

DOI: 10.1002/marc.((insert number))

## Communication

### Photoresponsive Gels Prepared by ROMP<sup>a</sup>

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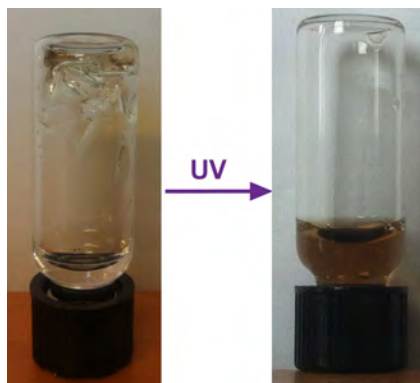
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This communication describes photoresponsive gels, prepared using ring-opening metathesis polymerization (ROMP), that dissolve upon irradiation with ultraviolet light. Exposure of mixtures of norbornene-type ROMP monomers and new photoreactive crosslinkers comprising two norbornene units bound through a chain containing *o*-nitrobenzyl esters (NBEs) to well-known ruthenium carbene catalysts gave crosslinked polymer networks that swelled in organic solvents or water depending on the structure of the monomer. These gels became homogeneous upon irradiation with UV light, consistent with breaking of the crosslinks through photolysis of the NBE groups. The irradiation time required for homogenization of the gels depended on the crosslink density and the structure of the photoresponsive crosslinker.



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<sup>a</sup> **Supporting Information** ((bold)) is available online from the Wiley Online Library or from the author.

## 1. Introduction

This communication describes ROMP-derived gels that degrade upon irradiation with UV light. Photodegradable polymers are an important class of materials that have target applications in the targeted delivery of therapeutics, tissue engineering, and the environmental degradation of packaging waste.<sup>[1-6]</sup> The advantages of light as a stimulus for these applications are its abundance as a natural source of energy, the tunable nature of its energy and intensity of light, its permeability through a variety of materials, and control over its spatial and temporal distribution.. Although photodegradable polymers encompass many material platforms, common among them is the appropriate incorporation of photocleavable chromophores into the structure of the material. For example, light-induced cleavage of photolabile groups on side chains or between blocks of a block copolymer<sup>[7,8]</sup> can disrupt block-copolymer (BCP) micelles,<sup>[9-15]</sup> and impart nanoporosity to microphase-separated films.<sup>[16-18]</sup> Light-induced cleavage of capping groups can induce spontaneous depolymerization of self-immolative polymers and yield rapid release of payload through dissolution of polymeric particles.<sup>[19-21]</sup> Removal of formally charged groups on side-chains bound to polymer backbones through photocleavable linkers yields light-induced changes in charge-charge interactions and disrupts layer-by-layer films.<sup>[22]</sup>

Along similar lines, incorporation of a stimuli-responsive chemical moiety into the structure of a chemical crosslinker can yield covalently crosslinked gels that degrade on-demand, with applications in the controlled delivery of molecules or cells.<sup>[23]</sup> Examples of stimuli successfully applied to photodegradable gels are changing pH,<sup>[24-26]</sup> introducing enzymatic activity,<sup>[27]</sup> or changing temperature.<sup>[28]</sup> A number of research groups have introduced photodegradable gels, almost exclusively prepared by free-radical polymerization, that have shown utility in the photopatterning of features in two or three dimensions,<sup>[3,29-32]</sup> control cell morphology, and the encapsulation and release of small molecules,<sup>[33,34]</sup> enzymes

and other proteins,<sup>[34-38]</sup> and cells.<sup>[39-42]</sup> More recently, an example of reversible addition-fragmentation chain-transfer polymerization (RAFT)-derived photodegradable hydrogels were reported.<sup>[43]</sup> In a different approach, photolabile groups can also be useful in revealing reactive functional groups such as amines to promote photoinduced cross-linking and subsequent post-cross-linking modification reactions.<sup>[44,45]</sup> The most common photolabile linkers in photodegradable gels contain *o*-nitrobenzyl (ONB) groups,<sup>[46,47]</sup> although there are other examples such as reversibly-photoresponsive anthracene or truxillate moieties.<sup>[48,49]</sup>

Well-known metal carbene catalysts developed for ring-opening metathesis polymerization (ROMP) have advantages such as high functional group tolerance, stable chain-ends for living polymerizations, and kinetics of initiation and propagation that are favorable for controlled polymerization and block-copolymer synthesis.<sup>[50,51]</sup> Our group and others have demonstrated the utility of ROMP as an alternative to radical polymerization of ONB-containing vinyl monomers,<sup>[52,53]</sup> which can be problematic because nitroaromatic rings can terminate the propagating radicals.<sup>[54]</sup> Despite the usefulness of ROMP, its use in the preparation of covalently crosslinked polymer networks is relatively rare, with several examples of hydrophobic thermosets<sup>[55]</sup> and hydrophilic hydrogel networks.<sup>[56,57]</sup> Our objective in this work was to demonstrate the potential utility of ROMP in the preparation of photodegradable gels.

