Photoswitching Cationic and Radical Polymerizations: Spatiotemporal Control of Thermoset Properties

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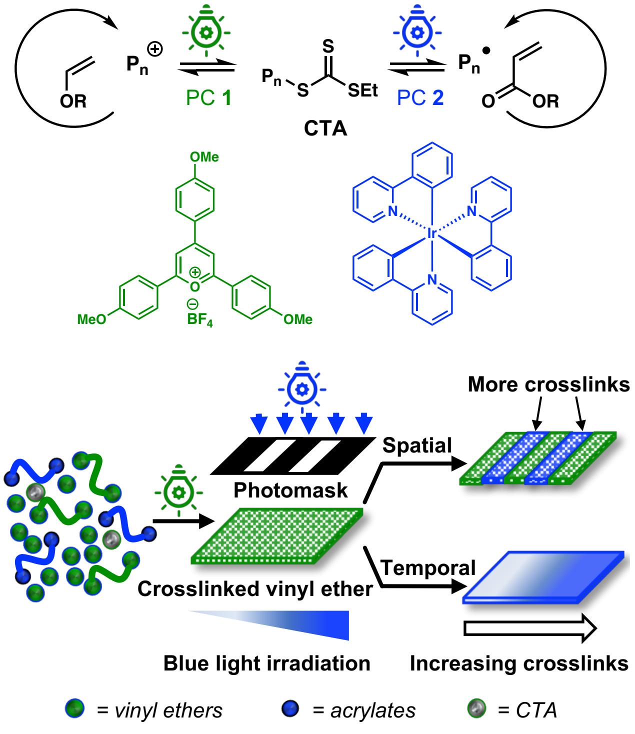
ABSTRACT: The ability to fabricate polymeric materials with spatially controlled physical properties has been a challenge in thermoset manufacturing. To address this challenge, this work takes advantage of a photoswitchable polymerization that selectively incorporates different monomers at a growing chain by converting from cationic to radical polymerizations through modulation of the wavelength of irradiation. By regulating the dosage and wavelength of light applied to the system, the mechanical properties of the crosslinked material can be temporally and spatially tuned. Furthermore, photopatterning can be achieved both on the macro scale and micro scale, enabling precise spatial control of crosslink density that results in high resolution control over mechanical properties.

Thermoset materials are a class of polymers that are hardened through irreversible crosslinking reactions. By forming covalent bonds between polymer chains, thermosets often possess strong and rigid structures. Because of their strong mechanical properties and chemical resistance, they are widely used in aerospace, construction, transportation and adhesives.[1, 2] However, it is challenging to produce thermosets composed of multiple materials while spatially controlling properties using conventional manufacturing methods.[3-5] For example, extrusion-based printing techniques can afford multimaterial structures quickly with little material waste, but the resulting architectures often possess poor mechanical properties due to the lack of interaction between different materials.[6, 7] Conversely, multimaterial vat polymerization can produce mechanically robust structures, but this technique typically requires several polymerization resins, adding time to the printing process and results in significant material waste.[8] Thus, there is a need to develop methodologies that enable selective transformations using a single resin to provide materials with spatially controlled properties.

Scheme 1. Tuning poly(IBVE) films mechanical properties by switching light.



Light is a powerful external stimulus to spatially and temporally control polymerizations.[9-20] Researchers have used light to control the polymerization of multiple types of monomers within a single photoresin.[5, 7, 21, 22] For example, the Boydston and Hawker groups have independently reported the use of two different wavelengths of light to spatially control the synthesis of epoxy-acrylate materials from a single photoresin.[21, 22] Another study conducted by Blinco, Blasco, Frisch, Barner-Kowollik and co-workers utilized wavelength-orthogonal ligation chemistry to selectively photocure multimaterial resist, fully independently of wavelength.[23] Because these methodologies are either photoinitiated or based on photodimerization, spatiotemporal control over chain growth is not possible.[24-26] Moreover, the epoxides and acrylates are not polymerized from the same growing chain ends, not allowing covalent linkages between the two polymer classes—this limits the structure integrity at the interfaces.[7] Therefore, the range of material properties that can be accessed is still limited. Thus, it is highly desirable to develop photoswitchable methodologies that have precise spatiotemporal control over polymer chain growth with expanded monomer scopes.

