

PAPER

Construction from destruction using a photo-triggered self-propagating degradable polyurethane as a one-pot epoxy

Yanhua Xu,^{‡a} Ephraim G. Morado^{‡a} and Steven C. Zimmerman^{*a}

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We report a photo-triggered, base generating, base propagating degradable polyurethane that is triggered by 365 nm UV light irradiation. A small area of this polyurethane material can be exposed to 365 nm UV light irradiation to generate basic species that can initiate base propagated degradation process within the bulk material leading to global degradation without the need of continuous UV irradiation. The polymer was synthesized by a polycondensation polymerization of a small amount of *o*-nitrobenzene diol **2**, a large amount of Fmoc-based diol **3** and hexylmethylenediisocyanate. Integrating both photosensitive and base-sensitive carbamate moieties into the polymer **1** backbone provides the UV light-triggered base propagating degradable polyurethane material. Degradation studies of polymer **1** using ¹H NMR and gel permeation chromatography (GPC) suggest that initial UV irradiation triggers the degradation of the photosensitive *o*-nitrobenzene carbamate linkages, releasing a primary amino group that causes a cascade of amines to form by further degrading the remaining Fmoc carbamate groups. A bulk polyurethane film was prepared using Fmoc-based triol **4** as monomer. UV-irradiation of a small localized area of the film initiates the propagation throughout leading to efficient bulk degradation of the entire material. The amine degradation products could be utilized to make a one-pot epoxy adhesive, showing a potential upcycling application of this self-propagating degradable polyurethane system.

Introduction

Light-responsive polymeric materials are used in a wide range of applications, including in tissue engineering, drug delivery, micro-robotics, photolithography and disposable plastics.^{1–8} Compared to other stimuli, light has the distinct advantage the wavelength, intensity, irradiation area, and time are easily tunable. Photo-triggered degradable polymers most often feature two general designs: the photocleavable moiety is (a) directly incorporated into the polymer main chain (chain-shattering)^{9–14} or as an end-cap (e.g., self-immolative)^{15–17} or (b) incorporated into the polymer as a pendant chain, whose photo-responsive group exposes a nucleophilic functional group on the pendant chain for intramolecular cyclization.^{18–21} The pendant chain photo-reaction may also expose an unstable quinone-methide structures within the polymer backbone^{22–25} and thereby breaking down the main chain.

Although there are other photo-labile protecting groups, the *o*-nitrobenzyl (ONB) group remains the most widely used photo-triggered moiety in large part because of its excellent performance, clean chemistry, well-studied mechanism, and ease of synthesis.^{26–33} The degradation of the ONB group

proceeds through a Norrish-type II reaction mechanism, which by virtue of being an intramolecular rearrangement, can easily occur in solution as well as in the solid state.³⁴ Particularly relevant to this study is a report by Fréchet and co-workers of the production of organic bases by UV irradiation of the *o*-nitrobenzyl carbamates of amines and diamines.³⁵

As noted above, both self-immolative polymers and chain-shattering degradable polymers have been shown to undergo successful photo-triggered degradation by incorporation of ONB groups within the polymer backbone or as a pendant chain. However, both types of degradable polymers still require a stoichiometric amount of stimulus for complete degradation and neither approach can achieve continuous macroscopic long-range degradation of the bulk material by localized light stimulation.

Adapted from small molecule amplifiers, novel self-amplifying degradable polymeric materials have been developed over the past few years.^{36–42} Previously we were able to develop a base-triggered, self-amplifying degradable polyurethane wherein addition of exogenous amines initiated an amplified degradation.⁴³ However, this trigger is not practical for a number of applications. We hypothesized that incorporating a small amount of an amine-protected ONB monomer via copolymerization would provide a light-triggered system with self-amplifying and self-propagating degradation properties.

^a Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA. E-mail: sczimmer@illinois.edu

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[‡] These authors contribute equally.

Herein, we report a material that undergoes a light-activated, macroscopic degradation through a long-range propagation mechanism upon exposure of a small area to UV light irradiation. However, the system is surprisingly found not to be self-amplifying. Polyurethanes were selected for this study because they are widely used and there is considerable interest in their degradation under mild conditions, particularly in the context of recycling or upcycling.⁴⁴⁻⁴⁷ As a proof of concept application, we show how to use the degradation products as precursors to a one-pot epoxy adhesive. The overall process of mild degradation of the polyurethane with subsequent upcycling into a high-performance adhesive demonstrates the potential for a new generation of sustainable polyurethane materials.

Results and discussion

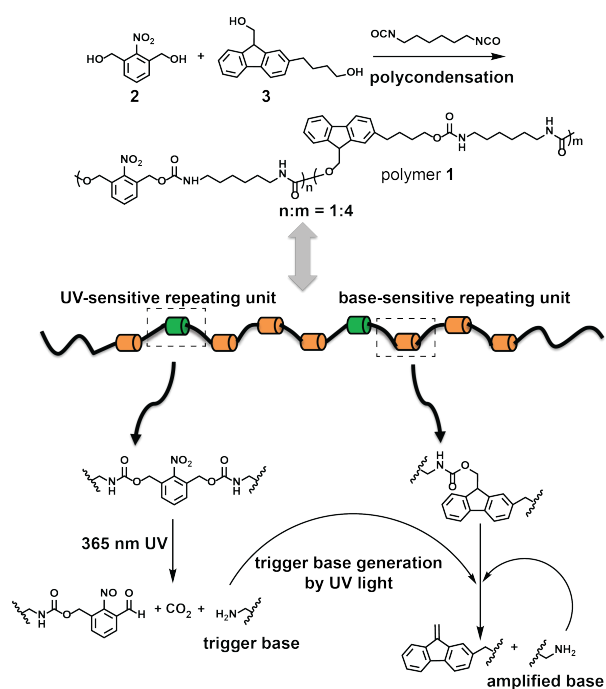


Fig. 1 Design of light-triggered base-propagating degradable polymer 1 by copolymerization (top) and its degradation mechanism initiated by 365 nm UV light irradiation (bottom).

Polymer 1 was prepared by copolymerization with the use of *o*-nitrobenzyl diol **2** (0.2 eq), Fmoc-based diol **3** (0.8 eq), hexylmethane diisocyanate, and 0.1 eq of dibutyltin dilaurate (DBTDL) as catalyst with *N*-methylpyrrolidone (NMP) as solvent at room temperature (Fig. 1). Linear polymer 1 contains two types of stimuli-responsive cleavable repeat units, one that is sensitive to 365 nm UV light, the other sensitive to base. With 365 nm UV light irradiation, one side of the *o*-nitrobenzyl carbamate undergoes photolytic cleavage through a Norrish-type reaction mechanism. Subsequent decarboxylation generates a primary amino group and a nitrosobenzaldehyde side-product. The exposed chain-end amino groups may act as the trigger to induce the degradation of a larger amount of the base-sensitive Fmoc carbamate units in the polymer backbone. The overall degradation scheme is outlined in Figure 1.

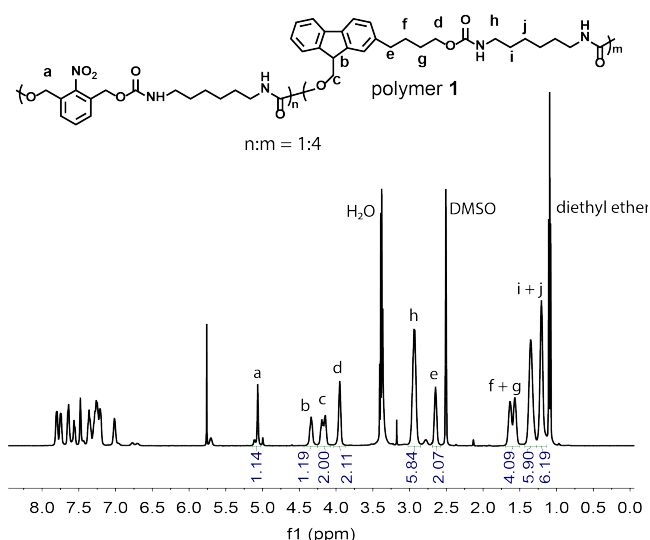


Fig. 2 ¹H NMR spectrum of polymer 1.

Polymer 1 was characterized using ¹H NMR, which clearly showed the incorporation of both **2** and **3**. Thus, resonances corresponding to the benzyl proton labelled **a** within the *o*-nitrobenzyl carbamate were observed at δ 5.07 ppm and methine and methylene protons labelled **b** and **c** from the Fmoc group were seen at δ 4.34 ppm and δ 4.15 ppm, respectively (Fig. 2). Comparison of the signal intensity of proton **a** and proton **b** in polymer 1 corresponded well with the 1:4 copolymerization feed ratio of nitrobenzyl diol monomer **2** to Fmoc diol monomer **3**. The number average molecular weight (*M_n*) of polymer 1 was determined by gel permeation chromatography (GPC) to be ca. 10 kDa with a dispersity (*Đ*) of 1.4 (Fig. S1). Polymer 1 was further analysed both by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), which revealed a glass transition temperature, *T_g* = 47 °C, and a thermal onset degradation temperature about 120 °C (Fig. S2 and S3). Polymer 1 was found to be stable for 48 h in the absence of light as indicating by its unchanged ¹H NMR spectra (Fig. S10).

The degradation of polymer 1 was studied using ¹H NMR. Thus, a solution of **1** (11 mg/mL) in DMSO-*d*₆ solution was prepared followed by 365 nm UV irradiation for 50 min, which caused a rapid decrease of proton **a** (Fig. 3a and Fig. S5), consistent with loss of the ONB carbamate structure. After the UV exposure, the polymer solution was allowed to react at room temperature and ¹H NMR spectra were taken at regular intervals for 25 h (Fig. 3b and Fig. S5). The ¹H NMR showed that the signal intensity for protons **b** and **c** decreased and a new signal at δ 6.25 ppm appeared and increased over 25 h, consistent with a dibenzofulvene unit generated from the Fmoc carbamate groups. Under the same conditions, control polymer **1c**, which lacks photosensitive carbamate repeat unit, showed no change in its ¹H NMR even after 80 min of UV irradiation followed by a 24 h incubation period (Fig. 3c).

Unlike our previously reported Fmoc containing polymer, the degradation kinetics of **1** with UV light irradiation did not show an exponential profile expected for a self-amplifying system (Fig. S6). One likely explanation is that the nitrosobenzaldehyde by-product generated in the photocleavage quenches a significant amount of liberated amino groups, preventing their reaction with base labile Fmoc group and thus deterring the amplified response. Although the complexity of the polymer system did not allow direct detection of such reaction products, two experiments support this hypothesis.

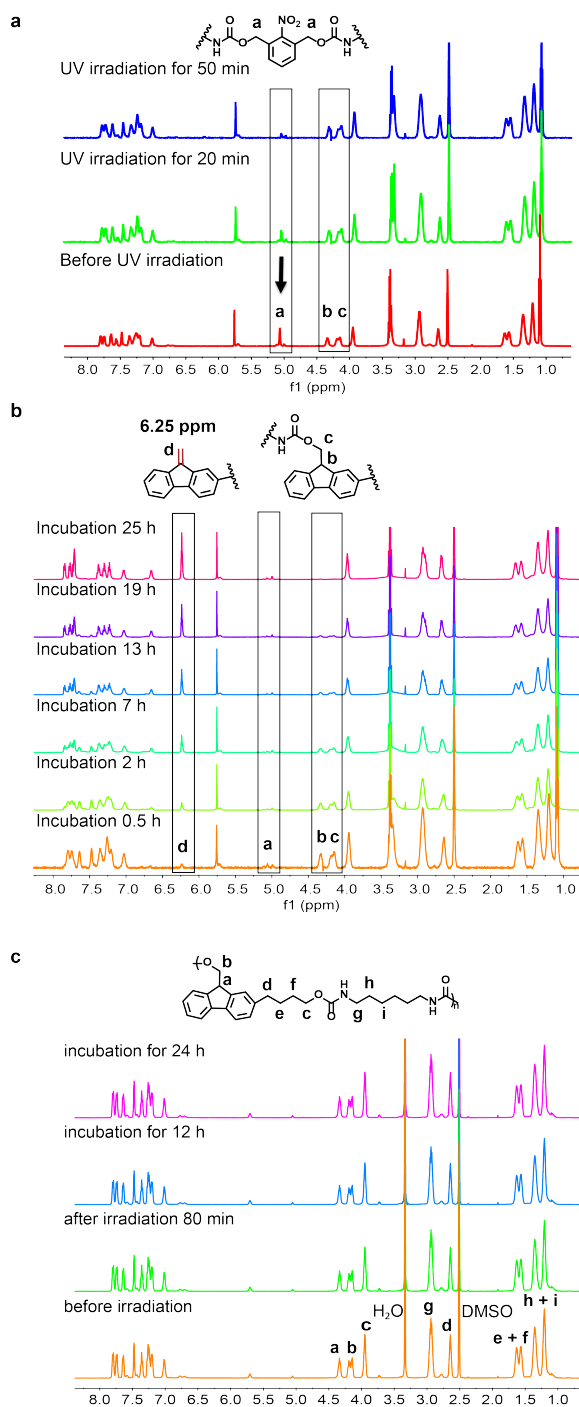


Fig. 3 (a) ¹H NMR degradation analysis of **1** under 365 nm UV light irradiation over 50 min. (b) ¹H NMR degradation analysis of **1** under incubation at room temperature over 25 h. (c) ¹H NMR degradation analysis of control polymer **1c**.

