

Functional Microcapsules via Thiol–Ene Photopolymerization in Droplet-Based Microfluidics

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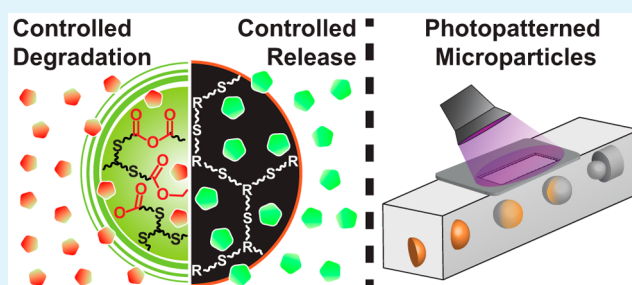
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S Supporting Information

ABSTRACT: Thiol–ene chemistry was exploited in droplet-based microfluidics to fabricate advanced microcapsules with tunable encapsulation, degradation, and thermal properties. In addition, by utilizing the thiol–ene photopolymerization with tunable cross-link density, we demonstrate the importance of monomer conversion on the retention of omniphilic cargo in double emulsion templated microcapsules. Furthermore, we highlight the rapid cure kinetics afforded by thiol–ene chemistry in a continuous flow photopatterning device for hemispherical microparticle production.

KEYWORDS: thiol–ene, microfluidics, encapsulation, degradable, photopatterning



Microcapsules hold great potential for applications involving the encapsulation, delivery, and release of actives in the fields of agriculture,¹ home care,² drug delivery,³ and cosmetics,⁴ with some commercial applications already in place. A variety of techniques, such as interfacial polymerization, complex coacervation, sol–gel encapsulation, and spray-drying have been used for the preparation of functional microcapsules.⁵ However, the size, shell thickness, and composition of the microcapsules obtained from these techniques vary significantly, limiting the usage of capsule technologies in many practical (or advanced) applications. Droplet-based microfluidics can overcome limitations associated with variability during microcapsule production by the precise control of multiphasic flows, leading to highly monodisperse multiple emulsion drops with fine-tunable size, morphologies, and compositions of each compartment; these emulsion drops have been utilized as templates to prepare functional microcapsules in which the chemical compositions of polymeric shells, shell thicknesses, and volume ratios of encapsulant to membrane can be fine-tuned.⁶ Traditionally, the polymeric shells in these emulsion-templated microcapsules^{7,8} are obtained by dissolving a polymer in a volatile solvent and allowing for solidification,⁹ through dewetting of a cosolvent to form polymersome shells from amphiphilic polymers,¹⁰ or direct photopolymerization of monomers.¹¹ Capsule shells fabricated from solvent approaches typically result in a nonhomogeneous structure during solidification; this leads to the undesired formation of small defects, and consequently, to loss of encapsulated active. By contrast, defect-free shell structures can be achieved by photopolymerization of monomers.¹² Although a wide variety of materials

have been examined for microparticle fabrication via photopolymerization, (i.e., methacrylates, acrylates, and cross-linkable poly(dimethylsiloxane) (PDMS)), many have intrinsic drawbacks. Methacrylates and acrylates suffer from inhibition of the polymerization by oxygen,¹³ polymerization induced stress development,¹⁴ incomplete reaction during curing,^{15,16} and most importantly, the formation of highly heterogeneous polymer networks.¹⁷ PDMS is capable of efficient photopolymerization but exhibits poor mechanical properties and poor solvent resistance leading to premature leakage of small actives that are highly diffusive.¹⁸ Thus, there remains an unmet need for a new tunable material platform for emulsion-based microcapsules that is photocurable, insensitive to oxygen, inexpensive, and modular in nature; this platform should possess tunable thermal-mechanical and chemical functionality, with simple processing conditions, in order to expand the range of possible applications.