## 2. Results and Discussion

Covalent polymer networks generally require a crosslinking molecule that contains two or more monomer moieties for linking individual polymer chains together. Our experimental design (**Figure 1**) was to incorporate photocleavable groups between norbornene units of a crosslinker suitable for ROMP. Upon copolymerization of a monomer with such a crosslinker, an insoluble network of polymer chains would be generated, which when swollen with organic solvent or water constitutes an organogel or hydrogel. Subsequent photolysis of

the photocleavable groups upon irradiation with light would break the links between polymer chains, disrupting the network and resulting in a mixture of soluble chains.

We therefore prepared photolabile crosslinkers **CL-1** and **CL-2**, each of which have two nitrobenzyl esters between the norbornyl monomeric moieties. The benzylic positions of **CL-1** have two hydrogen atoms, while the benzylic positions of **CL-2** have one hydrogen atom and one methyl group. Control crosslinker **CL-3** has an analogous chemical structure but lacks the nitrobenzyl ester units (**Scheme 1**). We chose this design for the photoresponsive crosslinkers, as opposed to having one nitrobenzyl group per crosslinker,<sup>[38,58]</sup> to both ensure equivalent reactivity of the two polymerizable termini of the cross-linker and increase the number of photolabile groups that could yield cleavage of the cross-link upon photolysis.

Protection of the phenol of 2-nitro-5-hydroxybenzaldehyde with tert-butyldimethylsilyl chloride (TBDMSCl) yielded silyl ether **1**, which sodium borohydride reduced to give nitrobenzyl alcohol **2**. We then acylated alcohol **2** with commercially available *exo*-5-norbornenecarboxylic acid using dicyclohexylcarbodiimide (DCC) activation to give nitrobenzyl ester **3**; esters derived from the *exo* diastereomer present less steric hindrance during ROMP than esters derived from the *endo* isomer.<sup>[59]</sup> Finally, fluoride-mediated deprotection of the silyl ether and alkylation of the resulting phenol **4** with 1,4-dibromobutane in the presence of potassium carbonate gave crosslinker **CL-1**. Synthesis of crosslinker **CL-2** proceeded in an analogous fashion, beginning with the preparation of **5** using a methyltitanium nucleophile,<sup>[60]</sup> followed by esterification of the benzylic alcohol and double alkylation of 1,4-dibromobutane with phenol following deprotection with TBAF. Preparation of photoinert crosslinker **CL-3** required only the double acylation of 1,4-butanediol with *exo*-5-norbornenecarboxylic acid.

**Figure 2** displays the solution-phase electronic absorbance spectra of **CL-1** and **CL-3**, as well as those of homopolymers of **Mono-1 (Poly-1)** and of **Mono-2 (Poly-2)**, as molar

extinction coefficient versus wavelength. These species represent the individual chromophores present in the polymer networks studied. Photoreactive crosslinkers **CL-1** and **CL-2** have similar absorbance spectra, with absorbance maxima near 310 nm, at which their molar extinction coefficients are  $\sim 10^4 \text{ M}^{-1}\text{cm}^{-1}$ , while their onset of absorbance is approximately 400 nm. Crosslinker **CL-3** and homopolymers **Poly-1** and **Poly-2**, each of which lack aromatic rings, have significantly blue-shifted and weaker absorbance, although they absorb light in the deep UV. These contrasts in spectral features allow for selective excitation of the photolabile nitrobenzyl aromatic rings in **CL-1** and **CL-2**.