First, degradation of a small molecule model system, which was characterized by HR-ESI-MS, shows the formation of both aldehyde and imine products, consistent with this mechanism of amine quenching (Fig. S4). Second, a control experiment involving addition of 5% hexylamine into polymer **1** (10 mg/mL in DMSO-*d*₆) to initiate the degradation was conducted in the absence of light. A faster degradation was observed and the kinetic data was successfully fit to

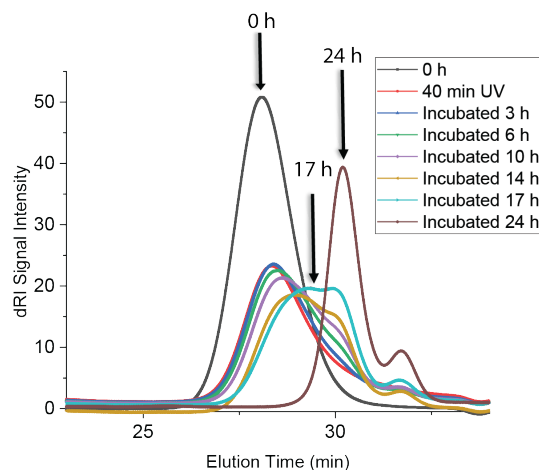


Fig. 4 GPC monitor of polymer **1** degradation overtime after being irradiated by UV light for 40 min.

autocatalytic equation S1 (Fig. S7 and S8). This key experiment shows that the polymer is able to exhibit amplified degradation in the absence of photolytic initiation. The amplified degradation observed upon addition of 5% hexylamine did exhibit a smaller ratio between k_2C_0 and k_1 values revealing a reduced amplification effect in comparison to our previously published system. This observation can be explained by the liberated amine species here being larger and less effective in abstracting protons. Indeed, larger degradation fragments were observed by mass spectrometry (Fig. S9).

The degradation of polymer **1** was further monitored by gel permeation chromatography (GPC). For these studies, **1** was dissolved in DMF with 0.1 M LiBr and irradiated at room temperature for 50 min with 365 nm UV light (190 mW, 1.5 mW/cm²) followed by 24 h incubation without light. The GPC trace at 40 mins irradiation time showed a less intense peak that had shifted to a slightly longer retention time $R_t = 30$ min after 24 h vs. $R_t = 28$ min for **1** before UV irradiation (Fig. 4). After 24 h only low molecular weight species were observed. A more detailed characterization of the degraded products was performed with high-resolution electrospray ionization mass spectrometry (HR ESI-MS), which indicated the formation of the amine species and non-fully degraded nitrobenzyl carbamate after degradation (Fig. S9). A peak corresponding to the nitrosobenzaldehyde by-product was not observed in the ESI-MS, likely because of its various extensive secondary side reactions such as imine formation, dimerization to azobenzenes, and further oxidation to the corresponding azoxy compound.^{35,48,49}

Encouraged by the results with polymer **1**, we prepared a cross-linked polyurethane gel **5** using Fmoc-based triol **4**. Bromothymol blue was added to the polymerization solution to colour the gel and aid in both visualizing the gel degradation and signalling the pH change (Fig. 5a). A yellow 500 μ m thick polyurethane film was formed after polymerization at room temperature for 24 h (Fig. S11). Immersion of the film in NMP solvent resulted in swelling without dissolving the film, indicating a cross-linked material. Further characterization of the film was achieved by attenuated total reflection infrared spectroscopy (ATR-FTIR) after the film was dried under high vacuum. Absorption peaks at 1692 cm⁻¹ and 1246 cm⁻¹ are assigned to the urethane groups and the peak at 1364 cm⁻¹ further showed the presence of the nitro groups (Fig. S12).

A degradation study of the cross-linked network **5** was conducted after swelling the gel with NMP. To demonstrate the

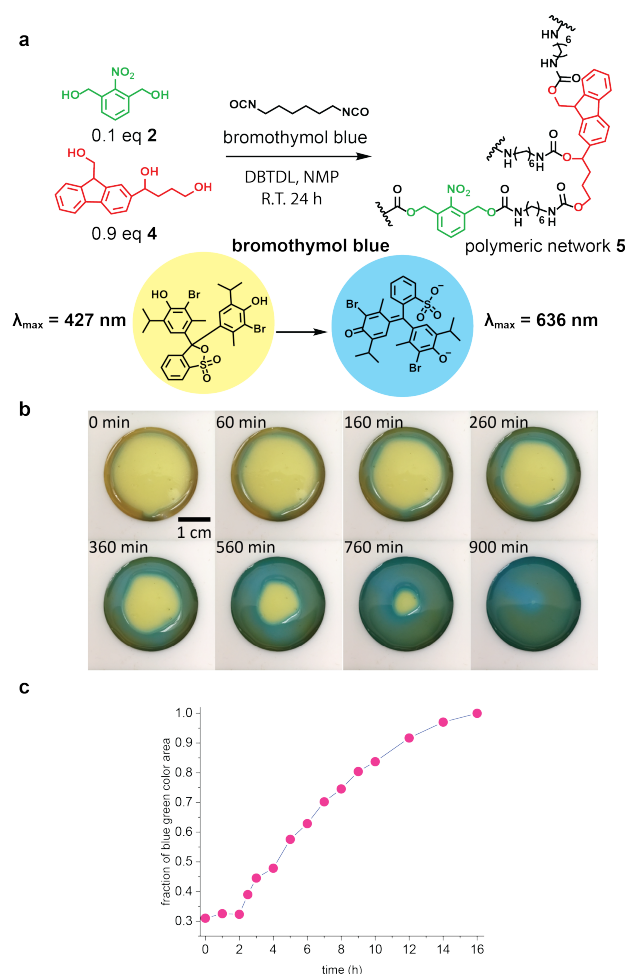


Fig. 5 (a) Synthesis of photo-triggered self-propagating degradable gel **5** with bromothymol blue as pH indicator. (b) Photographs of degradation of polymeric network **5** after a few mm of its outer edge were irradiated by UV light (190 mW, 1.5 mW/cm²) for 1 h. (c) Quantification of loss of yellow area versus time plot after UV irradiation. Lines added to guide the eye.

propagation of base within the bulk material, an aluminium shield cover was used to expose the periphery of the circular film to 365 nm UV light irradiation for 1 h (Fig. S13). The circular edge of the polymer film that was irradiated transitioned from a yellow gel to a brown solution. The inner edge of the irradiation area turned blue-green indicating base generation. Photographs of the film over time showed the blue-green color propagating inward accompanied by a gel to solution phase change (Fig. 5b and ESI video), suggesting the increasing amount of amine species generated during degradation propagation. In contrast, the control gel **5c** without photosensitive moiety incorporation was stable after UV light irradiation (Fig. S14).

The degradation area of the cross-linked network **5** was quantified using the color change of bromothymol blue from yellow to blue green with the use of Image-Pro Plus. As seen in Fig. 5c, there was a 2 h induction period where the yellow area remained the same after 1 h UV irradiation. The edges of the remaining film slowly turned green until finally the whole polymer was consumed by this green color and has fully transitioned into a liquid after 15 h. Despite

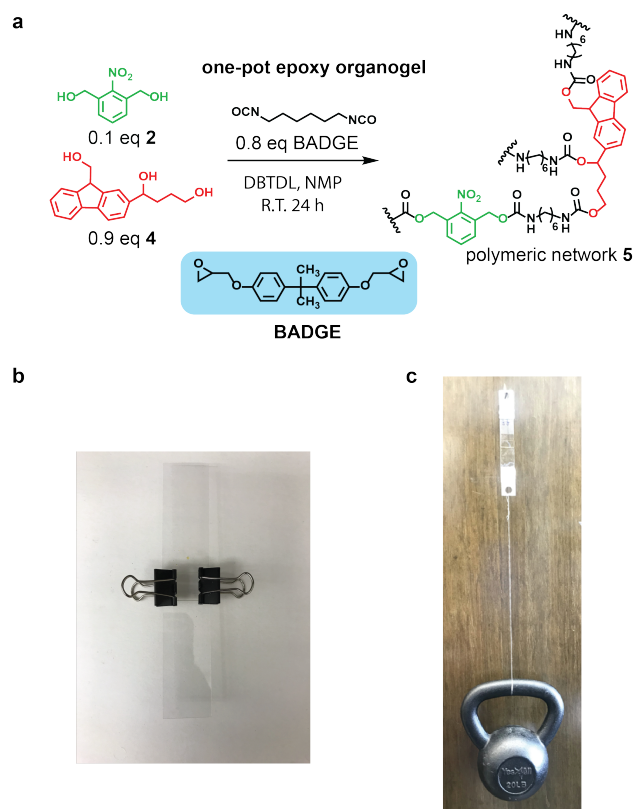


Fig. 6 (a) Synthesis of photo-triggered base-propagating degradable polymeric network **5** with BADGE epoxide monomer encapsulation (one-pot epoxy polyurethane organogel). (b) Preparation of adhesive sample with microscope slides and binder clips. The slices were cured at 95 °C under nitrogen in vacuum oven for 5 h. (c) Photograph of adhesive sample with a load of 20 lb kettlebell.

the long-range degradation supporting self-propagation, again an exponential rate profile was not observed so self-amplification was not demonstrated. The reasons for this observation may be the same as for the linear polymer, alternatively, the diffusion of amines may be rate limiting for this degradation, and large oligomeric amines containing unreacted *o*-nitrobenzyl moieties were observed by MS (Fig. S18). Nonetheless, long-range and complete degradation of the Fmoc units was ultimately achieved. The degradation products were characterized by HR-ESI-MS (see Fig. S17 and S18) with 6 major products observed (**D1-D6**). All six products contained the dibenzofulvene structure and amino functional groups generated by the base-triggered mechanism. Furthermore, degradation products **D3** and **D5** suggested the successful copolymerization and incorporation of ONB units.

Because polyurethane materials have broad application within society and, indeed, millions of tons are produced every year, there is an ongoing search for plausible solutions to their disposal.⁵⁰⁻⁵² One approach that was pursued here is to repurpose the degradation products. Thus, because the photo-triggered, self-propagating degradable polymeric gel **5** is able to generate a pool of amines, we sought to use it as a component of a one-pot epoxy in a proof of concept study. The chemistry, illustrated in Fig. S20 involves the destruction of the initial polyurethane gel to a mixture of amine

species that react with epoxy monomers encapsulated beforehand, thereby generating a strong adhesive.

To prepare the one-pot epoxy mixture, 0.8 equivalents of bisphenol A diglycidyl ether (BADGE) was added to form a polymeric organogel (Fig. 6a). The organogel described above was irradiated for 2 h with UV light ($\lambda_{\text{max}} = 365 \text{ nm}$) and allowed to stand at room temperature for 9 h, during which time a gel to solution transition was observed (Fig. S19). The resulting solution was concentrated to ca. 1 M and 10 mg of the mixture applied to glue together two microscope glass slides with a 25.4 mm x 12.7 mm overlap. The slides were held together with binder clips and heated to 95 °C for 5 h in an oven (Fig. 6b). A lap shear test was conducted to test the adhesive sample's strength but the glass broke before obtaining the maximum shear strength (Fig. S21). Although the glass substrate would shatter after reaching 2.2 MPa, it was observed that the lap joint samples were able to hold up to a 20 pound kettlebell (Fig. 6c and Fig. S21). In contrast, the control adhesive samples made with only the BADGE epoxide monomer or the polymer degradation solution showed very weak adhesion with the microscope glass sliding off when simply held vertical.

Conclusions

In summary, we successfully designed and synthesized a novel photo-triggered self-propagating degradable polyurethane that contains both photo and base-triggered repeat units. Upon treatment with UV irradiation, the ONB carbamate repeat unit degrades and forms primary amino groups, which could cause further degradation of Fmoc units without continuous UV-irradiation. However, strongly amplified degradation was not observed, in part because the amines may be quenched by reaction with the *o*-nitrosobenzaldehyde by-product. In addition, some of the released amines appear by MS to be oligomeric and might not be able to induce deprotonation of the Fmoc unit with high efficiency due to steric hindrance. Nonetheless, sufficient amines were generated to provide a self-propagating, long-range gel to solution transformation.

