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Backbone-Photodegradable Polymers by Incorporating Acylsilane Monomers via Ring-Opening Metathesis Polymerization

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Supporting Information Placeholder

ABSTRACT: Materials capable of degradation upon exposure to light hold promise in a diverse range of applications including biomedical devices and smart coatings. Despite the rapid access to macromolecules with diverse compositions and architectures enabled by ring-opening metathesis polymerization (ROMP), a general strategy to introduce facile photodegradability into these polymers is lacking. Here, we report copolymers synthesized via ROMP that can be degraded by cleaving the backbone both in solution and solid states under irradiation with a 52 W, 390 nm Kessil LED to generate heterotelechelic low-molecular-weight fragments. To the best of our knowledge, this work represents the first instance of the incorporation of acylsilanes into a polymer backbone. Mechanistic investigation of the degradation process supports the intermediacy of an α -siloxy carbene, formed via a 1,2-photo Brook rearrangement, which undergoes insertion into water followed by cleavage of the resulting hemiacetal.

Backbone-degradable polymers have been pursued for many biomedical, nanomaterials and environmental applications.¹⁻⁷ The past few years have witnessed research efforts aimed at developing ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) generated macromolecules with degradable backbones. The excellent functional group tolerance of the ROMP has resulted in its application towards a wide range of functional materials; however, there remains a lack of ROMP-generated polymers bearing degradable units embedded within carbon-carbon bonded backbone of these materials.⁸⁻¹⁰ Recently, monomer designs have produced polymers with degradable functionalities within the backbone, most notably enol ethers,^{11,12} acetals,¹³⁻¹⁵ amins,¹⁶ silyl ethers,^{17,18} and other functionalities (Figure 1A).¹⁹⁻²³ While these elegant examples demonstrated efficient acid- and/or base-triggered polymer degradation, the scope and applicability of these materials would be expanded by the development of other stimuli that trigger polymer degradation.

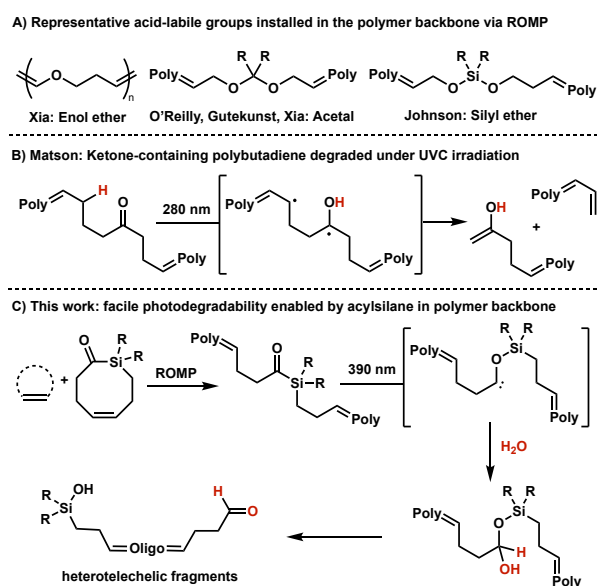
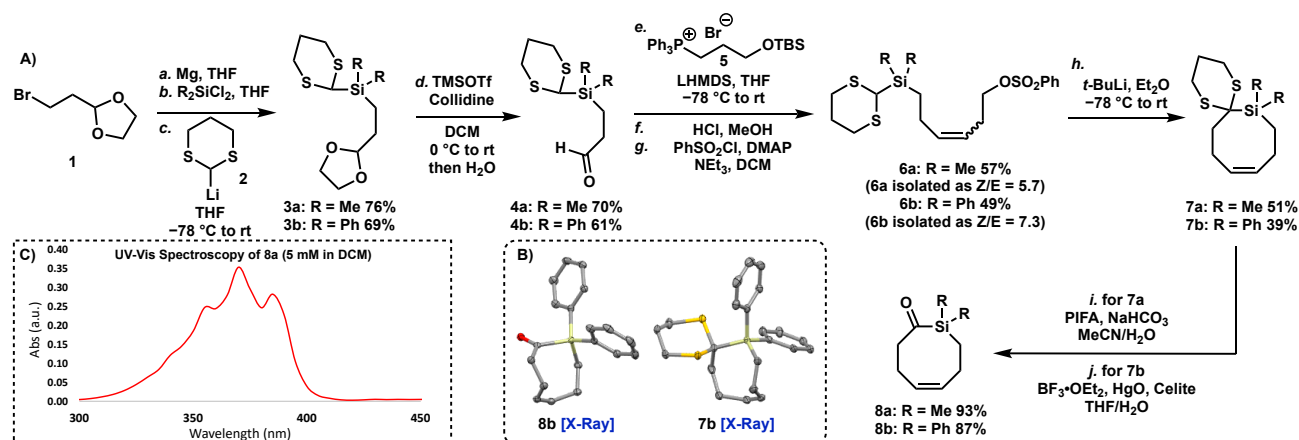