Thiol–ene photopolymerization—a robust, radical-mediated step polyaddition process—offers a promising route for the synthesis of microcapsules possessing the aforementioned properties;^{19,20} however, previous reports of thiol–ene polymerizations in microfluidics have primarily focused on the synthesis of solid microparticles.²¹ Multifunctional thiol and alkene monomers—a large number of which are commercially available—offer unparalleled control of thermal-mechanical properties, cross-link density, and incorporation of orthogonal chemistries while providing rapid polymerization kinetics

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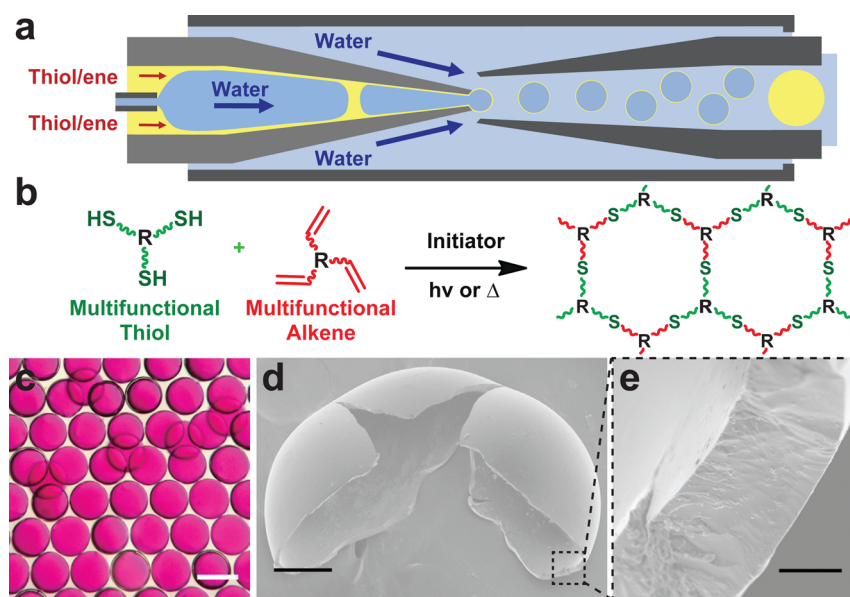
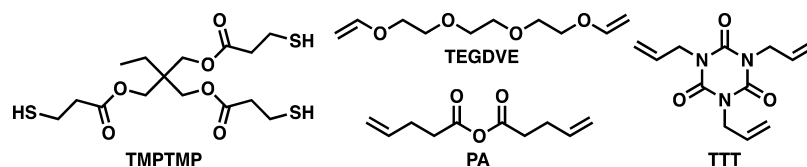


Figure 1. Production of thin-shell thiol-ene microcapsules. (a) Cross-sectional schematic of the glass capillary microfluidic device for preparation of thin-shell thiol-ene double emulsion drops. (b) General reaction scheme for the production of uniform thiol-ene networks. (c) Optical microscope image of monodisperse double emulsion drops produced; flow rates of the innermost aqueous phase (Q_I), middle thiol-ene monomer phase (Q_M), and outer aqueous phase (Q_O) were set at 500, 1000, and 10000 $\mu\text{L h}^{-1}$, respectively. Scale bar represents 300 μm . (d, e) Scanning electron microscope (SEM) images of dried microcapsules composed of TTT:TMPTMP at (d) low magnification (scale bar 100 μm) and at (e) higher magnification (scale bar 5 μm).

Scheme 1. Chemical Structures of the Monomers Employed for Thiol-ene Microcapsules and Microparticles



without the oxygen inhibition typically associated with other radical based polymerizations.¹⁹ Additionally, the onset of gelation during polymerization occurs at high conversion yielding low polymerization induced shrinkage and uniform network architecture.²²

In this paper, we describe a microfluidic approach for fabricating functional microcapsules via thiol-ene photopolymerization that show enhanced retention of an encapsulated model small active (fluorescein) that was previously shown to be highly permeable.²³ By inserting degradable anhydride monomers into the thiol-ene backbone, we demonstrate tailored release kinetics from a homogeneous degradable network, which aligns with the recent Microbead-Free Waters Act of 2015,²⁴ where all nondegradable plastic particles less than 5 mm are to be banned from sale in the United States.²⁴ We also show that thiol-ene microcapsules can be oxidized to tune the thermal-mechanical properties. Furthermore, we highlight the rapid cure kinetics afforded by thiol-ene chemistry in a continuous flow photopatterning device for hemispherical microparticle production.