As a proof of concept application, the degradable polyurethane system could be mixed readily with bisphenol A diglycidyl ether (BADGE) so that liberation of the amino groups can initiate polymerization yielding a high-performance adhesive. Improvements to this one-pot epoxy material are clearly needed to bring the reactions time down from hours to minutes or seconds. However, the approach indicates the potential application of these type of gel-based degradable polyurethanes for on-demand one-pot epoxy adhesives.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supplementary Information

Construction from destruction using a photo-triggered self-propagating degradable polyurethane as a one-pot epoxy

Yanhua Xu,[‡] Ephraim G. Morado,[‡] and Steven C. Zimmerman^{a*}

^aDepartment of Chemistry, University of Illinois, Urbana, Illinois 61801, United States.

[‡] These authors contribute equally

*Corresponding author (sczimmer@illinois.edu)

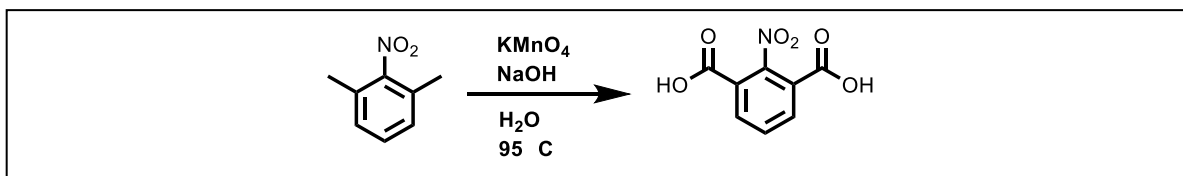
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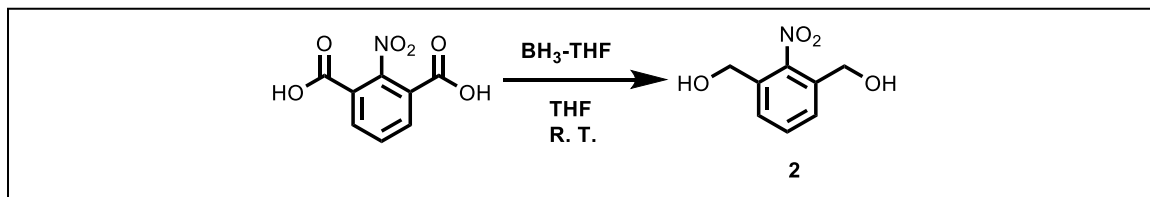
1. Materials and Instrumentation

All reagents were purchased from Acros Organics, Fisher Scientific, Chem-Impex International, AK Scientific, TCI America, or Sigma-Aldrich and used without further purification unless otherwise noted. Dried dichloromethane (DCM), pyridine, THF were obtained from an Mbraun solvent purification system. *N*-Methyl-2-pyrrolidone (NMP) was purified via vacuum distillation and stored in N₂ atmosphere with 20 wt% 3 Å molecular sieves. An UV light M365L2 (365 nm, 190 mW) from Thorlabs was used for photolysis experiments. NMR spectra were recorded using Varian U400, UI400, U500, VXR500, UI500NB, and CB500 (Bruker) spectrometers in the NMR laboratory, School of Chemical Science, University of Illinois and were processed with MestRec (v4.8.1.1) or MestReNova (v. 6.1.0). The NMR spectra were referenced to the residual proton solvent peak with coupling constants listed as Hertz (Hz). Mass spectral analyses were provided by the Mass Spectrometry Laboratory, School of Chemical Science, University of Illinois, using ESI on a Waters Micromass Q-ToF spectrometer, FD on a Waters 70-VSE spectrometer. Analytical gel permeation chromatography (GPC) experiments were performed on a hybrid system equipped with a Waters 1515 isocratic pump, a Waters 2414 refractive index detector, and a miniDAWN TREOS 3-angle laser light scattering detector (MALLS, Wyatt Technology, CA) with a detection wavelength of 658 nm. The MALLS detector was calibrated with toluene and was used to determine the absolute molecular weights. The mobile phase consisted of DMF containing 0.1 M LiBr with a flow rate of 1.0 mL/min at 50 °C using four Styragel columns (5 µm):HR 3, HR 4, and two HR 2. Absolute molecular weights of the polymers were determined based on the d_n/d_c value of each sample from the ASTRA software (version 6.1, Wyatt Technology CA) assuming 100 % mass recovery. The degradation of polymer **1** with GPC was conducted in DMF on a Tosoh Ecosec HLC8320GPC at 50 °C equipped with a reference columns (7.8 mm ID × 15 cm), guard column (6.0 mm ID × 4.0 cm × 5 µm) and two analytical columns (7.8 mm ID × 30 cm × 5 µm). The reference flowrate was set to 0.5 mL/min and the analytical column flowrate set to 1.0 mL/min. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q50 analyzer. About 5-10 mg of polymeric material were transferred to a platinum crucible and heated at a rate of 5 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured by Discovery DSC 250 from TA Instruments and T_g was calculated by half-height midpoint method on 2nd heating cycle with a heating rate 5 °C/min. Attenuated total reflection infrared spectroscopy (ATR-IR) was performed on a Nexus 670 ThermoNicolet Fourier Transform Infrared Spectrometer. Photographs were taken using an iphone 7S plus. The degradation kinetics of the crosslinked materials was quantified using Image-Pro Plus software adopting the procedure in Chapter 8: Color Segmentation in the user manual: Image-Pro Plus version 5.1 for Windows. All the data were developed and fitted using OriginPro 8.

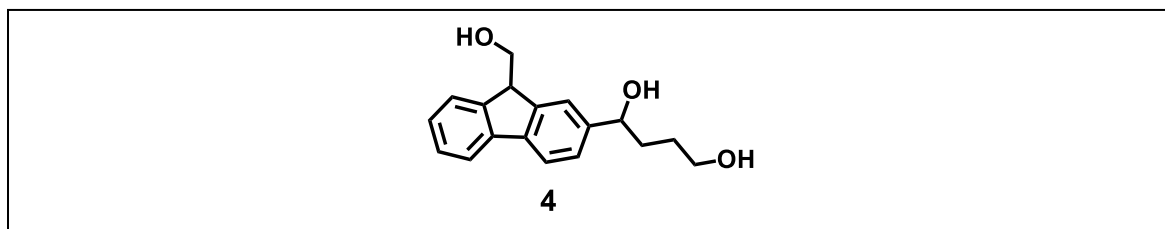
2. Monomer and Polymer Synthesis



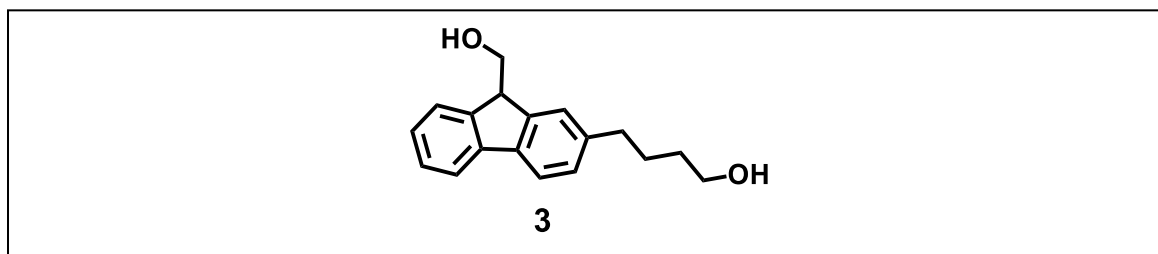
2-Nitroisophthalic acid. Synthesis and characterization of compound 2-Nitroisophthalic acid is described in S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.



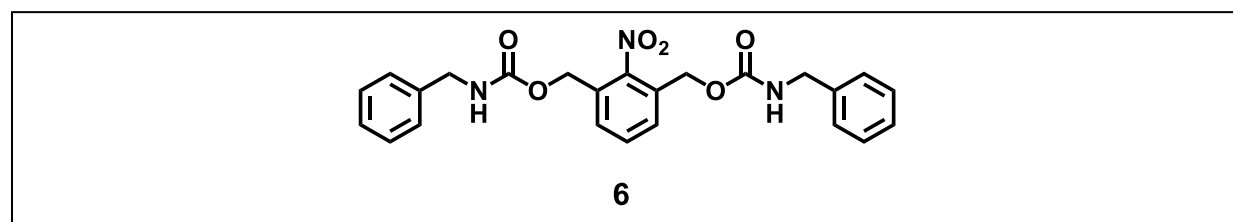
(2-Nitro-1,3-phenylene)dimethanol. Synthesis and characterization of monomer **2** is described in S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.



1-(9-(Hydroxymethyl)-9H-fluoren-2-yl)butane-1,4-diol. Synthesis and characterization of this compound as monomer **4** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.



4-(9-Hydroxymethyl)-9H-fluoren-2-yl)butan-1-ol. Synthesis and characterization of this compound as monomer **3** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.



(2-Nitro-1,3-phenylene)bis(methylene) bis(benzylcarbamate). In a 15 mL round bottom flask, **2** (0.37 g, 2 mmol) and benzyl isocyanate (0.24 mL, 2 mmol) was dissolved in dry DCM (10 mL) and stirred for 3 min at room temperature. Dibutyltin dilaurate (126 μ L, 0.2 mmol) was added using a micro syringe. The mixture was stirred at room temperature overnight before quenching with 3 mL H₂O. The reaction was extracted with DCM (5 mL) 3 times. The combined organic layer was washed with brine (5 mL), collected, dried over MgSO₄, and concentrated under vacuum. The crude product was purified *via* silica column chromatography eluting with 5% (v/v) methanol in DCM and 270 mg (30%) of product as a colorless liquid was obtained. ¹H NMR (500 MHz, CDCl₃): δ 7.50-7.26 (*m*, 13H), 5.24 (*s*, 4H), 4.37 (*s*, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 155.8, 149.0, 138.2, 131.2, 130.1, 130.0, 128.8, 127.8, 127.6, 62.8, 45.3. High resolution ESI-MS: Calculated for C₂₄H₂₄N₃O₆⁺ ([M+H]⁺): 450.1587; obtained 450.1668.

General synthetic procedure of photo-triggered self-propagating polymer 1. In a 5 mL glass vial, **2** (9.15 mg, 0.05 mmol) and **3** (53.67 mg, 0.2 mmol) were dissolved in NMP (0.2 mL) at room temperature. Hexamethylene diisocyanate (42 μ L, 0.258 mmol) and dibutyltin dilaurate (12 μ L, 0.019 mmol) were added in sequence and the mixture was stirred at room temperature for 24 h. Benzyl alcohol (10 μ L) was added and stirred for 1 h to quench the polymerization reaction. The polymer was further purified via precipitation by dissolving the polymer in 50% (v/v) methanol in DCM (2 mL) and adding the solution dropwise in diethyl ether (8 mL). The resulting precipitate solution was subjected to centrifugation and the excess solvent was decanted, which is a process that was repeated 3 times. The purified precipitate was dried under high vacuum to afford 70 mg (67%) of product as a white solid. GPC analysis (DMF): Mn = 10 kDa; Mw = 14 kDa; PDI = 1.4.

General synthetic procedure of control linear polymer 1c. Synthesis of **1c** was performed based on previously reported procedure. Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.

General synthetic procedure of photo-triggered self-propagating polymeric network 5. In a 5 mL glass vial, monomer **2** (9.15 mg, 0.05 mmol) and monomer **4** (128 mg, 0.45 mmol) were dissolved in dry NMP (0.5 mL) at room temperature. Hexamethylene diisocyanate (88 μ L, 0.55 mmol), dibutyltin dilaurate (40 μ L, 0.064 mmol), and 0.05 mL of bromothymol blue indicator stock solution in NMP (1 mg/ 1 mL) were added in sequence and stirred at room temperature for 15 min. The solution was quickly transferred to a circular PTFE mold (2.2 cm diameter and 500 μ m thickness) and covered by a glass slide equipped with a PTFE sheet. This mixture was cured at room temperature in a vacuum oven under N₂ atmosphere for 24 h.

General synthetic procedure of photo-triggered self-propagating polymeric network 5 with encapsulation of epoxide monomer (one-pot epoxy organogel). In a 5-mL glass vial, monomer **2** (9.15 mg, 0.05 mmol) and monomer **4** (128 mg, 0.45 mmol) were dissolved in dry NMP (0.55 mL) at room temperature. Hexamethylene diisocyanate (88 μ L, 0.55 mmol) and dibutyltin dilaurate (40 μ L, 0.064 mmol) were added in sequence. Finally, 2,2-Bis(4-glycidyloxyphenyl)propane (136 mg, 0.4 mmol BADGE) was added and the solution was stirred for 15 minutes at room temperature. 0.2 mL reaction solution was quickly transferred to another 5 mL vial, reacting at room temperature under nitrogen for 24 h.