Figure 1. Design of backbone-degradable polymers via ROMP

Given the high spatial and temporal tunability as well as the non-invasive nature of light, photodegradability is a highly desired trait. In 2017, Matson and coworkers reported the ROMP of an unsaturated cyclic ketone and 1,5-cyclooctadiene.²⁴ The resulting polymer was degraded through a Norrish photocleavage using UVC light with a peak emission at 280 nm (Figure 1B). Inspired by this study, ROMP monomers were designed for polymers that degrade under less invasive, longer-wavelength irradiation, which would potentially be compatible with biomedical applications. Common photolabile scaffolds that absorb >300 nm light,²⁵ such as *o*-nitrobenzyl derivatives, have been incorporated into cross-linkers for core-degradable complex polymer architecture synthesized using ROMP.²⁶⁻²⁹ However, it remains challenging to design cyclic monomers containing these large scaffolds while maintaining the requisite strain energies for efficient ROMP with widely used monomers (e.g. cyclooctene-type and norbornene-type monomers).

Scheme 1. (A) Synthetic routes to cyclic acylsilane monomers^a; (B) Crystal structures of **7b** and **8b** determined by X-ray crystallography; (C) UV-Vis spectrum of **8a** that has a broad absorption in the range of 300–400 nm.



^aHydrogen atoms and solvents are omitted for clarity in the crystal structure of **7b** and **8b**; thermal ellipsoid plot is drawn at 50% probability.

Acylsilanes are attractive for such photolabile polymers, because of their long wavelength UV-absorption profile (350–420 nm) and potential cleavage mechanisms. These silicon-based moieties can be cleaved through either a Norrish-type homolysis or through the insertion of an α -siloxy carbene, generated via a 1,2- photo Brook rearrangement, into water followed by collapse of the hemiacetal (Figure 1C).^{30,31} Either degradation mechanism can enable access to end-functionalized fragments for further chemical modifications.

Additionally, polymers prepared by radical polymerization,³² with acylsilane in their sidechains, underwent chemical changes upon UV irradiation.^{33,34} Moreover, the small size of the acylsilanes was expected to enable straightforward design and synthetic planning of the proposed monomers. Thus, it was envisioned that eight-membered-ring acylsilane-based cyclic olefins would undergo efficient ROMP with other monomers and render a photodegradable polymer backbone.