To fabricate thiol-ene double emulsion drops, we use a glass capillary microfluidic device containing two tapered cylindrical glass capillaries—one for the injection, and the other for collection as shown in Figure 1a. The detailed procedure for preparing the device can be found in the Supporting Information. The tapered capillaries are aligned by insertion within a square capillary whose inner diameter is slightly larger

than the outer diameter of the cylindrical capillaries. The injection capillary is treated with *n*-octadecyltrimethoxysilane to modify the surface hydrophobic and the collection capillary is treated with 2-[methoxy(polyethyleneoxy)propyl] trimethoxysilane to make it hydrophilic. Additionally, a small cylindrical capillary is inserted into the injection capillary for the injection of an aqueous phase that forms the innermost drop of the double emulsions. The photocurable thiol-ene resin consisting of the thiol trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) and either tri(ethylene glycol) divinyl ether (TEGDVE), triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (TTT), or 4-pentenoic anhydride (PA) pairs shown in Scheme 1, is injected through the injection capillary. The hydrophobic treatment of the injection capillary facilitates pluglike flow with preferential wetting of the thiol-ene phase around the capillary. We inject an aqueous surfactant solution as the continuous phase through the interstitial space between the square and collection capillaries. The pluglike stream of encapsulated drops from the injection capillary break up into monodisperse double emulsion drops with a thin thiol-ene layer by shearing of the aqueous continuous phase. The resulting drops then flow through the collection capillary and are photocured with UV light (Figure 1b) to yield thin-shell microcapsules as shown in the optical microscope image of Figure 1c. The resulting microcapsules are 300 μm in diameter (Figure 1d) with a shell thickness of approximately 8 μm as shown in the scanning electron microscope images of Figure 1d, e. On the basis of the