General synthetic procedure of control polymeric network 5c. Synthesis of control polymeric network **5c** with monomer **4** is described in Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.

3. GPC of polymer 1

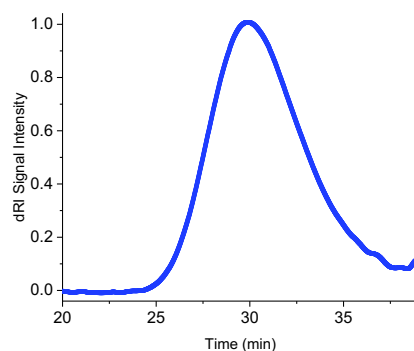


Fig. S1 Representative GPC elution curve of photo-triggered self-propagating degradable polymer **1**. $M_n = 10$ k, PDI = 1.4.

4. Supplemental DSC of Polymer 1

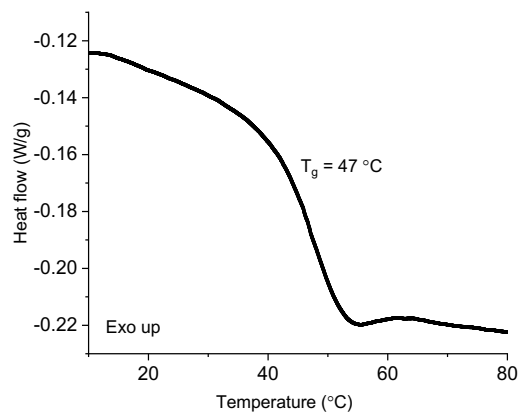


Fig. S2 DSC of photo-triggered self-propagating degradable polymer **1**. “Exo up” indicates that the direction of exothermic heat flow is up. T_g was calculated by half-height midpoint method on 2nd heating cycle with a heating rate is 5 °C/min.

5. Supplemental TGA of Polymer 1

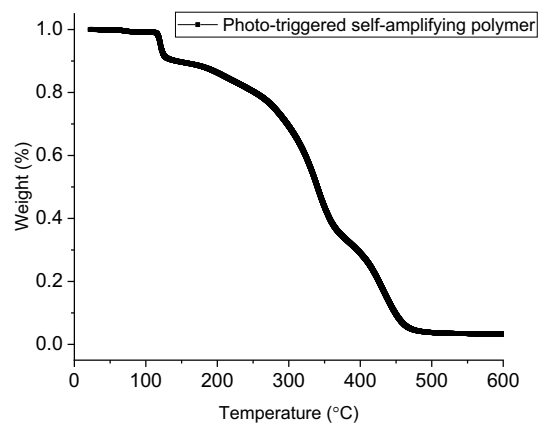
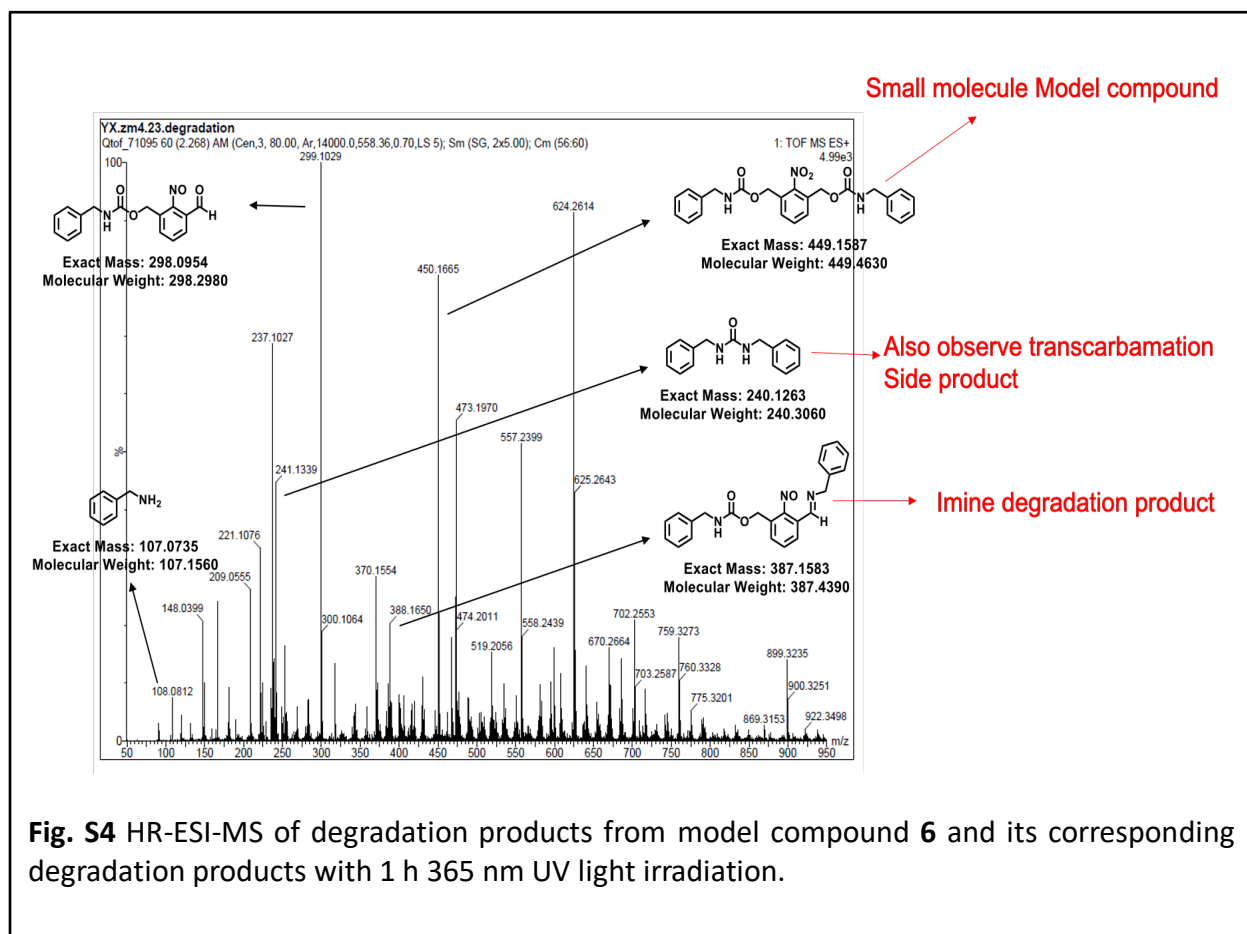


Fig. S3 TGA data of photo-triggered self-propagating degradable polymer **1** with ramping temperature at the rate of 5°C/min. The temperature for 5% weight loss is 120 °C.

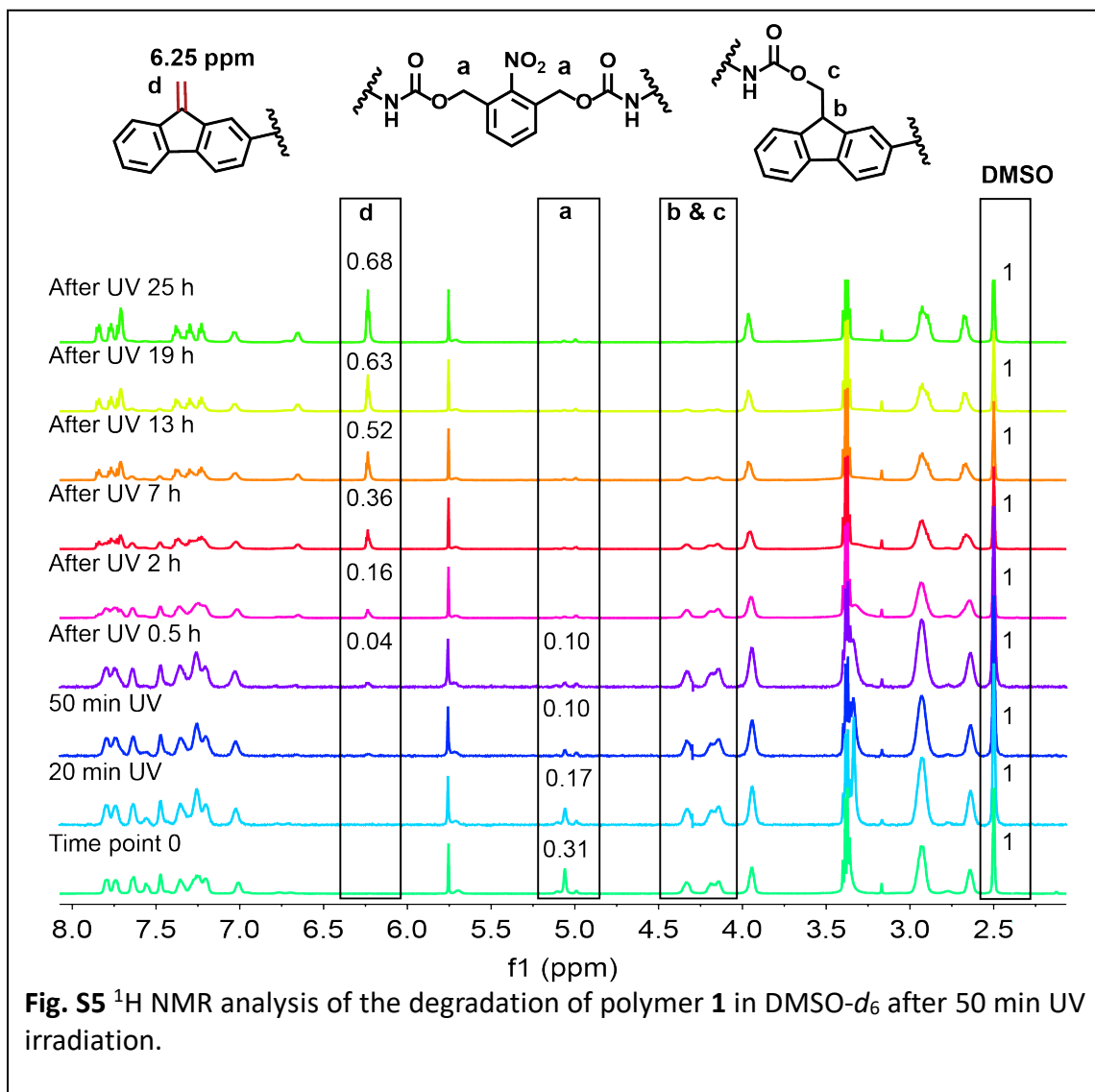
6. ESI-MS of degraded products of 6



7. NMR and GPC Degradation Study of Linear Polymer 1

General procedure for the ^1H NMR analysis of photo-triggered degradation of polymers.

A 5 mL vial was charged with about 5.4 mg of polymer and 0.5 mL (11 mg/mL) $\text{DMSO}-d_6$. This mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. An ^1H NMR of the polymer sample was performed before UV exposure, and after 20 and 50 min UV irradiation. The degradation kinetics of the polymer was monitored by obtaining the relative ratios between the Fmoc unit elimination product with proton signal at δ 6.25 ppm with respect to the $\text{DMSO}-d_6$ peak at different time points over 25 h.



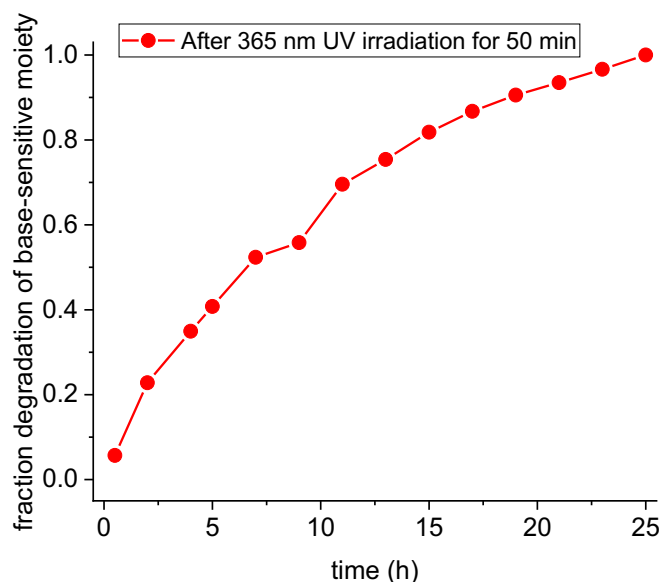


Fig. S6 ^1H NMR degradation kinetics of base-sensitive Fmoc repeat unit in polymer **1** in $\text{DMSO-}d_6$ after 50 min UV irradiation.

General procedure for the photo-triggered degradation of linear polymer **1** by GPC.

A 10 mg/ mL solution of polymer **1** in DMF with 0.1 M LiBr was prepared and was filtered through a 0.45 μm syringe filter. The polymer solution was irradiated for 50 min by 365 nm UV light before taking 50 μL aliquots at various time points for GPC analysis.