Table 1. Copolymerization of cis-cyclooctene and cyclic acylsilane monomers via ROMP

entry	polymer	acylsilane monomer	[Ru]	[8] ₀ + [9] ₀ (M)	([8] ₀ + [9] ₀)/[Ru] ₀	M _n ^b (kDa)	\bar{D} ^b	Yield (%) ^c	acylsilane mol% ^d
1	P1	8a	G2	1.0	100	38.0	1.73	83	22
2	P2	8a	G2	1.0	200	40.4	1.75	84	20
3	P3	8a	G2	1.0	400	52.3	2.01	79	22
4	P4	8a	G3	1.0	400	44.3	1.86	72	21
5	P5	8a	G2	1.0	1000	76.5	2.08	77	20
6	P6	8b	G2	1.0	100	48.8	1.82	85	24
7	P7	8b	G2	1.0	200	60.8	1.99	85	21
8	P8	8b	G2	1.0	400	85.9	1.81	82	20
9	P9	8b	G2	1.0	1000	99.2	1.78	79	20

^aConditions: CHCl₃, room temperature, N₂ atmosphere, 30 min, then quenched with ethyl vinyl ether (EVE). ^bDetermined by GPC-RI detector in THF with polystyrene standard. ^cPolymer precipitated with methanol and dried *in vacuo*. ^dMole percentage of acylsilane units in the copolymers as determined by ¹H NMR spectroscopy.

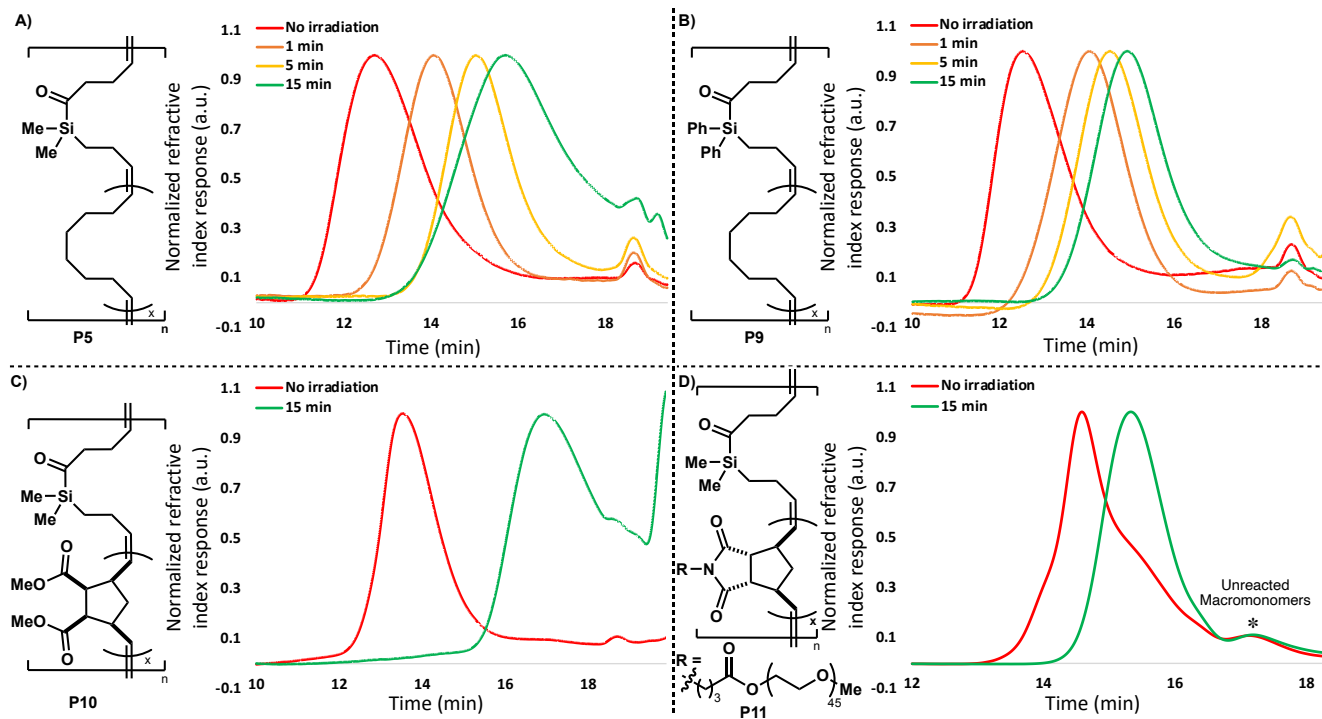


Figure 2. Photodegradation of acylsilane copolymers (A) **P5**; (B) **P9**; (C) **P10**; (D) **P11** in solution and GPC traces in THF; all irradiation studies were conducted on polymer solutions with a 52 W Kessil PR160L-390 nm LED lamp.