Our first studies focused on the gelation and photochemical disruption of organogels comprising **CL-1** and ROMP monomer **Mono-1** (Figure 1), the butyl ester of 5-norbornenecarboxylic acid to form **OG-1**. For control experiments, we also prepared samples of **OG-3**, which comprised **Mono-1** and **CL-3**, the crosslinker lacking nitrobenzyl groups. In a straightforward procedure, dissolution of the monomer and crosslinker in dichloromethane at predetermined concentrations in a glass vial followed by addition of a commercially available ruthenium carbene catalyst (either Grubbs 2<sup>nd</sup> or 3<sup>rd</sup> generation catalyst) at room temperature yielded gels. We executed these polymerization reactions using 25–100 mg of monomer at concentrations in the hundreds of millimolar, and varied the ratio of crosslinker to catalyst as well as the ratio of monomer to catalyst. Whether gelation occurred depended strongly on the initial conditions of the reaction. Consistent with previous studies as well as theory concerning network formation, significant gelation only occurred when the crosslinker:catalyst ratio was greater than 1.<sup>[56,57]</sup> In addition, an initial concentration of catalyst of greater than 6 mM was required in order for efficient gelation at the relatively low concentrations of monomer used in these experiments (0.09–0.51 M), suggesting the importance of competitive macrocyclicization at these low monomer concentrations.<sup>[56]</sup> Gelation was observed within 15 minutes, except at a low ratio of crosslinker:catalyst (1.2), which required up to 30 minutes. We purified these gels by Soxhlet extraction with

dichloromethane. Removal of solvent *in vacuo* yielded xerogels that could be re-swollen with solvents of moderate polarity such as THF, dichloromethane, or benzene, whereas highly polar solvents such as methanol and water did not swell these materials. Gels with higher crosslink densities (3.0) were mechanically tougher than those with lower crosslink densities (1.5).

Crosslinker **CL-1** was also effective at inducing gelation of a hydrophilic monomer to yield hydrogels. Using the same polymerization procedures as described above for organogels, we prepared insoluble gels **HG-1** in dichloromethane that also swelled in water with oxanorbornene derivative **Mono-2** as the monomer, which Tew and coworkers previously reported for the preparation of ROMP hydrogels.<sup>[56,57]</sup> Upon swelling these materials in D<sub>2</sub>O for 1 hour, <sup>1</sup>H NMR analysis of the liquid phase revealed the presence of 2-dimethylaminoethanol, indicating that hydrolysis of some of the ester moieties occurs in water. Over the course of approximately 1 week, however, we did not observe any significant qualitative change of the hydrogels due to this background reaction.

To characterize the effects of nitrobenzyl photolysis on these crosslinked ROMP networks, we irradiated macroscopic swollen organogels with UV light. Samples were fabricated by swelling dry samples of **OG-1** in benzene. In each of these examples, we used polymer networks synthesized using an initial monomer concentration of 0.25 M and an initial catalyst concentration of 8 mM. We then irradiated these samples in benzene, contained in a glass vial, with wavelengths of light greater than 320 nm and monitored the sample visually for the absence of insoluble gel. We chose benzene because of its strong C-H bonds that radical intermediates are unlikely to cleave homolytically. Consistent with our experimental design, samples of **OG-1** turned yellow, which is characteristic of the photochemical byproducts of the nitrobenzyl esters. The gels became mechanically weaker during irradiation, consistent with decreasing the crosslink density of the materials. As summarized in **Table 1**, the time required for samples of benzene swollen **OG-1** to dissolve

completely in response to irradiation depended strongly on the crosslinker:catalyst ratio used in ROMP gelation reaction. With a crosslinker:catalyst molar ratio of 1.5, complete dissolution occurred in 16 hours, while a samples with a crosslinker:catalyst ratio of 3.0 did not dissolve completely even after 50 hours of UV irradiation. A sample of **OG-3**, which comprises **Mono-1** and **CL-3**, persisted as an insoluble gel upon irradiation with UV light under identical conditions. As expected, a  $^1\text{H}$  NMR spectrum of a sample of **OG-1** after irradiation and complete dissolution of gel were consistent with the spectrum of **Poly-1** (Figure 3). Control samples of **OG-1** and **OG-3** in benzene stored in the dark showed no observable change.

Irradiation of hydrogel **HG-1** (crosslinker:catalyst ratio of 1.5) in glass vials at  $\lambda > 320$  nm yielded gels that increased their swelling ratio by a factor of two within three hours (see supporting information). Complete dissolution of the gel, however, was not observed within 50 hours of irradiation under these conditions. Efforts to increase the rate of dissolution of otherwise identical hydrogel samples by using a quartz cuvette and deep UV light from a Rayonet photochemical reactor, however, did not result in increasing swelling of water-swollen **HG-1**, but instead induced deswelling of either gel **HG-1** or **HG-3** (prepared using **CL-3**), yielding in each case insoluble particles. As ES quartz transmits light with wavelengths as short as 190 nm, we attribute the observed deswelling of **HG-1** and **HG-3** to an increase in cross-link density due to background photochemical reactions, perhaps resulting from resulting from photoinduced electron transfer from the tertiary amines and subsequent radical reactions.<sup>[61]</sup>