8. NMR Degradation Study of Linear Polymer **1** With Base Addition

General procedure for ^1H NMR analysis of base-triggered degradation of polymer **1**.

A 5 mL vial was charged with about 5 mg of polymer **1** and 0.5 mL $\text{DMSO-}d_6$. This mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. An ^1H NMR of the polymer degradation was performed after addition of 5% hexylamine corresponding to Fmoc repeating unit concentration. The degradation kinetics of the polymer was monitored by obtaining the relative ratios between the Fmoc unit elimination product at δ 6.25 ppm with respect to the $\text{DMSO-}d_6$ peak at different time points. The degradation percentage versus time data was used to fit a sigmoidal degradation equation and k_1 as well as k_2 value was calculated.²

$$\frac{c}{c_0} = \frac{k_1 + k_2 c_0}{k_1 e^{(k_1 + k_2 c_0)t} + k_2 c_0} \quad (\text{S1})$$

Where c is the concentration of the base-triggered degradable Fmoc repeat unit with its initial

concentration value being c_0 . The c_0 values used were 0.019 M. After fitting the degradation data with addition of 5% hexylamine as base into equation S1,

$$k_1 = 3.4 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 = 0.20 \text{ M}^{-1} \text{ min}^{-1},$$

$$k_2 c_0 = 3.8 \times 10^{-3} \text{ min}^{-1}$$

$$k_2 c_0 > k_1, \frac{k_2 c_0}{k_1} = 1.12$$

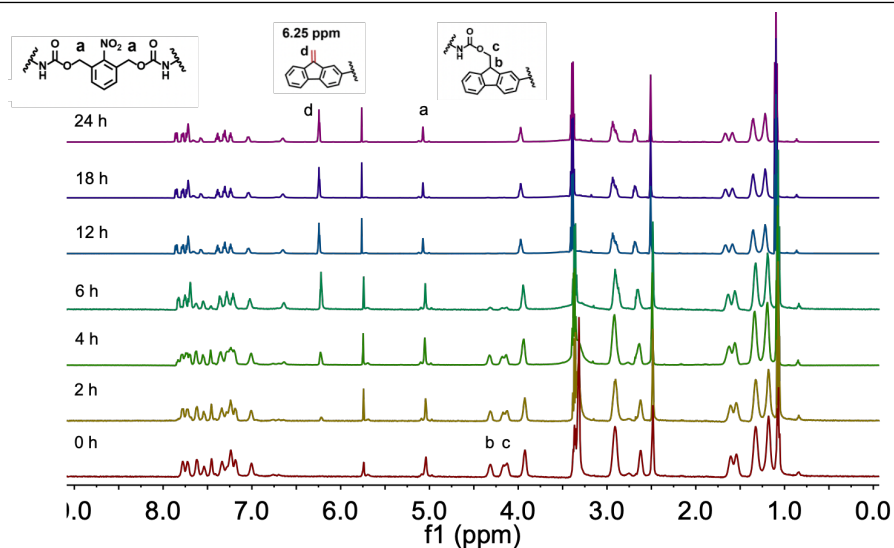


Fig. S7 ^1H NMR degradation study of polymer **1** with 5 % hexylamine added corresponding to Fmoc repeating unit.

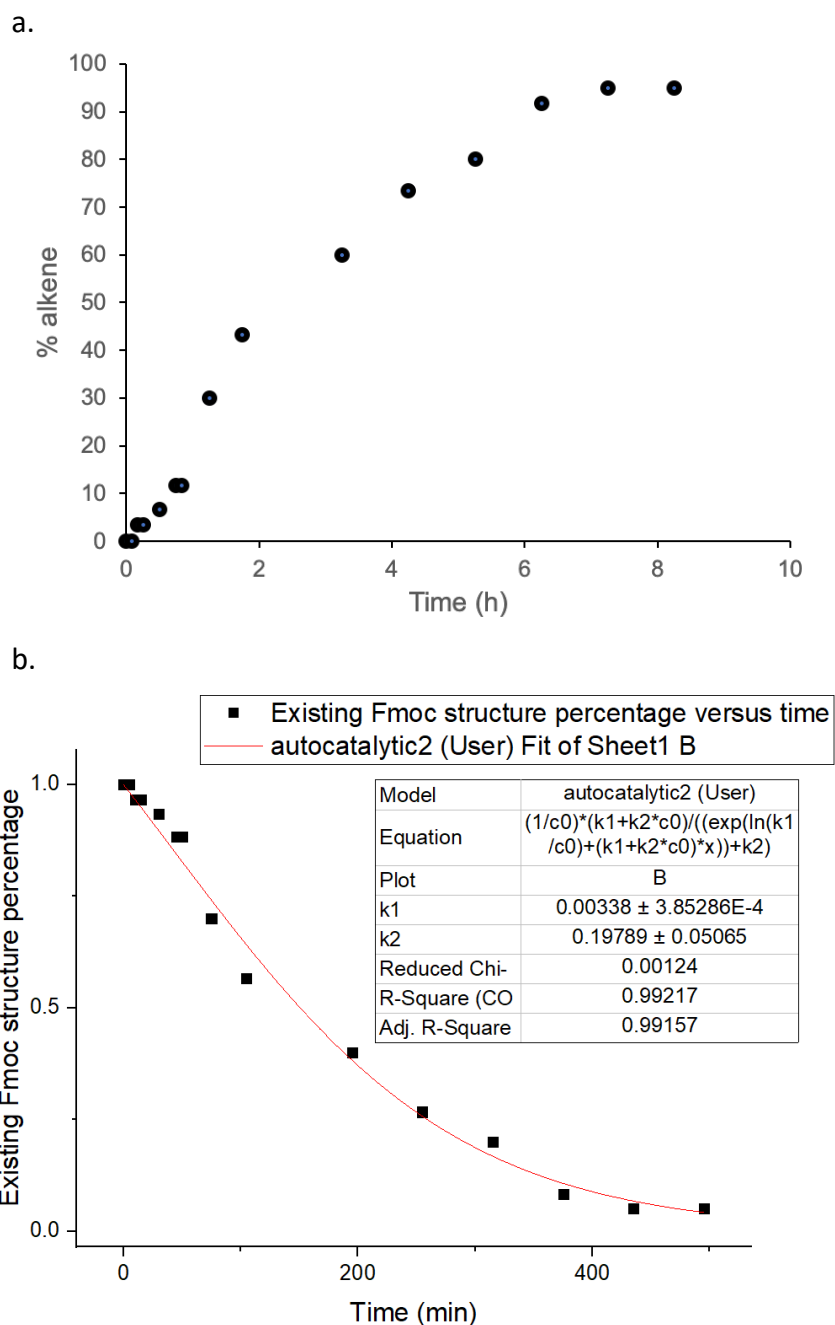


Fig. S8 (a) Degradation percentage of polymer **1** versus time with addition of 5 % hexylamine corresponding to Fmoc repeat unit. The percent conversion of Fmoc moiety to alkene were determined by the absolute ratio between the alkene peak (δ 6.25 ppm) and DMSO- d_6 over time. (b) Representative data fitting of degradation of Fmoc repeat unit with addition of 5 % hexylamine as trigger. The Fmoc repeat unit concentration is 19 mM solution in DMSO- d_6 at 25 °C. The red line represents the fitting curve of the data to equation S1 ($R^2 = 0.992$).

9. ESI-MS Analysis of the Degradation Products from Polymer 1

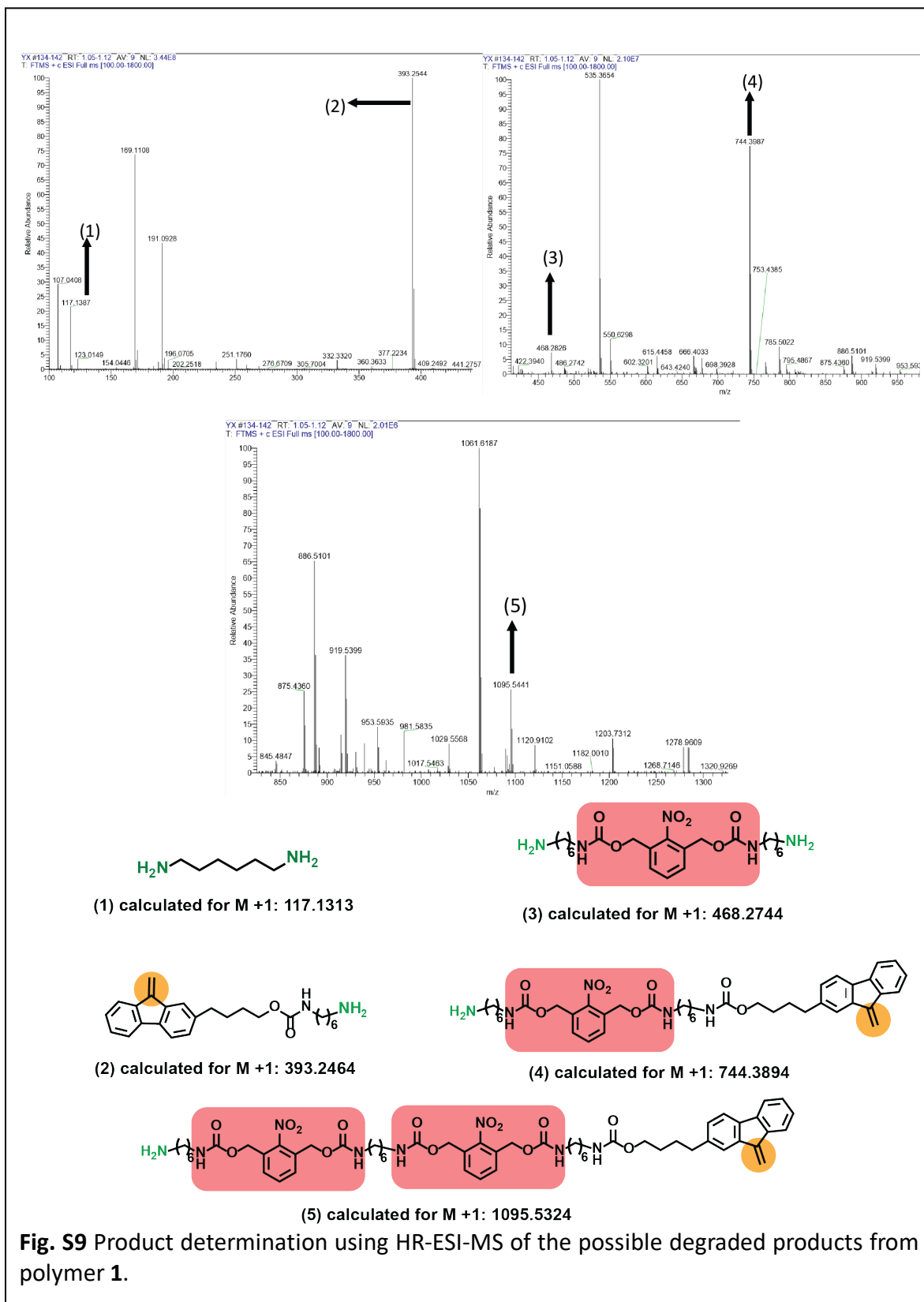
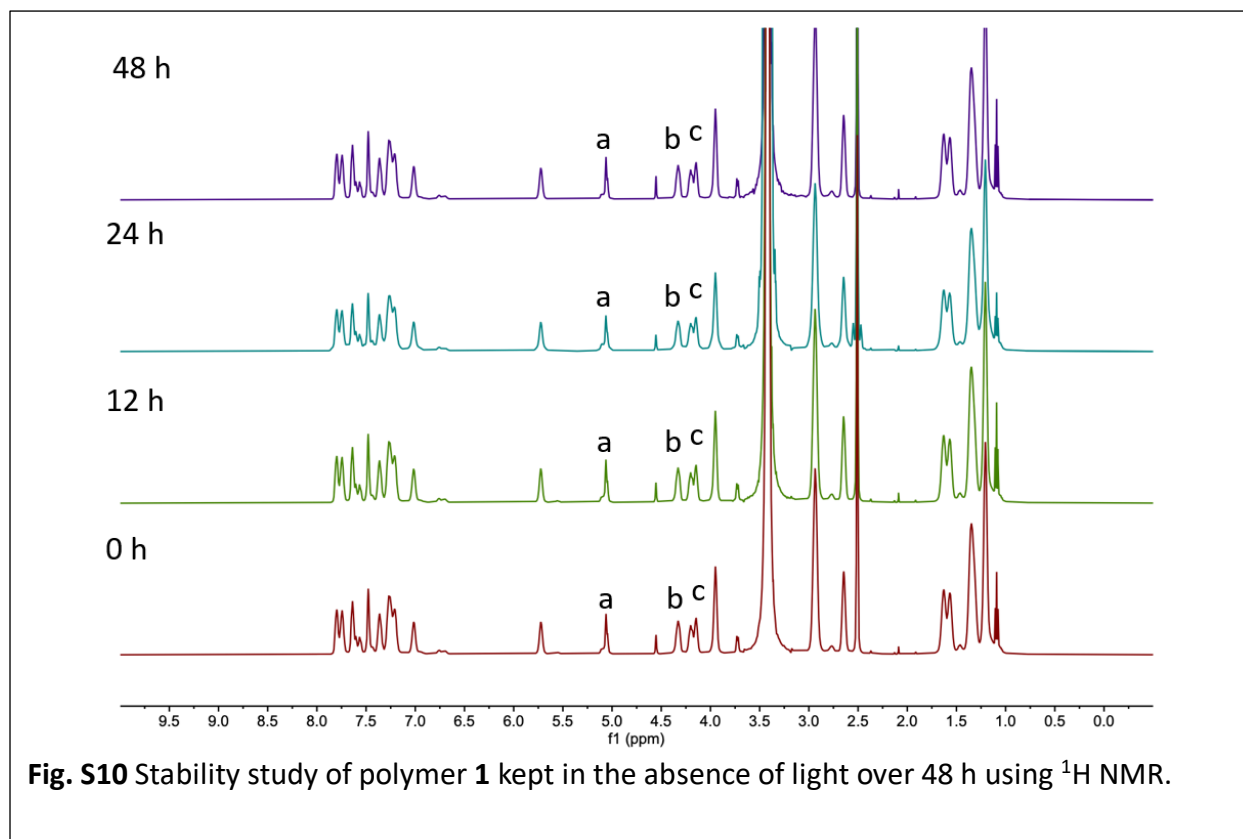


Fig. S9 Product determination using HR-ESI-MS of the possible degraded products from polymer 1.