Spirodithianes **7a** and **7b** were readily synthesized through classical chemical transformations (Scheme 1A). Subjecting **7a** oxidative cleavage with PIFA yielded cyclic acylsilane **8a** in 93% yield. However, the same oxidative conditions led to complete decomposition of **7b**. Alternative conditions using mercury oxide were thus employed for **7b**, which generated acylsilane **8b** in 87% yield. These synthetic routes afforded cyclic acylsilane monomers **8a** and **8b** in 14% and 7% overall yields, respectively. Finally, the structure of **8b** was determined by X-ray crystallography (Scheme 1B). Monomer **8a** absorbs at a long-wavelength UV λ_{max} between 350–390 nm (Scheme 1C).

The calculated strain energies of **8a** and **8b** are -0.97 kcal/mol and -5.05 kcal/mol, respectively (See Supporting Information, Figure S1). Thus, homopolymerization of **8a** and **8b** are not thermodynamically favorable and were unsuccessful experimentally. Without homopolymerization, it becomes feasible to insert and modulate the distribution of cleaving points along a long polymer chain by copolymerizing these monomers with common ROMP monomers (cis-cyclooctene and norbornene-type monomers). Thus, polymer backbones can be cleaved when only a very small fraction of foreign monomers is added to minimize alteration of the polymer composition and properties. A 1:3 ratio monomers **8a/b**: cis-cyclooctene (**9**) underwent efficient copolymerization within 30 min using 2nd-generation Grubbs' catalyst (**G2**) in chloroform (Table 1). Catalyst loadings were varied with the $([8]_0+[9]_0)/[\text{Ru}]_0$ ratio ranging from 100 to 1000 (Table 1, entries 1–3 and 5–9). Copolymers from **8a** or **8b** (**P1-9**) consisting of >20 mol%

acylsilane were generated in high yields in all cases. When $([8]_0+[9]_0)/[\text{Ru}]_0 = 400$, **P3** was obtained in 79% yield with $M_n = 52.3$ kDa, $D = 2.01$, and 22% acylsilane incorporation (Table 1, entry 3). The same catalyst loading of 3rd-generation Grubbs' catalyst (**G3**) delivered **P4** in 72% yield with $D = 1.86$ and similar M_n and acylsilane ratio (Table 1, entry 4).

Photodegradation reactions of the copolymers were then examined. As a control experiment, the homopolymer of **9** was subjected to irradiation conditions (1 mg/ml in CHCl_3 , irradiated with a 52 W Kessil PR160L LED lamp with a peak emission at 390 nm). As expected, no degradation was observed by gel permeation chromatography (GPC) analysis (Figure S4). In contrast, exposure of a chloroform solution of dimethyl acylsilane-containing **P5** to the irradiation using the same LED source resulted in gradual decreases in molecular weight with increased irradiation periods (Figure 2A). Significant decreases in molecular weight and broadened molar mass distributions were observed after 15 min of irradiation: $M_n = 6.0$ kDa, $D = 3.86$ (peak cutoff at 19 min) compared to $M_n = 76.5$ kDa, $D = 2.08$ before irradiation. Notably, no significant degradation was observed in rigorously dried and degassed CHCl_3 , suggesting that the initial photochemical reaction was reversible in absence of water and air (Figure S8). When diphenyl acylsilane-containing **P9** was subjected to the same conditions in benchtop chloroform, the molecular weight decreased from $M_n = 99.2$ kDa to $M_n = 13.9$ kDa after 15-min irradiation (Figure 2B). In contrast to **P5**, the molar mass distribution of **P9** broadened only slightly (D changes from 1.78 to 1.88 after 15-

min irradiation), consistent with a more block-like copolymerization in **P9**.