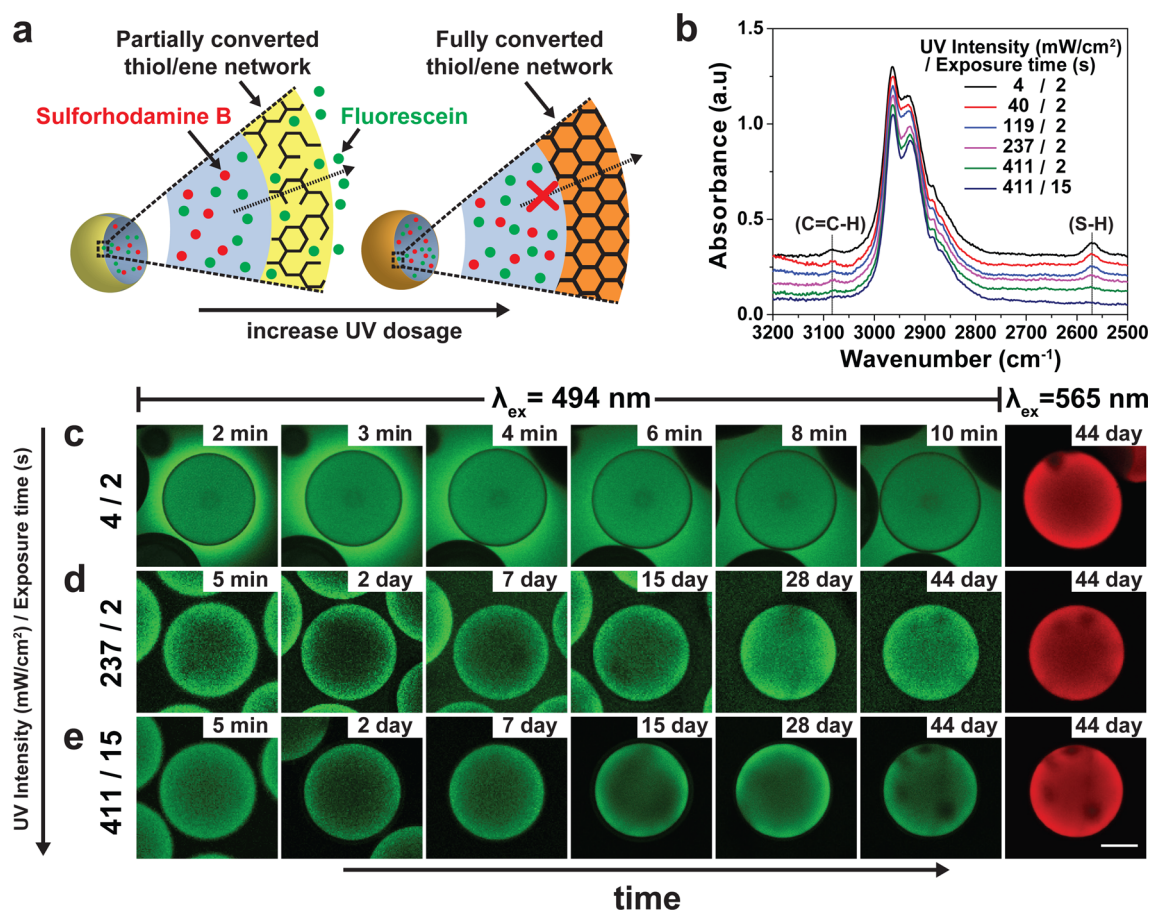


Figure 2. Effect of monomer conversion on the retention of small actives in thiol-ene microcapsules. (a) IR spectra of the resulting microcapsules after different cure conditions. (b) Scheme representing partially and fully converted thiol-ene network in microcapsules. (c–e) Fluorescence images of microcapsules encapsulating both fluorescein ($\lambda_{\text{ex}} = 494$) and sulforhodamine B ($\lambda_{\text{ex}} = 565$ nm) at different curing conditions: (c) 4 mW cm⁻²/2 s, (d) 237 mW cm⁻²/2 s, and (e) 411 mW cm⁻²/15 s. Scale bar represents 100 μm.

ratio of core volume to microcapsule volume, the loading capacity of the aqueous encapsulant phase is estimated to be around 85%.

The ability to produce a highly impermeable, yet homogeneous membrane with thiol-ene photopolymerization offers new opportunities for encapsulation and retention of small molecules in polymer microcapsules. To validate this capability, we prepared double emulsion microcapsules with different monomer conversion of the thiol-ene shell (TTT-TMPTMP, 1:1 SH:ene ratio) while encapsulating both fluorescein (green dye) and sulforhodamine B (red dye) as representative small actives as shown in Figure 2a. These two dyes exhibit different octanol/water partition coefficients ($\log P_{\text{oct/wat}}$): sulforhodamine B (hydrophilic, $\log P_{\text{oct/wat}} = -2.02$)²⁵ and fluorescein (omniphilic, $\log P_{\text{oct/wat}} = 0.34$).²⁶ Among these two model molecules, fluorescein was previously shown to completely leak within 24 h from double emulsion microcapsules with photopolymerizable acrylate shells without the additional reinforcement of fluorocarbon oil within the polymerized shell.²³

To study the effect of thiol-ene monomer conversion on the retention of these two types of small actives, we prepared sets of microcapsules with different extent of cure by independently varying the UV intensity and the cure time from 4–411 mW cm⁻² and 2–15 s, respectively. To determine conversion, we use Fourier-transform infrared spectroscopy (FT-IR) to monitor the consumption of thiol at 2570 cm⁻¹ and ene at

