediated acrylate homopolymerization are largely orthogonal, independent reactions that minimally interfere with each other during the polymerization. During the initiation of the first thiol–Michael polymerization stage, if any radical species associated with the photobase are generated, they will readily react to initiate the radical homopolymerization, thereby eliminating the desired orthogonality of the dual cure process. As a result, the desire for a wavelength-selective sequential polymerization significantly restricts the viable types of initiation systems. In particular, photobase generators must be selected such that there are no radical

intermediates formed during the photobase generation. As such, NPPOC-protected TMG was selected to photoinitiate the first thiol–Michael stage since it does not form radicals and also generates a “super base”, i.e., the guanidine species (high- pK_a organic base), which is a highly efficient thiol–Michael catalyst.^{37,38} For the second-stage radical initiation, many deep UV radical photoinitiators are viable, and Irgacure 2959 was selected as a representative photoinitiator. NPPOC-TMG and Irgacure 2959 are an ideal initiator pair for this wavelength-selective polymerization dual cure process because of their UV–vis light absorption characteristics as well (Figure 1). To demonstrate the orthogonality of the NPPOC-TMG and Irgacure 2959 initiation systems, off-stoichiometric monofunctional small molecule model compound reactions (butyl 3-mercaptopropionate:butyl acrylate with a molar ratio of 1:2) were performed and monitored by NMR spectra in solvent-free conditions at room temperature (Figures S3 and S4). After the 20 mW/cm² 400–500 nm light exposure, complete consumption of the thiol and 50% consumption of acrylate were found. Photolysis of the NPPOC-TMG induced a stoichiometric thiol–Michael reaction, and no acrylate homopolymerization was observed under these conditions. Subsequently, the same sample was exposed to 365 nm light, and the disappearance of the acrylate in the 5.7–6.5 ppm region indicated complete reaction of the residual acrylate.

After confirming the orthogonal initiation processes in small molecule model compounds, the NPPOC-TMG/Irgacure 2959 initiation system was performed to form two wavelength-controlled cross-linked polymer networks. Real-time Fourier transform infrared (FT-IR) was used to monitor the thiol (2500–2600 cm⁻¹) and acrylate peaks (790–830 cm⁻¹) in off-stoichiometric PETMP/TCDDA polymerization systems during the photopolymerization process. Upon 400–500 nm irradiation, the photobase generator, NPPOC-TMG, is cleaved and releases TMG. Then, TMG catalyzes the first-stage thiol–Michael polymerization, which leads to the formation of a loosely cross-linked step-growth network. In the PETMP/TCDDA systems, for thiol–acrylate ratios of 1:1.5 (a), 1:2 (b), and 1:3 (c), all of the thiol species and an equivalent molar amount of the acrylate species were consumed in the first stage thiol–Michael polymerization after 400–500 nm irradiation (Figure 3). Subsequent exposure to 365 nm light leads to radical generation from cleavage of the Irgacure 2959 which initiates the second-stage acrylate homopolymerization. After the photobase triggered stoichiometric thiol–Michael polymerization, whatever excess acrylate functional groups were originally in the system remain unreacted until exposure to the lower wavelength. In the control group (d) with no radical initiator, no second-stage polymerization was observed despite exposure to 365 nm irradiation, which further demonstrates that the NPPOC-TMG and any of its photoreaction side products do not affect the second stage radical polymerization. Thus, a UV radical initiator is necessary.

To analyze the polymer structure and to ensure a suitable material is formed at each stage of the reaction, the Flory–Stockmayer equation (eq 1) was implemented to determine the gel point conversion for the initial thiol–Michael step-growth polymerization for each stoichiometric ratio. Here, f_{thiol} and f_{vinyl} are the functionalities of the two monomers, and r_0 is the molar ratio of functional groups present ($r_0 = 1$).

$$\alpha = \frac{1}{\sqrt{r_0(f_{\text{thiol}}-1)(f_{\text{vinyl}}-1)}} \quad (1)$$

Theoretically, to achieve gelation at full conversion, the value of α , i.e., the conversion of the limiting functional group, has to be smaller than one. Hence, control over the state of the intermediate material following the Michael addition stage, i.e., whether it is a viscous gel or a cross-linked solid resin, is achieved simply by adjusting the ratio of the thiol to the acrylate functional groups. In this case, for the 1.5:1 and 2:1 molar ratios of thiols to acrylate functional groups in the diacrylate (TCDDA):tetrathiol (PETMP) mixtures ($\alpha < 1$), gelled, cross-linked networks are predicted to be formed and realized in actuality when these ratios are polymerized.