Our group has developed a polymerization process where we can change monomer selectivity at a growing polymer chain end by switching the mechanism of polymerization through

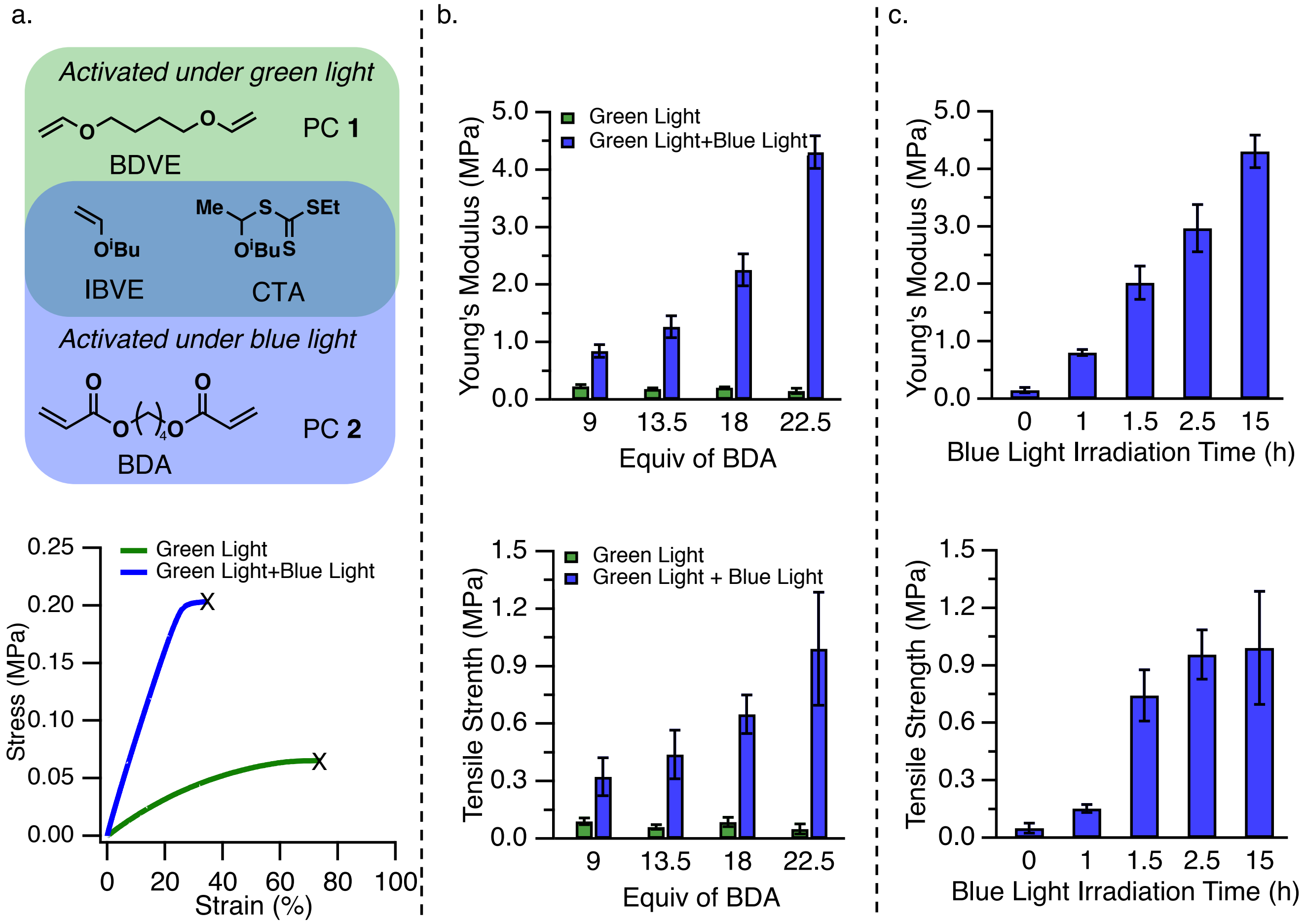


Figure 1. (a) Top: materials used to make poly(vinyl ether) films. Bottom: stress-strain curves of films synthesized using 9 equiv of BDA to 100 equiv of IBVE either under green light exposure (30 min) or green light (30 min) and blue light (15 h). (b) Young's modulus and tensile strength at break of poly(vinyl ether) films using different equivalences of BDA. (c) Young's modulus and tensile strength at break of poly(vinyl ether) films formed upon exposure to green light for 30 minutes and subsequent exposure to blue light for varying amount of time.

modulation of the wavelength of irradiation.[27, 28] Specifically, we developed a reversible addition-fragmentation chain-transfer (RAFT) polymerization that could switch between controlled cationic polymerization of vinyl ethers and radical polymerization of acrylates (Scheme 1).[29-32] Under green light irradiation, excitation of the photocatalyst 2,4,6-tris(p-methoxyphenyl) pyrylium tetrafluoroborate (PC **1**) led to reversible oxidation of the trithiocarbonate chain transfer agent (CTA) to give a stable trithiocarbonyl radical and an oxocarbenium ion that selectively initiates polymerization of vinyl ethers. In contrast, excitation of the reducing photocatalyst Ir(ppy)$_3$ (PC **2**) under blue light reduced the CTA to generate radical chain end that induced the radical polymerization of acrylates. Using this photoswitchable RAFT methodology, we were able to covalently link vinyl ethers and acrylates within growing polymer chains and build block polymers in one pot.

We hypothesized that we could extend this methodology to control the crosslink density of thermoset materials. We posited that irradiating a resin containing both vinyl ethers and acrylates along with CTA, PC **1**, and PC **2** with green light would selectively promote cationic polymerization and give a crosslinked poly(vinyl ether) film—upon