10. Stability Study of Polymer 1 by ^1H NMR

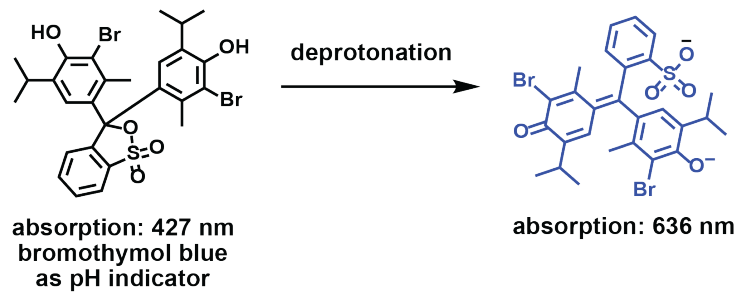
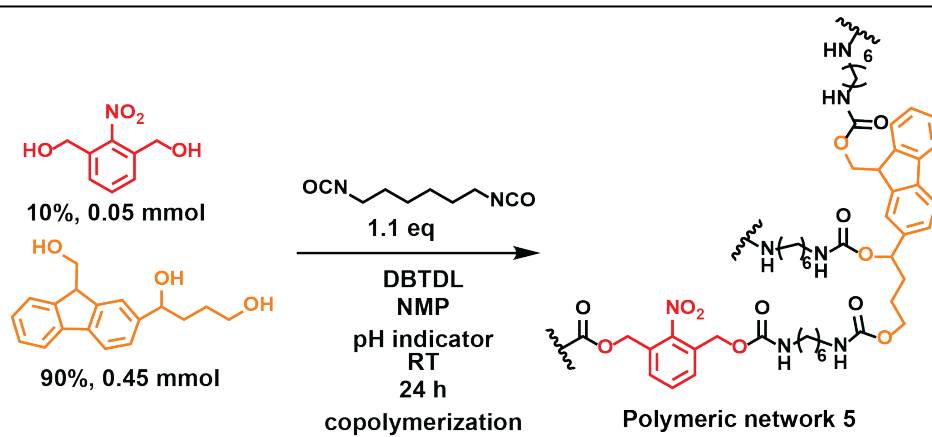
General procedure for the ^1H NMR analysis of stability of polymer 1.

A 5 mL vial was charged with about 5 mg of polymer 1 and 0.5 mL $\text{DMSO}-d_6$. The mixture was sonicated for 5 min and transferred to an NMR tube using a 1 mL syringe. The sample was kept in the dark and ^1H NMR of the polymer sample was performed at different time points over 48 h.



11. Synthesis and Characterization of Polymeric Network 5

a



b

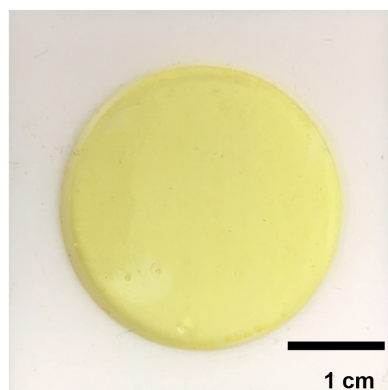
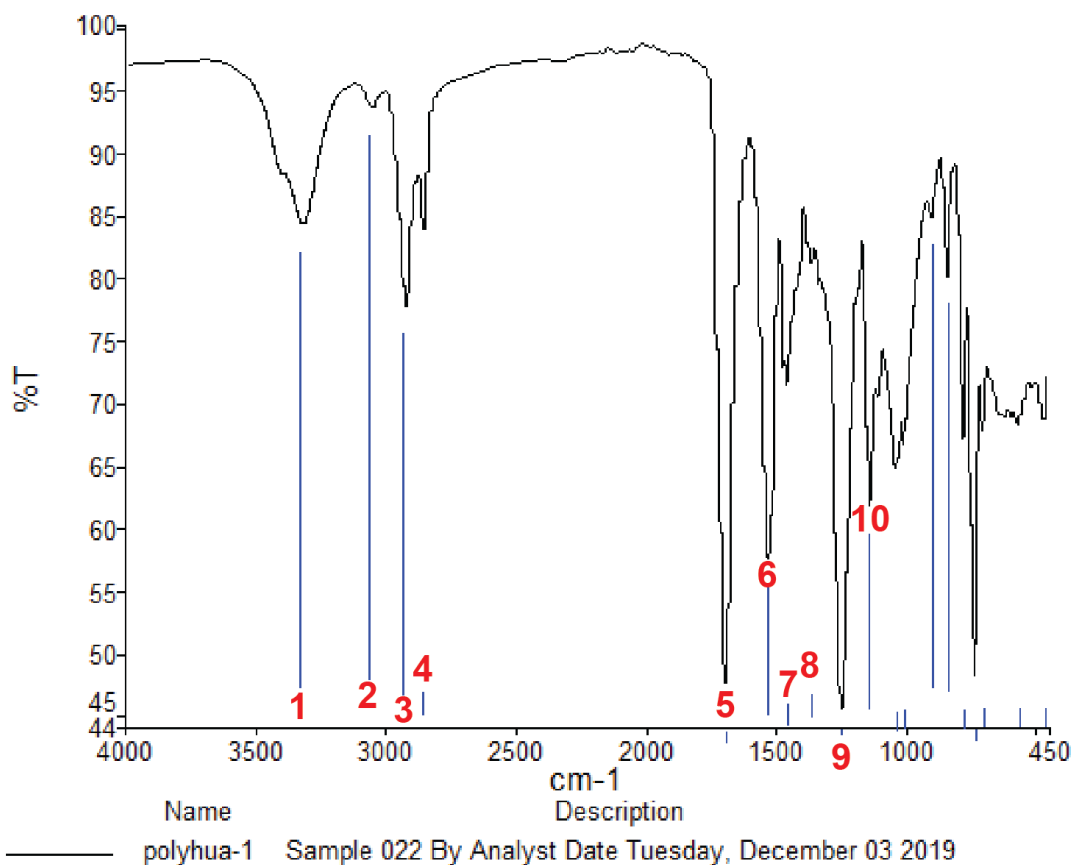


Fig. S11 (a) Synthesis of photo-triggered self-propagating degradable polymeric network 5. (b) Visual observation of the organogel in the circular Teflon mold.

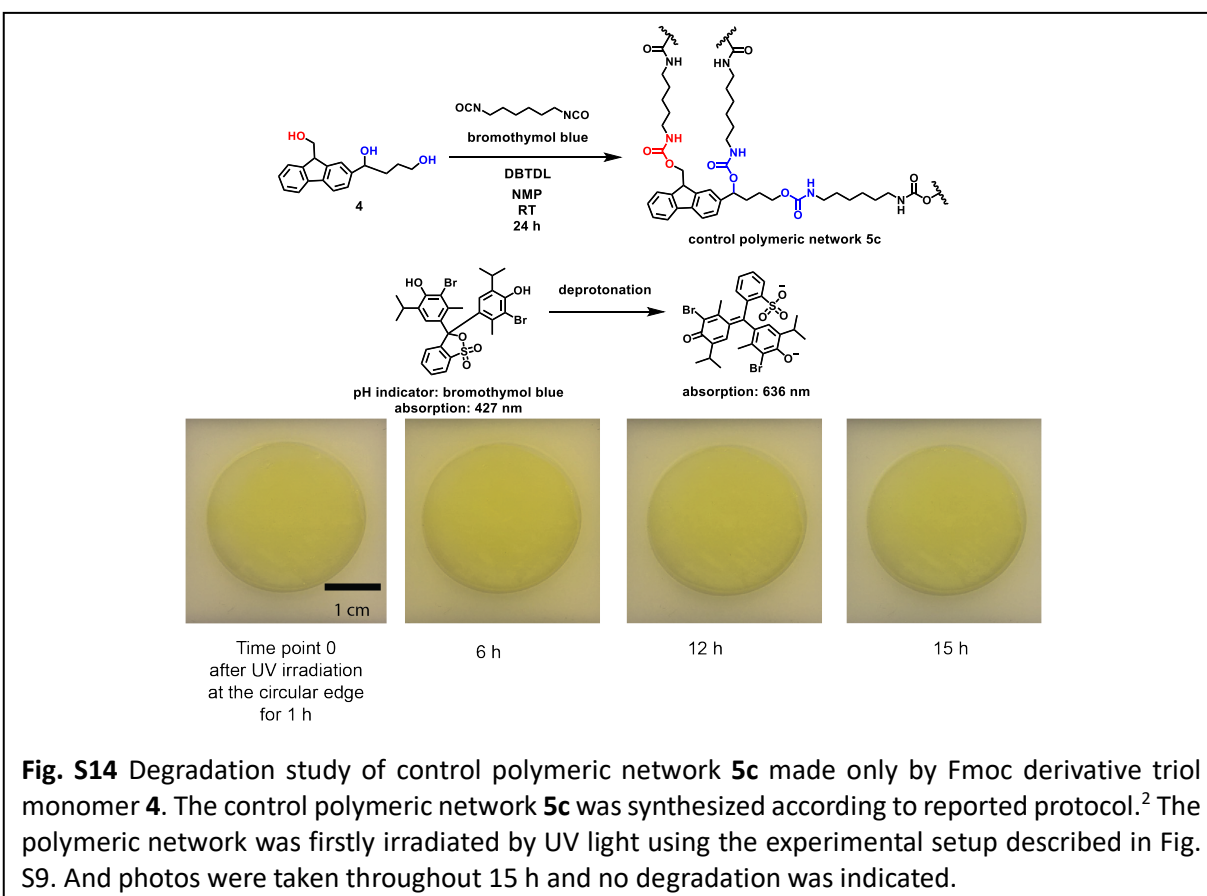
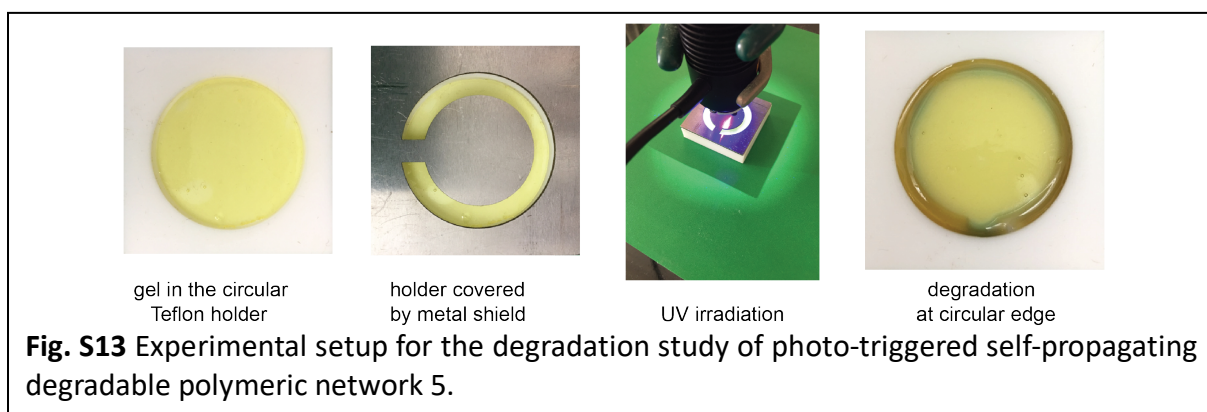


Peak Number	X (cm-1)	Y (%T)	Functional group
1	3324.06	84.54	O-H
2	3056.26	93.87	=C-H
3	2928.71	77.89	-C-H
4	2856.74	84.08	
5	1692.24	47.53	C=O in -NH-CO-O-
6	1525.22	57.73	N-H bending in -NH-CO-O-
7	1455.43	71.5	
8	1364.91	81.44	N-O symmetric stretch in NO ₂
9	1245.5	45.55	C-O in -NH-CO-O-
10	1136.39	61.94	C-N

Fig. S12 Attenuated total reflection IR spectrum of photo-triggered self-propagating degradable crosslinked polymer network 5.