3085 cm⁻¹ under various polymerization conditions as shown in Figure 2b. Microcapsules cured under low intensity for short durations (4 mW cm⁻², 2 s) result in ~10% conversion and a partially cured membrane as indicated by the significant residual thiol and ene peaks in the IR spectra of Figure 2b. Increasing the cure intensity and curing time results in higher conversion, with 90% conversion of the monomers after curing under 411 mW cm⁻² for 15 s. By monitoring the leakage of dyes from microcapsules with different cure dosage via confocal laser microscopy over two months, we show that controlling the monomer conversion of the thiol-ene network results in microcapsules with tailored release as shown in the series of fluorescent images of Figure 2c–e and Figure S1. For microcapsules exposed to low UV intensity (4 mW cm⁻², 2 s), an immediate release of fluorescein was observed within 10 min, while sulforhodamine B was completely retained after 44 days as shown in the fluorescence images of Figure 2c. Fluorescein's $\log P_{\text{o/w}}$ value of 0.34 signifies that this dye can readily diffuse through both oil and water phase leading to rapid permeation through the incompletely cured membrane. By contrast, ionically charged sulforhodamine B with a $\log P_{\text{o/w}}$ value of -2.02 is unable to diffuse through the membrane resulting in complete retention within the capsule shell. The long-term retention of sulforhodamine B in microcapsules cured under low UV dosage also indicates that these microcapsules do not have physical defects such as holes, cracks, or voids as both dyes are not simultaneously released.