Rheology during Two-Stage Photopolymerization

In real-time rheological experiments, two PETMP–TCDDA systems with different functional group ratios (thiol-to-acrylate 1:1.5 and 1:2) were used. Time-dependent elastic (G') and viscous (G'') moduli were evaluated for 400–500 nm induced thiol–Michael stage and the subsequent 365 nm homopolymerization stage. It is shown that upon exposure to 400–500 nm light the elastic (G') and viscous (G'') moduli increased dramatically. The storage modulus exceeded the loss modulus, an indication of gelation, after approximately 100 s of irradiation for both the 1:1.5 and 1:2 systems (Figure 4a,c). Thus, both stoichiometric ratios formed gelled, cross-linked polymer networks ($G' > G''$) after the thiol–Michael stage. However, the 1:2 system had a lower final storage modulus (0.7 MPa) than the 1:1.5 system (1.7 MPa) due to the increased, unreacted acrylate excess in this curing stage. After initiating the acrylate polymerization with 365 nm light, the elastic modulus (G') of the film increased by 3-fold due to the formation of a more highly cross-linked material for both stoichiometries (Figure 4b,d). Different from the first thiol–Michael stage, the 1:2 system showed a much higher final modulus as compared to the 1:1.5 system. This phenomenon is explained by the higher final cross-linking density in the 1:2 system due to more extensive acrylate homopolymerization. These results indicate that the polymer properties of both photocontrolled stages can be manipulated and programmed by controlling the stoichiometric ratio in these systems. As compared to the kinetics measured by FT-IR, the photopolymer evolution was assessed by real-time rheological traces over a similar curing time. These traces exhibited comparable polymerization time scales under similar irradiation conditions (Figure S5).

Thermomechanical Performance

Thermomechanical transitions and behavior of the dual wavelength initiated resins were investigated using dynamic mechanical analysis (DMA) in tension mode. To investigate the NPPOC-TMG photo-initiation effect on the thiol–Michael network behavior, 1:1 stoichiometric PETMP/TCDDA formulations were cured with 1 wt % TEA and 2 wt % NPPOC-TMG (under 400–500 nm light), and the corresponding polymerization kinetics are shown in Figure S5. During the photoinitiation process, if even a small amount of radicals are generated, acrylate homopolymerization will occur in parallel with the thiol–Michael

polymerization, which, as a result, would form a less homogeneous polymer network with different T_g , T_g width, and elastic modulus values as compared to the polymerization that would only be base-catalyzed, thiol–Michael polymerizations. DMA results indicated that whether the stoichiometric network is formed from photoinitiation of NPPOC-TMG or catalyzed directly by triethylamine addition, nearly identical polymer networks are formed as evidenced by equivalent T_g and elastic modulus, which further indicates that there is no radical homopolymerization during the NPPOC-TMG photoinitiation.

Similar to the rheological traces, the 1:1.5 (thiol-to-acrylate ratio) and 1:2 PETMP/TCDDA systems were also analyzed by dynamic mechanical analysis (DMA) experiments to determine the mechanical performance of the material at each of the two distinct stages. Table 1 presents the glass transition temperature (T_g) and rubbery moduli for materials after both reaction stages. In Figure 5a (1:1.5 system) and Figure 5b (1:2 system) representative curves are presented for the second heating cycle in the DMA. The second heating cycle is used to eliminate the effects of additional reaction associated with the trapped radicals from the acrylate homopolymerization stage. For both stoichiometries the thiol–Michael reaction resulted in polymer networks with a relatively low T_g . Subsequently, after the acrylate homopolymerization occurred, the 1:1.5 system and 1:2 system exhibited a 30 and 50 °C T_g increase, respectively, as a result of the increased stiffness and higher cross-link density achieved in both resins. Increased storage moduli are also observed after the acrylate reaction in both systems. A greater increase in the storage modulus and T_g is observed in systems with a larger initial acrylate excess due to the expanded capacity for these resins to increase their cross-link density during the acrylate homopolymerization.

Wavelength-Selective Polymerization Diversity

Initiation System Diversity—The kinetic, rheological, and thermomechanical experiments indicated that combining NPPOC-TMG and Irgacure 2959 initiation, cleaved with different wavelengths (400–500 and 365 nm), enables control of the distinct dual cure network (thiol–Michael polymerization and radical homopolymerization) formation. However, the generalization of this concept is not limited to the NPPOC-TMG and Irgacure 2959 pair. By changing the photobase–radical initiator combinations, the initiation conditions necessary for achieving the desired two-stage polymerization are quite flexible. For example, the use of a photosensitizer such as ITX (isopropylthioxanthone, absorption ends at 440 nm) enables NPPOC-TMG to respond to even longer wavelengths of light (455 nm LED light) to initiate the first thiol–Michael polymerization (Figure S6). Here, exploiting the absorption difference of NPPOC-TMG and a visible light radical initiation system based on camphorquinone (CQ) (Figure 6a), a different wavelength-selective polymerization is realized with a reversal in the induction sequence, where 365 nm is used to initiate the first-stage thiol–Michael polymerization and 400–500 nm light is used to initiate the second-stage radical polymerization. Because of a minimal but finite absorption of CQ at 365 nm and due to the potentially photosensitization effects of NPPOC structure, extended 365 nm irradiation will generate radical species as well as the desired TMG. Fortunately, the ability for the thiol–Michael reaction to proceed for extended periods of time in the dark is useful in overcoming this problem. Even with only limited exposure time, the photogenerated base will initiate the thiol–Michael polymerization by forming long-lived