Following the efficient photodegradation of the copolymers of cyclic acylsilanes and cis-cyclooctene, copolymerization reactions of **8a** and norbornene-type monomers were tested. When the copolymer **P10**, prepared from a 1:1 molar ratio of **8a** and norbornene dimethyl carbate (**10**), was subjected to 390 nm irradiation, nearly complete degradation of the pristine polymer was achieved after 15 min of irradiation, accompanied by the emergence of low-molecular-weight peaks eluting after 20 min. (Figure 2C). Finally, 15 min of irradiation resulted in a decrease in peak degree of polymerization (DP) from about 30 to 5 for bottlebrush copolymer **P11** containing methyl polyethylene glycol sidechains, (Figure 2D, DP of copolymers were estimated from homopolymerization of the macromonomer with targeted DP, see supporting information for details).

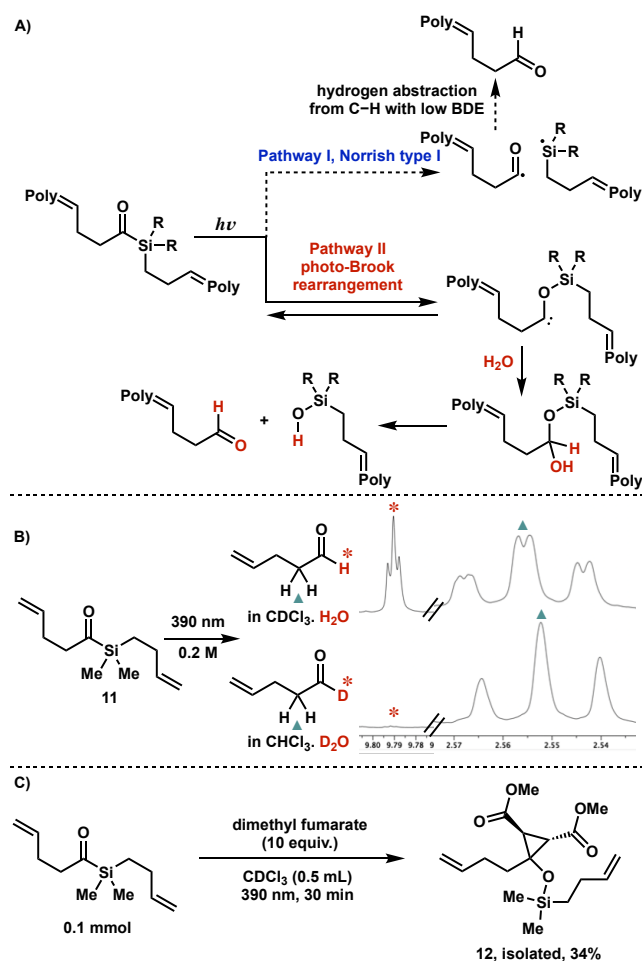


Figure 3. (A) Possible photodegradation mechanisms of acylsilane polymers; (B) Deuteration experiments in support of pathway II; (C) Photolysis of **11** in the presence of dimethyl fumarate led to cyclopropanation product.