switching to blue light the dormant polymer chains would be reduced and the acrylate crosslinker would be incorporated into the films. Significantly, the acrylate crosslinker would only be incorporated where the blue light was irradiated, and the amount of crosslinking should be directly proportional to the dosage of the light that a particular area receives. This methodology would enable us to spatially and temporally control the crosslink density and, therefore, mechanical properties of poly(vinyl ether) films.

To assess if we could use light to influence the mechanical properties of poly(vinyl ether) films, we made a solution containing isobutyl vinyl ether (IBVE), PC **1**, PC **2**, CTA, 1,4-butanediol divinyl ether (BDVE), and 1,4-butanediol diacrylate (BDA) (Figure 1a). We anticipated that irradiating this solution with green light would activate the oxidizing PC **1** and lead to the cationic polymerization of IBVE and BDVE, thereby forming crosslinked poly(IBVE) films. By subsequently irradiating the solution with blue light, we sought to activate the reducing PC **2** and polymerize BDA crosslinker through a radical mechanism. Because the films exposed to green and blue light would have acrylate crosslinks in addition to BDVE crosslinks, we expected these films to be stiffer than the films formed solely under green light irradiation. Using 9 equiv of BDA relative to 100 equiv of IBVE, a poly(IBVE) film with a stiffness (Young's modulus, *E*) of 0.2 MPa was formed upon irradiating the solution with green light for 0.5 h (Figure 1a, green trace). Successively irradiating this film with blue light for 15 h increased *E* to 0.8 MPa (Figure 1a, blue trace). Moreover, we observed a significant increase of carbonyl resonance signal on IR spectra after blue light irradiation. (Figure S9). This preliminary result is consistent with the idea that after the cationic polymerization, exposure of the film to blue light promoted the photocontrolled radical polymerization and incorporated the acrylate crosslinker to increase the crosslink density of the material.