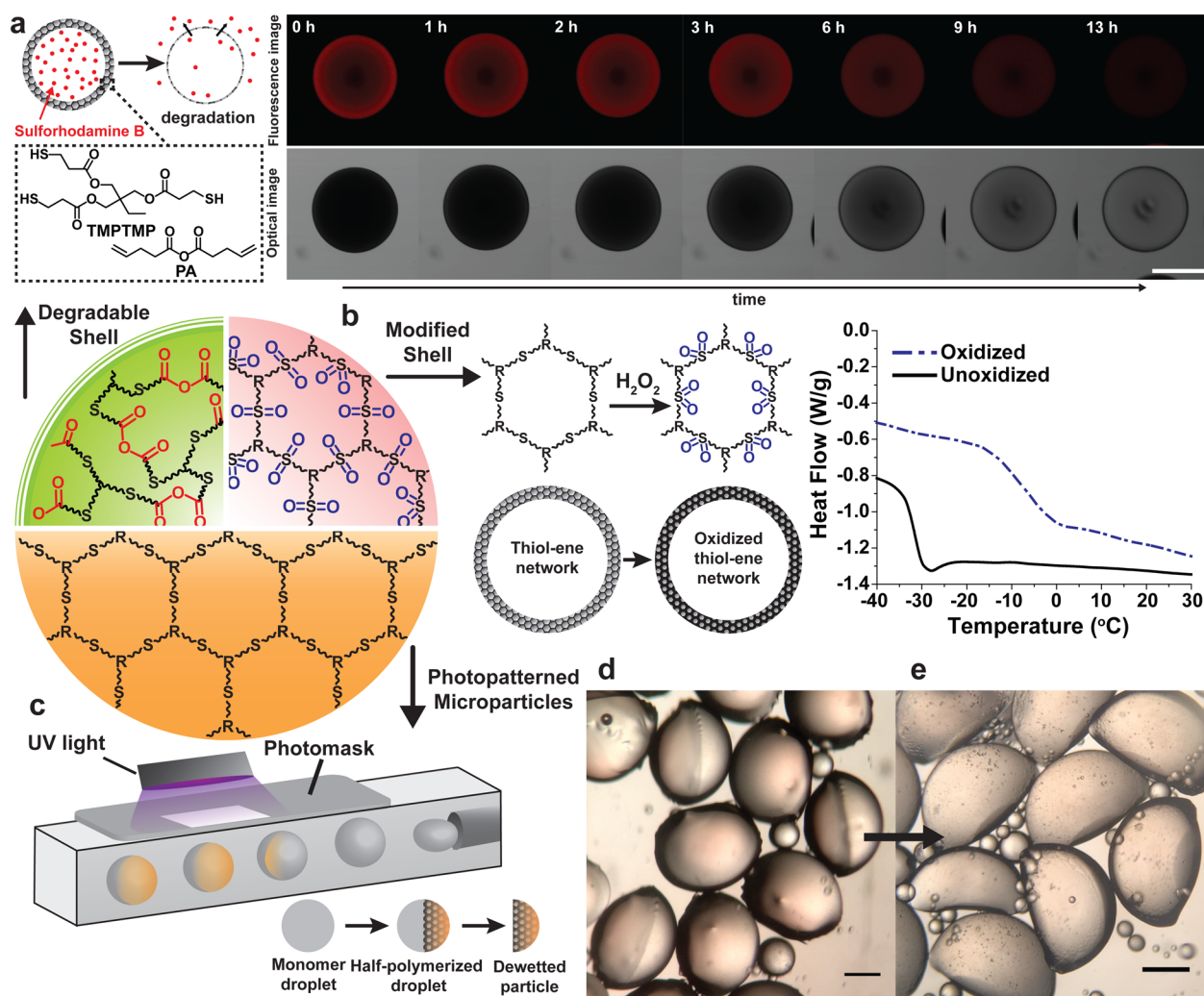


Figure 3. (a) Monomers used to prepare degradable microcapsules encapsulating aqueous solution of sulforhodamine B (red). The series of fluorescence (top) and optical (bottom) images on the right shows full retention of the dye within the microcapsule up to 3 h in DI water and subsequent gradual release due to surface erosion of the shell. Scale bar represents 50 μm . (b) Conversion of thiol-ene (sulfide) network into oxidized thiol-ene (sulfone) networks with hydrogen peroxide treatment. The plot on the right shows the differential scanning calorimetry (DSC) data before and after oxidation. (c) Scheme of a continuous photopatternable droplet device and the resulting particles (d) before and (e) after dewetting. Scale bars represent 500 μm .

The retention of fluorescein was substantially improved under medium UV intensity (237 mW cm^{-2} , 2 s) as shown in Figure 2d, where the onset of fluorescein release occurred between 2 and 7 days. The leakage still occurs, but at a much slower rate likely due to a higher ($\sim 60\%$) yet incomplete conversion of the thiol-ene monomers as indicated by the IR spectrum. Improved retention of both dyes for up to 44 days was achieved under high UV intensity and extended duration (411 mW cm^{-2} , 15 s) to ensure high conversion ($\sim 90\%$) of the membrane as shown in Figure 2e. The improved retention is further shown by dye release profiles of microcapsules at 2 and 44 days (Figure S2). These results indicate that the highly uniform polymer network provided by thiol-ene chemistry enables encapsulation and enhanced retention of omniphilic actives in microcapsules. Notably, fluorocarbon triple emulsions were required to achieve similar retentions in acrylate based capsules; however, these triple emulsions were sensitive to surfactant selection and are environmentally unfriendly.²³

Although the previous monomer set provided microcapsules for long-term retention, the versatility of thiol-ene provides

facile design of microcapsules with controlled degradation and subsequent release of actives via judicious choice of monomer. Inspired by the work of Shipp et al.,²⁷ we polymerized 4-pentenoic anhydride (PA) with TMPTMP, as shown in Scheme 1, to fabricate a degradable thiol-ene anhydride membrane. We encapsulated an aqueous solution of Sulforhodamine B because of its inability to permeate through a polymer membrane unless a significant void is formed, which is achieved in this case via surface erosion of the membrane. We monitored the leakage of sulforhodamine B using confocal laser microscopy and observed full retention up to 3 h and subsequent gradual disappearance of the dye from the capsule as shown in the fluorescence and optical images of Figure 3a. These results are in good agreement with literature, as within 15 h, significant degradation of the membrane has occurred leading to release of the encapsulated dye.