Mechanistic investigation was conducted to provide insights into the photodegradation process of the acylsilane units in the solution. Pathways that involve a photogenerated radical^{35–38} or carbene^{39–42} are possible (Figure 3A). In pathway I, the acylsilane undergoes a Norrish type-I fragmentation to effect acyl and silyl radicals upon irradiation. The acyl radical can abstract a hydrogen atom from C–H bonds with low bond

dissociation energies (BDE) (such as allylic C–H bonds) and lead to aldehyde products. In pathway II, an α -siloxy carbene is generated *via* a 1,2-photo Brook rearrangement of the acylsilane followed by subsequent insertion into water and cleavage of the hemiacetal. $^1\text{H-NMR}$ spectroscopy revealed the formation of aldehydes during the irradiation of acylsilane-containing polymers. However, this observation alone cannot distinguish one mechanism from the other as both pathways produce aldehyde products. Thus, a D_2O -saturated polymer solution was selected for photodegradation. If pathway I is operative, the aldehyde hydrogen would be a proton, whereas deuterium incorporation would occur if pathway II is operative. Due to the existence of multiple aldehyde peaks in the $^1\text{H-NMR}$ spectra and low signal-to-noise ratio of the degraded polymer samples, studies were carried out using model compound **11**. Two samples with the same concentration were prepared using 1) H_2O -saturated CDCl_3 and 2) D_2O -saturated CHCl_3 as solvents. After irradiation, 4-pentenal was obtained as the major product in 1). In 2); however, only C1-deuterated 4-pentenal was observed, which is evident from the disappearance of the C1 proton peak (indicated by a red star, Figure 3B) and loss of J-coupling between C1 and C2 protons (indicated by a green triangle, Figure 3B) in the $^1\text{H-NMR}$ spectra (Figure 3C). Moreover, cyclopropanation product was not observed in the post-irradiation mixture. In contrast, photolysis of **11** in the presence of an electron-deficient alkene, dimethyl fumarate, led to **12** as the major product (Figure 3C). Again, the intramolecular cyclopropanation product was not observed in the post-irradiation mixture, likely the result of unfavorable cyclopropanation reaction of nucleophilic α -siloxy carbenes and unactivated alkenes. Collectively, these results support pathway II as the operative mechanism of acylsilane photodegradation in CHCl_3 .

Following the studies conducted in solution, photodegradation was probed in the solid state. Films of the copolymer of **8a** and **9**, 0.14 mm in thickness, were prepared through solution casting and exposed to 390 nm LED irradiation. Consistent with the results in solution degradation studies, gradual decreases in molecular weight and broadened molar mass distributions were observed after increased irradiation time (Figure 4A). The copolymer from **8a** and dicyclopentadiene (**13**) was also prepared (Figure 4B). Thermogravimetric analysis (TGA) of the polymer sample revealed the onset of thermal degradation (5% weight loss) occurred above 240 °C (Figure S13), indicating the complete incorporation of monomers into the polymer networks. The copolymer was then irradiated under 390 nm light for 30 min. and its surface morphology was characterized by scanning electron microscope (SEM). Before irradiation, SEM showed smooth areas along with wrinkles on the surface of the sample (Figures 4C and S14). In stark contrast, noticeable cracks and cavities emerged on the surface after irradiation (Figures 4D and S15). The post-irradiation sample was subjected to sonication in THF, resulting in fracturing after the sonication. The supernatant was analyzed by GPC, UPLC-MS and NMR (Figures S17-S19), which showed polymer fragments dissolved in THF (Figure 4D). The remaining solids were dried *in vacuo*, and a weight loss of 28% was noted compared to the pristine sample. Control experiments with polymer samples that underwent no irradiation showed no weight loss after sonication. The photodegradation shown here would potentially be utilized to upcycle the highly cross-

linked and mechanically strong polydicyclopentadiene at the end of its lifecycle.

In conclusion, cyclic acylsilane monomers for ROMP were successfully designed and synthesized. Efficient copolymerization of acylsilane monomers with common ROMP monomers was achieved. The resulting polymers were easily degraded under 390 nm irradiation both in solution and solid states, highlighting the untapped potential of acylsilanes as photocleavable groups. Low-molecular-weight fragments, with asymmetrically functionalized aldehyde and silanol end-groups, were generated from the photodegradation processes. The formation of the heterotelechelic fragments provides opportunities for post-degradation chemical upcycling. Mechanistic investigation revealed the α -siloxy carbene as a key intermediate in the degradation and adventitious water as a reaction component. These results will inform the synthesis of photoresponsive materials for use in sustainable materials and biomedical applications. The mechanistic insights garnered here also pave the way for α -siloxy carbene-mediated diversification of acylsilane-containing polymers in the future.