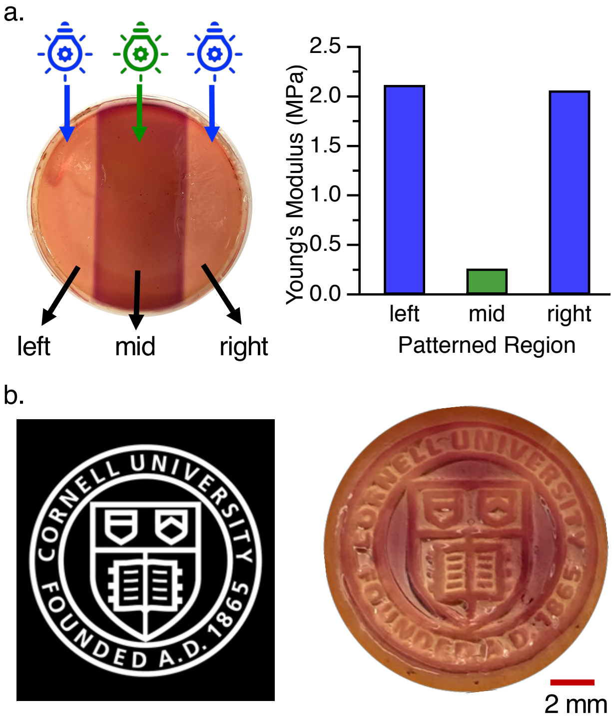


Figure 2. Spatial control of mechanical properties of poly(IBVE) films: (a) Mid section exposed to only green light has a lower Young's modulus compared to the outer sections exposed to both green and blue light. (b) Poly(IBVE) film was exposed to green light and then moved to collimated blue light covered by a photomask depicting the Cornell logo (left).

Next, we sought to systematically tune the mechanical properties of poly(IBVE) films by altering the amount of acrylate crosslinker incorporated under blue light irradiation. We speculated that the amount of acrylate that is added into the film would depend upon both the equivalence of BDA present in solution and the blue light irradiation time. Thus, we began by varying the ratio of BDA to IBVE and assessed the mechanical properties of the films formed under green and blue light irradiation (Figure 1b). Increasing the amount of BDA in four different solutions ranging from 9 to 22.5 equiv did not result in measurable differences in *E* or tensile strength (TS) at break of films formed under green light irradiation. However, subsequent irradiation of these films with blue light for 15 h resulted in substantial differences between materials synthesized with varying molar quantities of BDA. While the films synthesized with 9 equiv of BDA had an *E* of 0.8 MPa and a TS of 0.3 MPa, the films synthesized with 22.5 equiv of BDA exhibited an *E* of 4.3 MPa and a TS of 0.9 MPa (Figure 1b). These results show that the amount of acrylate crosslinker present in solution influences the mechanical properties of poly(IBVE) films during exposure to blue light irradiation.

To further probe the influence of acrylate crosslinker incorporation on the mechanical properties of these poly(IBVE) films, we varied the dosage of blue light applied to the film to temporally control the final crosslink density of the material. We analyzed the mechanical properties of films synthesized with 22.5 equiv of BDA under green light irradiation (0.5 h) followed by exposure to blue light for variable amounts of time (Figure 1c). We found that the Young's modulus of the material increased as the time of irradiation with blue light increased—for example, increasing the time of light exposure from 0 to 15 h led to a 40 fold increase in *E* (0.1 MPa to 4.3 MPa). These results demonstrate that by taking advantage of the photocontrolled radical polymerization process we can precisely control the crosslink density of our films.