12. Degradation Study of Degradable Polymeric Network 5.

A dye solution was prepared by dissolving 1 mg of bromothymol blue in 1 mL NMP. About 5 mL of dye solution was used to swell the gel for 3 h. A circular aluminum cutout was pressed against the gel to obtain a circular gel with a 29 mm diameter. The gel was then placed onto a 29 mm diameter Teflon mold and covered with an aluminum shield that only exposed the edge of the gel. The gel was irradiated by UV light for 1 h and allowed to degrade and photos were taken every 10 min. The fraction of color change (the area with color change to green blue) of the gel was quantified and plotted against time using an Image-Pro-Plus software. Quantification of degradation area percentage through Image-Pro-Plus was conducted using reported procedure.²



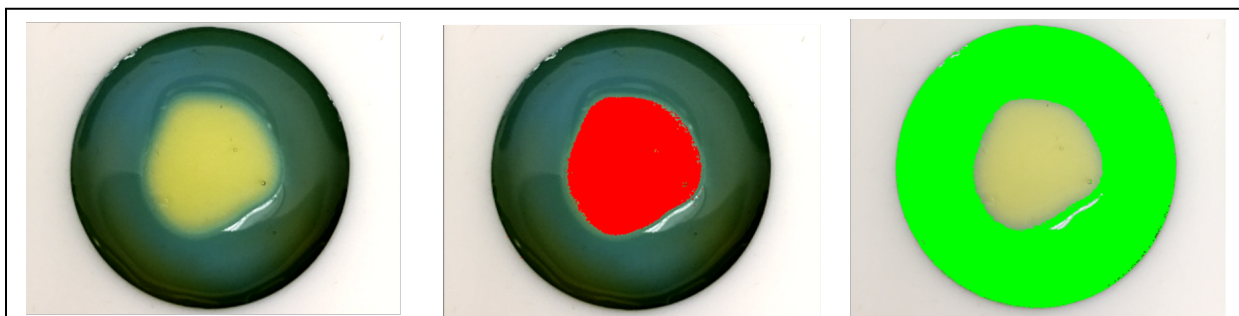


Fig. S15 Example of performing non-degraded yellow area color and degraded non-yellow area color segmentation in Image-Pro-Plus.

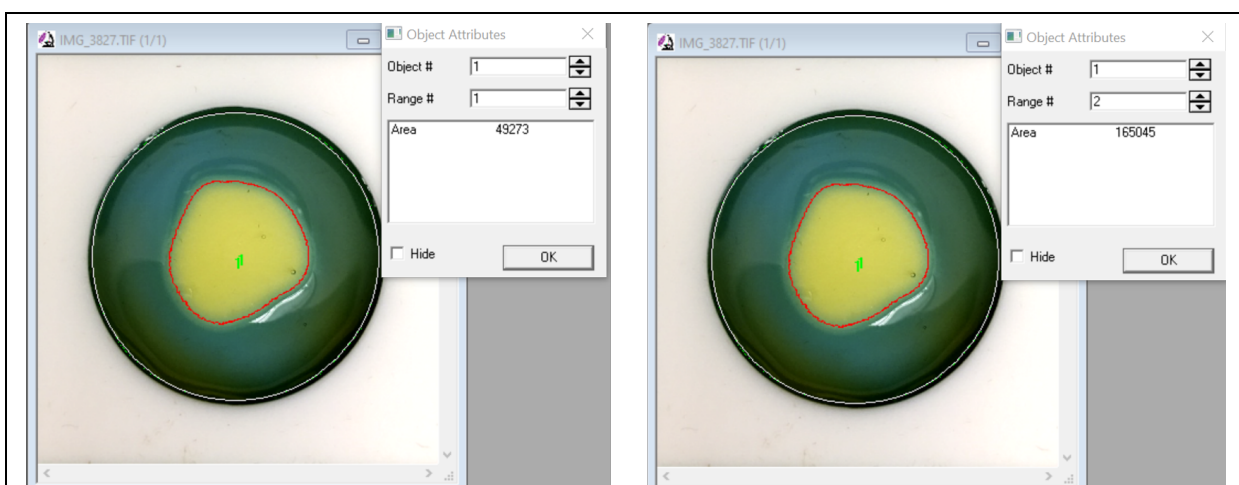


Fig. S16 Example of counting the area of non-degraded yellow area(left) and degraded non-yellow area(right) in Image-Pro-Plus.

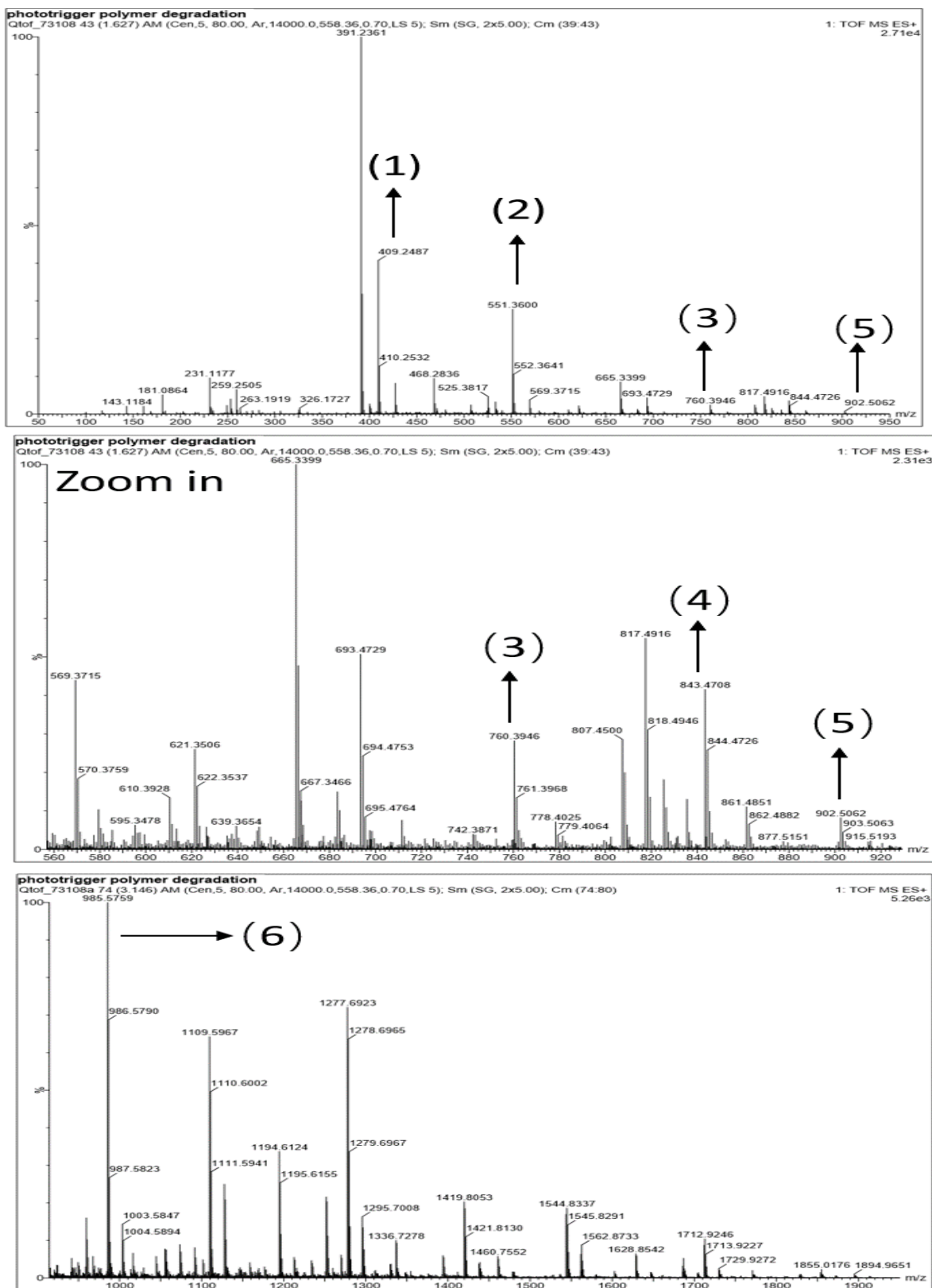


Fig. S17 HR-ESI-MS of degradation product from 5.