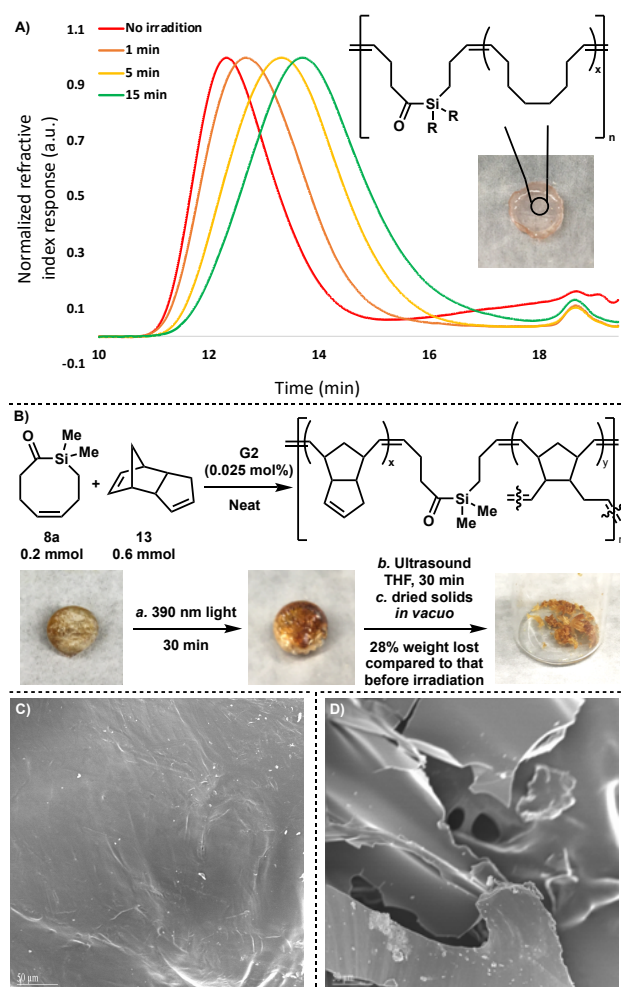


Figure 4. Photodegradation of acylsilane copolymers in the solid state; all irradiation studies were conducted with a 52 W Kessil PR160L-390 nm LED lamp: (A) Irradiation studies of polymer films and GPC traces in THF; (B) Irradiation studies of polydicyclopentadiene containing acylsilane; (C) SEM image of the copolymer sample before irradiation showed

smooth surface; (D) Holes and cracks emerged from the surface as shown by SEM image of the copolymer sample after 30 min irradiation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, supplemental figures, compound characterization data and spectra (PDF)

Accession Codes

CCDC 2089618 and 2089621 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

B.H. and F.D.T. are named inventors on a patent application filed by The Regents of the University of California on the monomers and copolymers described in this work.

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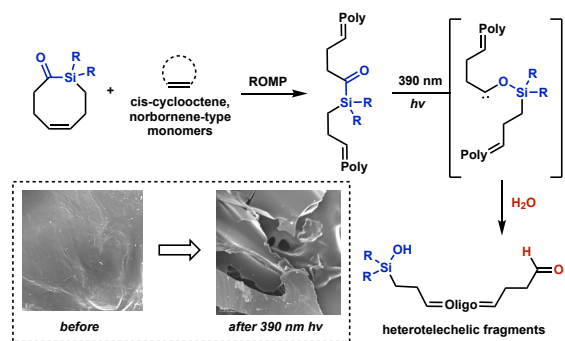


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