In addition to affording temporal control of crosslink density, we were able to gain spatial control through the use of photomasks. After irradiating a reaction solution containing 22.5 equiv of BDA with green light for 0.5 h, we covered the middle (mid) section of this film with a mask and exposed the outer sections (left and right) to blue light for 2.5 h. We expected that the outer regions would have different mechanical properties compared to the mid-section. As shown in Figure 2a, the stiffness of the mid-section, which was only exposed to green light, is 0.3 MPa while the outer sections exhibit an increased stiffness of 2 MPa due to the inclusion of acrylate crosslinkers. Noticeably, the boundaries between the soft and stiff domains remain clear, implying that high resolution on the spatial control of mechanical properties is achievable. Moreover, we found the adhesion between different regions remains strong (Figure S8). The material broke at the soft region instead of at the interface during the dynamic mechanical analyzer characterization. These results demonstrate our ability to spatially control the mechanical properties of poly(IBVE) films by using green and blue wavelengths of light to alter the acrylate crosslinking.

To examine the resolution of crosslinked domains with different mechanical properties more specifically, we used photomasks to create domains with different crosslink densities. A crosslinked poly(IBVE) film formed via irradiation of a reaction mixture with 18 equiv of BDA under green light for 0.5 h. Then, we exposed the film to blue light covered by a photomask depicting the Cornell logo (Figure 2b). After blue light irradiation for 15 h, we obtained a poly(IBVE) film with a 1 mm feature size pattern. Furthermore, we scaled down the feature size of the photomask and made an array of 500 micron squares (Figure 3a).[33] The boundaries between domains with different degrees of crosslinking in the poly(IBVE) film still remained distinguishable based on optical microscope images (Figure 3b). In an effort to quantify the resolution of domain boundaries in terms of mechanical properties, we performed nanoindentation experiments on the poly(IBVE) film from Figure 3b across different regions. From typical load-displacement indentation curves (Figure 3c), we calculated the hardness (*H*) and reduced modulus (E_r). The *H* values of the regions exposed and unexposed to blue light are calculated to be 16.36 ± 0.95 MPa and 0.70 ± 0.14 MPa respectively, and the E_r values are 36.69 ± 2.06 MPa and 1.83 ± 0.12 MPa respectively, illustrating this poly(IBVE)'s dramatic increase in stiffness after blue light exposure. We also indented across the different crosslink domains on this poly(IBVE) film and mapped their physical properties