intermediates (i.e., the thiolate anion and a carbanion), which are negligibly influenced by oxygen or quenched by any radical-type recombination or other termination reactions. As such, these anionic intermediates enable the thiol–Michael reaction to proceed in the dark and achieve a high final conversion even with only a relatively short exposure period. Thus, a limited 365 nm exposure duration was implemented in the 1:1.5 PETMP-TCDDA system. After 30 s of 365 nm light irradiation at 20 mW/cm², the thiol conversion was only 20–30% immediately after the light was extinguished. But due to the effective living nature of the thiol–Michael reaction, the thiol conversion continued and ultimately achieved nearly quantitative conversion (Figure 6b). As a consequence, no obvious radical homopolymerization was detected in the UV light-triggered thiol–Michael stage. Subsequently, the intermediate thiol–Michael resin was exposed to 400–500 nm light to initiate the acrylate homopolymerization as triggered by CQ/EDAB. As compared to Irgacure 2959, the CQ/EDAB system is a relatively less efficient photoinitiating system, resulting in a slower second stage polymerization as shown in the kinetic plots. To overcome this drawback, high-intensity light was used to accelerate the second-stage radical polymerization. Further, we were also able to combine NPPOC-TMG with a radical thermal initiator (e.g., AIBN) to achieve a photoinitiated first-stage resin with tunable properties and then thermally cure the intermediate material to form a more highly cross-linked polymer network, which has the potential to be applied in adhesives, 3D printings, and other applications.

Polymerization System Diversity—In addition to the ability to utilize different initiation systems, this generalized approach can be further implemented in other fundamentally distinct polymerization systems, where anion-mediated reactions are used as a first stage (e.g., thiol–epoxy reaction, aza-Michael addition, for example) and radical-mediated reactions are used as the second stage (e.g., thiol–ene reaction, thiol–yne reaction, methacrylate homopolymerization, etc.). To demonstrate one such extension, we created a thiol–Michael (first stage) and thiol–ene (second stage) hybrid polymer system (Figure 7). NPPOC-TMG and Irgacure 2959 initiation systems were utilized to photoinitiate the PETMP/TCDDA/TATATO system with a functional group ratio of 2:1:1 thiol:acrylate:ene. The real-time rheological development was investigated for the polymerizations at both wavelengths (400–500 and 365 nm which initiated the thiol–Michael and thiol–ene polymerizations, respectively) and is presented in Figure S8. In Figure 7a, after the 400–500 nm initiated thiol–Michael stage, all of the acrylate moieties were reacted with equimolar thiol consumption. However, compared with the thiol–Michael/ acrylate homopolymerization two-stage systems, the subsequent 365 nm initiated thiol–ene reaction achieved only a limited thiol conversion (around 80%). This behavior is attributed to the reduced mobility of the reactive ends and the presence of a base which may also have a negative effect on the thiol–ene reaction rate and final conversion. As such, a lower T_g and elastic modulus are observed for the thiol–Michael/thiol–ene hybrid as compared to the thiol–Michael/ acrylate hybrid (Figure 7b).

CONCLUSIONS

In conclusion, by exploiting the photoresponsive properties of a novel initiation system (i.e., NPPOC-TMG/Irgacure 2959), the thiol–Michael click reaction and subsequent acrylate radical homopolymerization have been engineered to form a wavelength-selective dual cure polymer network. The 400–500 and 365 nm lights were implemented to control the sequential two-stage network construction in an orthogonal manner with high wavelength selectivity in each stage as confirmed by polymerization kinetics measurements. It was also demonstrated that tuning of the properties of the intermediate material and the final polymer is realized by manipulating the ratio of the thiol and acrylate functionalities. In addition to the thiol–acrylate polymerization system, a similar initiation system could also be used to initiate controllably many other types of polymerizations including the thiol–Michael/thiol–ene system demonstrated here.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

UV-vis absorption spectra for the photobase generator NPPOC-TMG that is used for the first stage and the radical generator Irgacure 2959 that is used for the second stage. The blue (400–500 nm) and red (365 nm) regions indicate the two light sources used for the dual cure photopolymerization.