We further explore the utility of thiol-ene networks in emulsion templated microcapsules by demonstrating their ability to be postfunctionalized through very efficient reactions. We first prepared double-emulsion microcapsules consisting of

TEGDVE and TMPTMP to fabricate low glass transition ($T_g = -36\text{ }^\circ\text{C}$) temperature microcapsules. Then, we modified the sulfide linkages present in the capsule shell into sulfone linkages with H_2O_2 using the protocol recently highlighted by Podgórski et al.²⁸ Upon simple incubation of the microcapsules with H_2O_2 for 24 h, an increase in T_g from $-36\text{ }^\circ\text{C}$ to $-8\text{ }^\circ\text{C}$ was observed as shown in the differential scanning calorimetry plot of Figure 3b. This oxidation can be applied to networks derived from other thiol–ene monomer pairs to even increase the glass transition temperature up to $120\text{ }^\circ\text{C}$ higher than the original network.²⁸ This result indicates that the microcapsule shell can be postmodified to achieve tunable thermomechanical properties enabling technologies ranging from cosmetics to high performance coating–applications that require a range of service temperatures.

Finally, we exploit the rapid cure kinetics of thiol–ene based systems by demonstrating the production of photopatterned microparticles in a continuous process. A single emulsion droplet generator was outfitted with a steel photomask placed to expose half the channel width to UV light as shown in Figure 3c. The monomer combination TEGDVE:TMPTMP was used with the addition of a colorless spiropyran, Photorome I, which undergoes a photoinduced color change upon exposure to UV light. A certain percentage of Photorome I is irreversibly converted into a colored state which allows for visual contrast between the polymerized and nonpolymerized sections of the microparticles (Figure S3). As the droplets pass under the photomask, a color change was observed in the UV exposed half of the droplet, as shown in the optical image of the collected droplets in Figure 3d. Collection of the photopatterned microparticles in deionized water without presence of any surfactants to stabilize the drop allows the nonpolymerized oil portion to dewet and form polymerized hemispherical particles as shown in the optical image of Figure 3e. This simple demonstration exploits the rapid cure kinetics of thiol–ene photopolymerization which can yield new asymmetric or three-dimensional structures from emulsion drops. We anticipate that this approach will afford new tools for the polymer and colloid community with applications in particle self-assembly, drug delivery, and diagnostics.

In summary, thiol–ene chemistry was exploited in droplet based microfluidics to fabricate microcapsules with tunable encapsulation, degradation, and thermal properties. This work demonstrates the importance of monomer conversion on the retention of omniphilic cargo in double emulsion templated microcapsules. The wide range of commercially available thiol–ene monomers enabled easy incorporation of degradable anhydride linkages within the thiol–ene membrane–generating degradable microcapsules. The thiol–ene membrane itself can be oxidized to improve thermal/mechanical properties of the microparticles. Lastly, the rapid cure kinetics show great promise in generating photopolymerizable microparticles with complex geometries via continuous flow photomasking. The strategies of utilizing thiol–ene chemistry in fabrication of advanced microcapsules/particles outlined in this work are general and can be further extended to many biological applications including tissue engineering,²⁹ and immobilization of peptides and dyes within gels.³⁰ Moreover, while allyl and vinyl ethers were primarily discussed in this work, other alkenes such as norbornenes, n-vinyl amides, N-substituted maleimides or acrylates can be used to tune reactivity, release kinetics, and provide new network architectures with different reactive handles for simple postpolymerization modification or

sequestration. The rapid cure kinetics, ease of fabrication, and wide range of commercial monomers suggest unprecedented opportunities for designer emulsions with well-defined network architectures.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b16382.

Additional experimental details, expanded release profiles, and macroscopic images (PDF)

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Notes

The authors declare no competing financial interest.

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