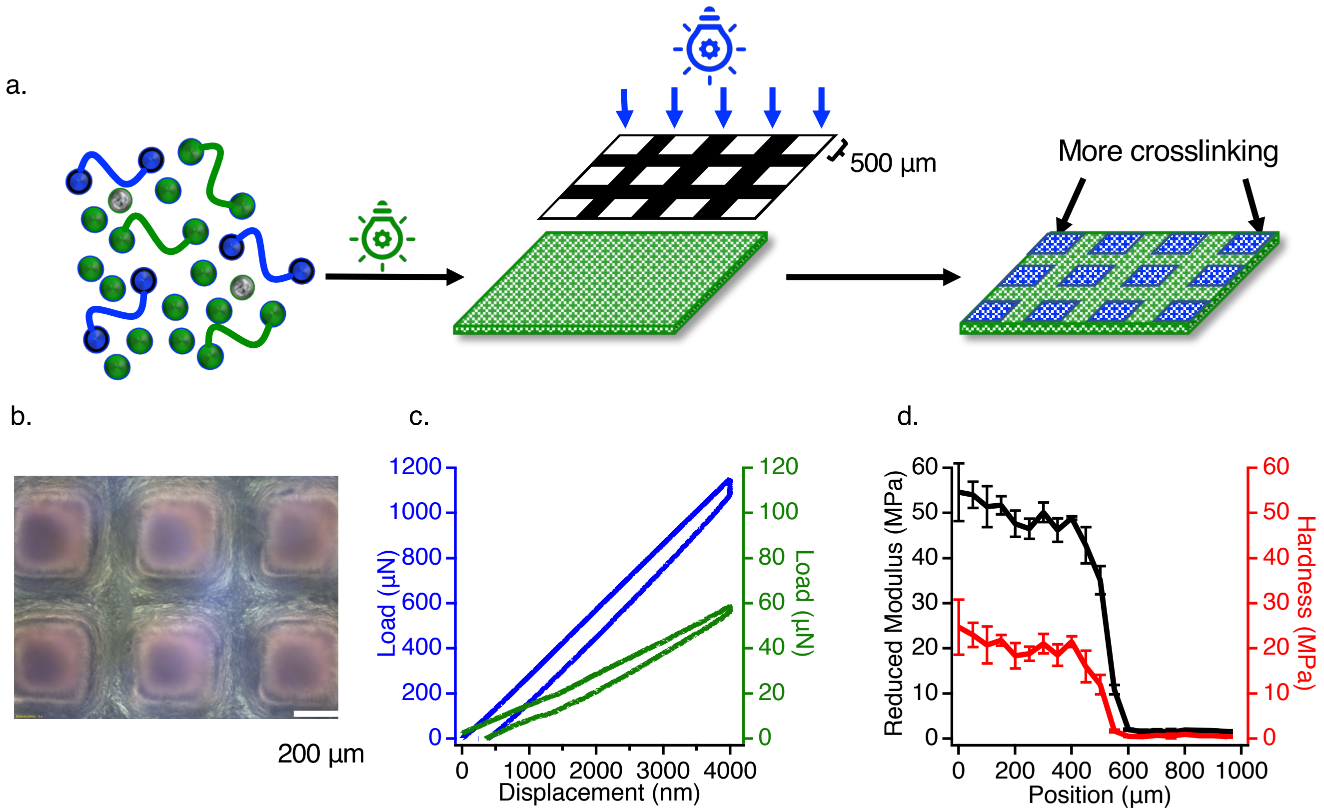


Figure 3. (a) Spatial control of poly(IBVE) film crosslink density by irradiating with green light and collimated blue light with a photomask having 500 microns square size. (b) Microscope image of poly(IBVE) film made in (a). (c) Load-displacement indentation curves from different regions of poly(IBVE) film in (b), which were exposed to green light (green trace) and both green and blue light (blue trace). (d) Reduced modulus (black trace) and hardness (red trace) mapping results across different exposure regions of poly(IBVE) film in (b); the position starts in a region after both green and blue exposure, and moves to a region with only green light exposure.

(Figure 3d). Two clearly distinct regions with nominally homogenous mechanical properties were observed. These nanoindentation measurements provide insight into the microscale resolution of spatial control of crosslink densities achievable through switching light irradiation. We expect the resolution of this approach to be limited by the wavelength of the irradiation.[34]

In summary, we developed a photoswitchable methodology that could selectively polymerize vinyl ethers or acrylates to give crosslinked materials within a single photoresin. The mechanical properties of the crosslinked polymers were easily tuned by changing the amount of acrylate crosslinker and irradiation time. By using photomasks, we created crosslinked domains with distinct mechanical properties with microscale resolution. In the future, we will expand this methodology to 3D materials. We envision that the low viscosity of the vinyl ether resins will help decrease the 3D printing time.[35] Also, combining with oxygen-tolerant RAFT polymerization will expand the potential applications for 3D printing.[10] Overall, the spatiotemporal control of crosslink density in this system will allow multimaterial 3D printing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Reagent and analytic information, general procedures, and additional studies.

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Notes

The authors declare no competing financial interest.

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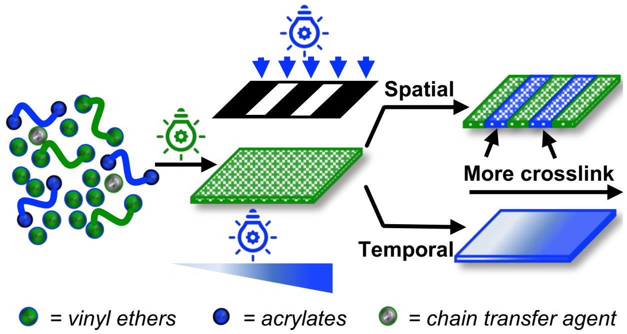
TOC Graphic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