Figure 3.

Thiol and acrylate functional group conversion versus time for wavelength-selective off-stoichiometric PETMP/TCDDA thiol-Michael polymerization systems: (a) thiol-acrylate ratio = 1:1.5; (b) thiol-acrylate ratio = 1:2; (c) thiol-acrylate ratio = 1:3; (d) control group with no radical initiator for second stage polymerization with a thiol-acrylate ratio = 1:1.5. All samples were composed of 2 wt % NPPOC-TMG and 1 wt % Irgacure 2959 (plot d only has NPPOC-TMG) and cured with 20 mW/cm² 400–500 nm light during the first thiol-Michael stage and 50 mW/cm² 365 nm light during the subsequent acrylate radical polymerization stage (dark region indicates dark condition without any induction light).

Figure 4.

Evolution of elastic (G') and viscous (G'') moduli as a function of time. (a) 400–500 nm irradiation for the 1:1.5 (thiol-to-acrylate ratio) system and (b) subsequent 365 nm irradiation, (c) 400–500 nm irradiation for the 1:2 (thiol-to-acrylate ratio) system, and (d) subsequent 365 nm irradiation. All samples were composed of 2 wt % NPPOC-TMG and 1 wt % Irgacure 2959 and cured with 20 mW/cm² 400–500 nm light during the first thiol–Michael stage and 20 mW/cm² 365 nm light during the subsequent acrylate radical polymerization stage (frequency and strain conditions depicted in the Materials and Methods section).

Figure 5.

Tan δ and storage modulus plots for (a) an acrylate to thiol ratio of 1.5:1 and (b) for an acrylate to thiol ratio of 2:1 in the PETMP/ TCDDA system. Both resin systems were composed of 2 wt % NPPOC-TMG and 1 wt % Irgacure 2959 and cured with 20 mW/cm² 400–500 nm light during the first-stage thiol–Michael polymerization and 50 mW/m² 365 nm light during the second-stage radical polymerization. Representative curves are presented as the second cycle in the DMA.

Figure 6.

CQ/EDAB/NPPOC-TMG as a combined initiation system for wavelength-selective two-stage polymerizations. (a) UV-vis absorption spectra of camphorquinone (CQ) and the photobase NPPOC-TMG. The blue (400–500 nm) and red (365 nm) regions indicate the two light sources used for the dual cure photopolymerization. (b) Plots of thiol and acrylate conversion versus time for CQ/EDAB/NPPOC-TMG controlled wavelength-selective polymerization in the 1:1.5 PETMP/TCDDA resin. The resin was composed of 2 wt % NPPOC-TMG and 3 wt % camphorquinone (CQ) and 3 wt % EDAB (CQ-EDAB molar ratio equals 1.1:1) cured with 20 mW/cm² 365 nm light during the first-stage thiol–Michael polymerization and 50 mW/m² 400–500 nm light during the second-stage radical polymerization.

Figure 7.

(a) Plot of acrylate and thiol conversion versus time in a thiol–Michael/thiol–ene type dual cure polymer network in PETMP/TCDDA/ TATATO (functional group molar ratio = 2:1:1). (b) Tan δ and storage modulus plots for the first stage and second stage in thiol–Michael/thiol ene hybrid system. The resin was composed of 2 wt % NPPOC-TMG and 1 wt % Irgacure 2959 cured with 20 mW/cm² 400–500 nm light during the first-stage thiol–Michael polymerization and 50 mW/m² 365 nm light during the second-stage thiol–ene radical polymerization.

Scheme 1.
Mechanism of Wavelength-Selective Thiol-Michael/Radical Homopolymer Network Formation Controlled with Different Wavelength Induction Lights (400–500 and 365 nm)

Table 1

Summary of DMA Results for a Series of Off-Stoichiometric PETMP/TCDDA Polymerizations Composed of 2 wt % NPPOC-TMG and 1 wt % Irgacure 2959 and Cured with 20 mW/cm² 400–500 nm Light during the First-Stage Thiol–Michael Polymerization and 50 mW/ m² 365 nm Light during the Second-Stage Radical Polymerization

acrylate:thiol	400–500 nm thiol–Michael stage		365 nm radical homo stage	
	T_g (°C)	modulus (MPa)	T_g (°C)	modulus (MPa)
1:1	26 ± 2	8 ± 1	26 ± 2	8 ± 1
1.5:1	2 ± 1	5 ± 1	34 ± 2	18 ± 1
2:1	–5 ± 2	2 ± 1	62 ± 3	23 ± 2