In order to improve upon the reluctance of these photoresponsive samples containing **CL-1** to dissolve upon UV irradiation, we prepared organogels (**OG-2**) and hydrogels (**HG-2**) with **CL-2** using the same general procedure described above for gelation with **CL-1**. Kasko and coworkers have noted that acrylic-based gels with nitrobenzyl-containing crosslinking units respond more rapidly when the benzylic positions of the nitobenzyl esters are

monomethylated than when they are not.<sup>[40]</sup> Consistent with this precedent, the complete dissolution of **OG-2** and **HG-2** each required less than two hours of irradiation to dissolve in benzene or water, respectively. These times for light-induced solubilization are greater than one order of magnitude faster than that required for **OG-1** and **HG-1** (**Table 1**).

### **3. Conclusions**

We have developed new ROMP-derived organogels and hydrogels that incorporate photolabile norbornene-based crosslinkers. UV irradiation induces dissolution of these gels, with sensitivity to light that depend both on the structure of the nitrobenzyl photocleavable group and the crosslinker:initiator ratio used in their preparation. Adventitious features of our approach are the living nature, simple procedure, mild conditions, and fast kinetics of ROMP, in addition to the rapid kinetics of photoinduced gel dissolution with highly photoresponsive crosslinker **CL-2**.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author

Acknowledgements: This material is based upon work supported by a National Science Foundation CAREER award (DMR-1151385). J. L. was supported by the Beckman Scholars Program.

Received: Month XX, XXXX; Revised: Month XX, XXXX; Published online:

DOI: 10.1002/marc.((insert number))

Keywords: ring-opening metathesis polymerization (ROMP), gels, photochemistry, crosslinking, hydrogels



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## Figures and Table

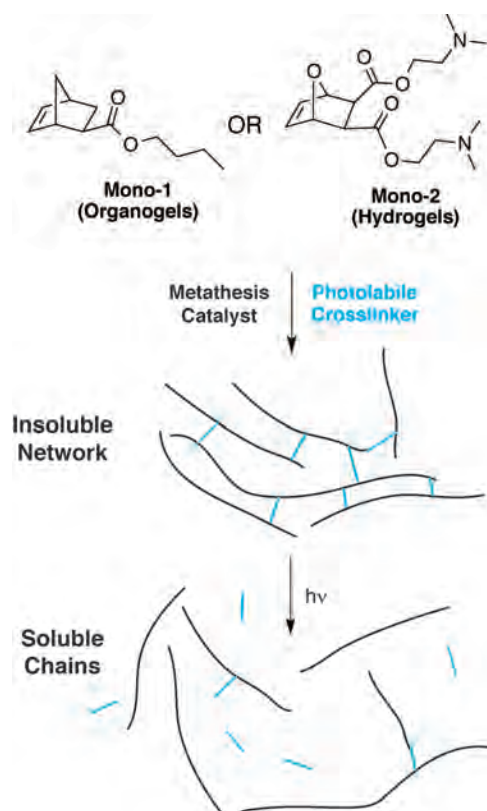
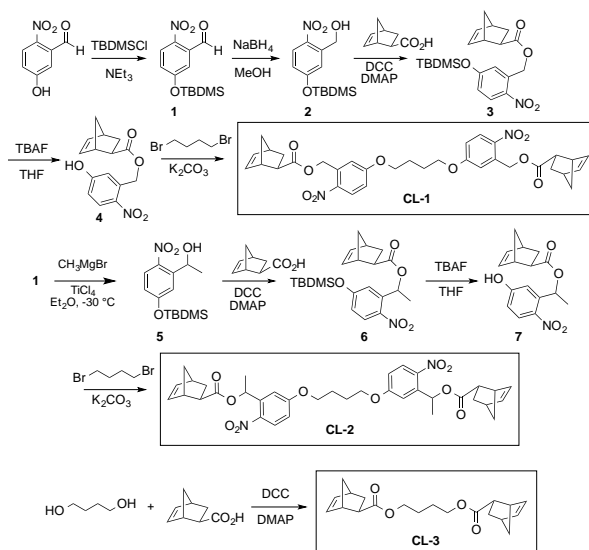


Figure 1. General design of ROMP gels that dissolve upon irradiation with UV light.



Scheme 1. Synthesis of photolabile crosslinkers **CL-1** and **CL-2** and photoinert crosslinker **CL-3** for use in ring-opening metathesis polymerizations.

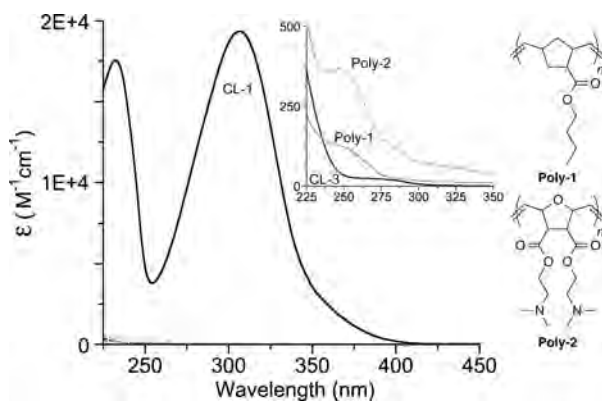


Figure 2. UV/vis absorbance spectra of crosslinkers **CL-1** (solid black line) and **CL-3** (dotted black line), and homopolymers **Poly-1** (solid gray line) and **Poly-2** (dotted gray line). Except for **Poly-2** (in water), all samples were dissolved in THF.

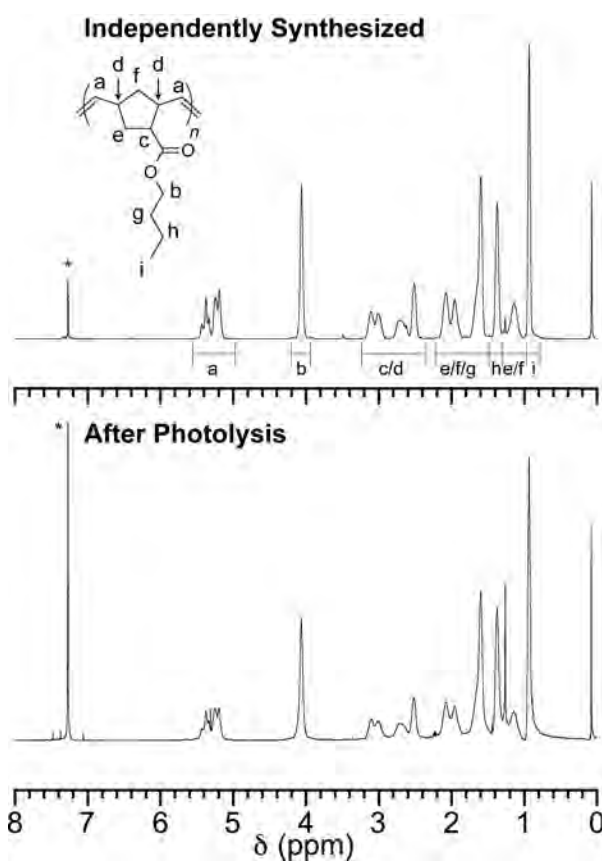


Figure 3.  $^1\text{H}$  NMR spectrum of sample of independently synthesized **Poly-1** in  $\text{CDCl}_3$  (top) and **OG-1** in  $\text{CDCl}_3$  after UV-induced gel dissolution (bottom).  $\text{CHCl}_3$  is indicated with \*.

*Table 1.* Irradiation time required to dissolve ~ 2.0 mg of gel using  $\lambda > 320$  nm from a 200 W Hg/Xe lamp

| <b>Gel<sup>a)</sup></b> | <b>Monomer</b> | <b>Crosslinker</b> | <b>CL:I<br/>[M/M]</b> | <b>Time Required<br/>[Hours]</b> |
|-------------------------|----------------|--------------------|-----------------------|----------------------------------|
| OG-1                    | Mono-1         | CL-1               | 3.0                   | > 50                             |
| OG-1                    | Mono-1         | CL-1               | 1.5                   | 16                               |
| HG-1                    | Mono-2         | CL-1               | 1.5                   | > 50                             |
| OG-2                    | Mono-1         | CL-2               | 1.5                   | 0.75                             |
| HG-2                    | Mono-2         | CL-2               | 1.5                   | 1.25                             |

**Light-responsive gels** combine ROMP with novel photoresponsive bis(norbornene) crosslinkers containing photolabile nitrobenzyl esters. Upon addition of commercially available ruthenium carbene catalysts, gelation is complete in a matter of minutes. Irradiation with UV light causes ROMP-derived organogels or hydrogels to swell and dissolve due to photolysis of the nitrobenzyl groups in the crosslinkers.

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