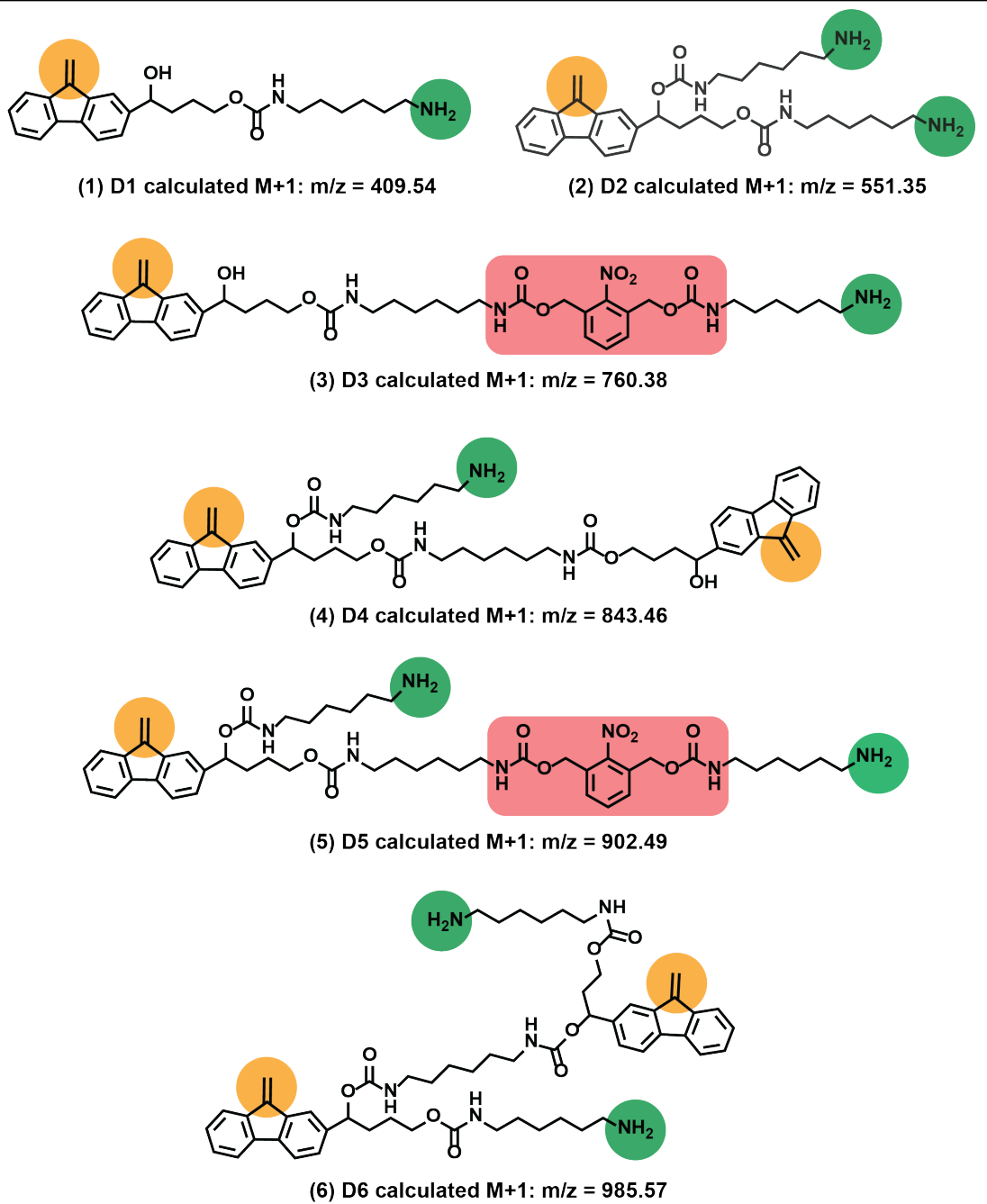
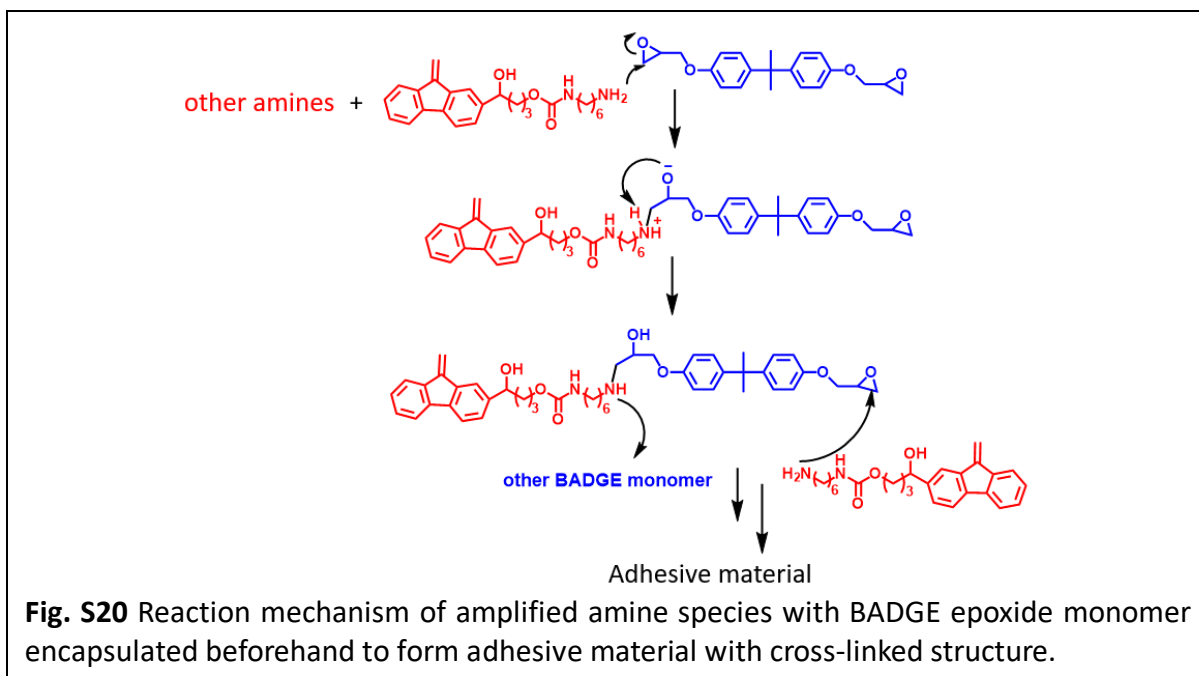
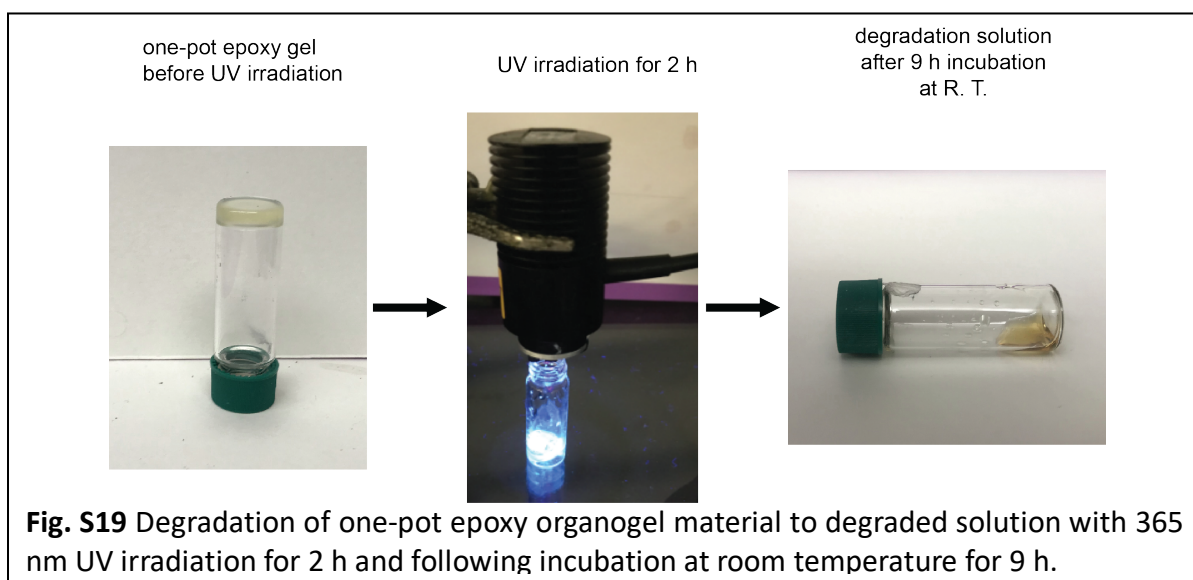


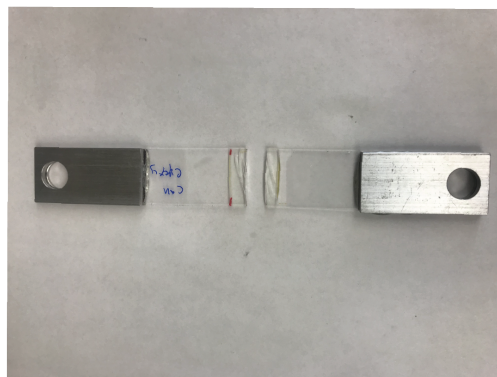
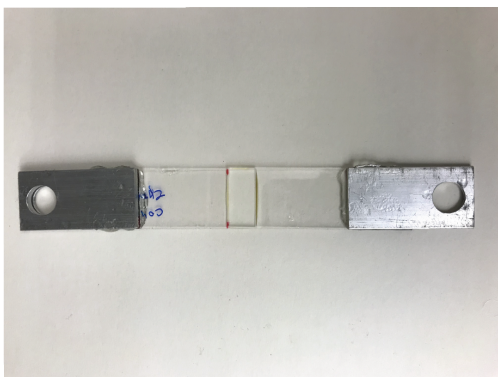
Fig. S18 Corresponding degradation product structures of 5.

13. Degradation of one-pot epoxy polyurethane organogel and synthesis of adhesive

The crosslinked gel 5 with BADGE epoxide monomer encapsulation beforehand (one-pot epoxy polyurethane organogel) was swelled in 0.2 mL of NMP and was irradiated by 365 nm UV light for 2 h. After irradiation, the gel swollen was allowed to degrade at room temperature. After 9 h the gel transitioned into a liquid and was concentrated by removing excess NMP by purging with N₂ until about 1 M concentration of degraded amine solution. About 10 mg of degradation mixture were applied to stick together two glass slides with 1 inch × 0.5 inch overlap. The glass slides were held together with binder clips and cured in an oven at 95 °C.



a



b

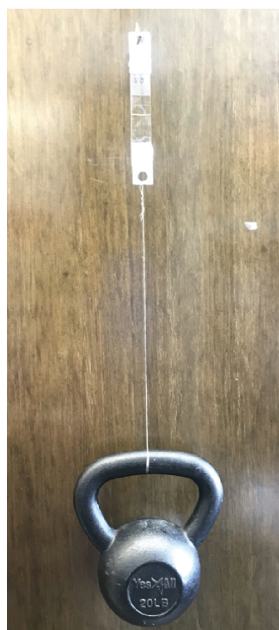
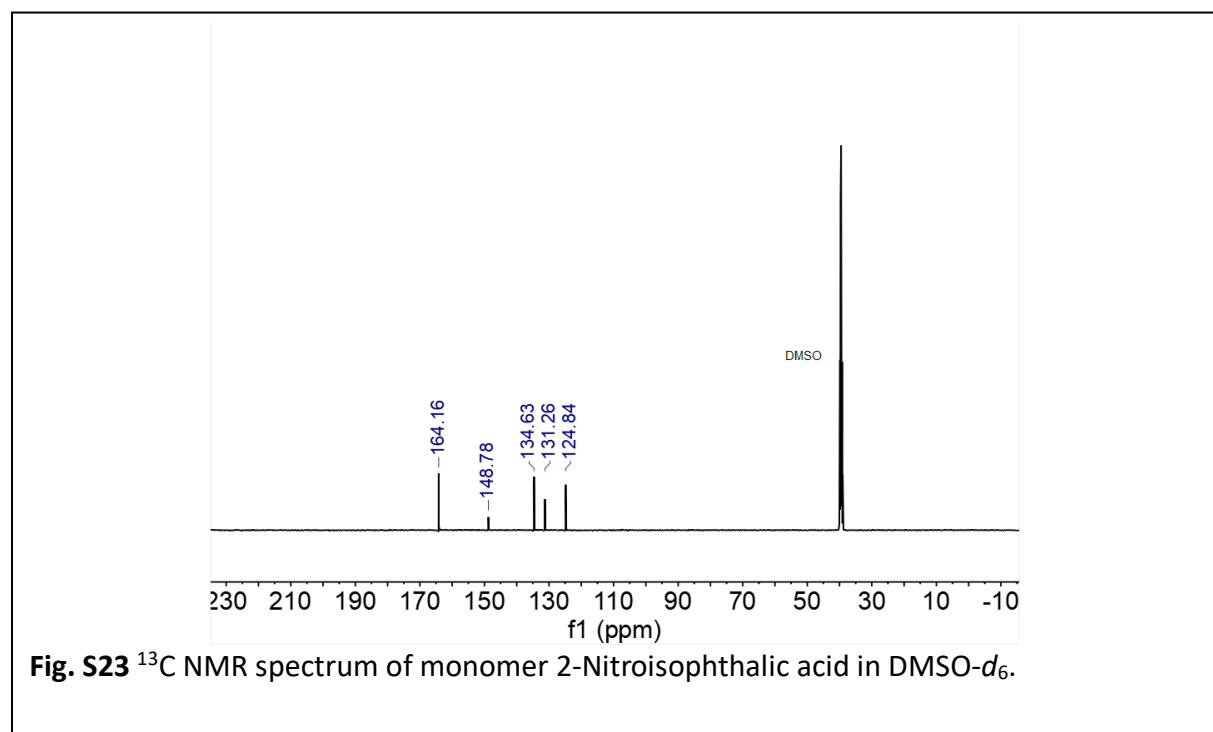
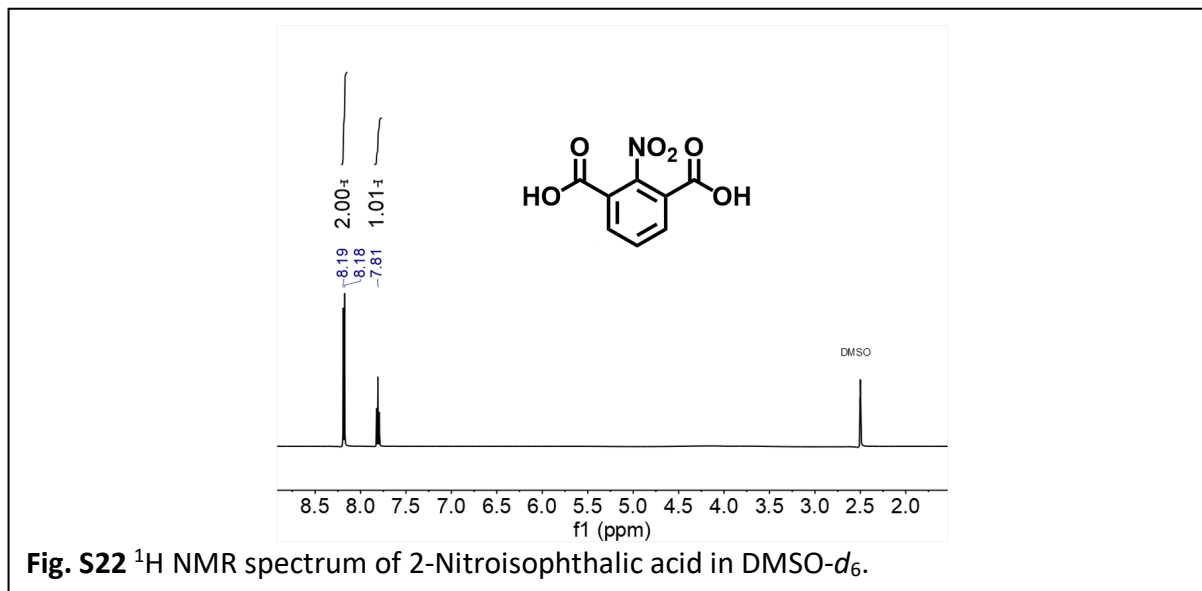


Fig. S21 (a) Left: the adhesive sample prepared for lap shear test. Right: the microscope glass substrate got broken after shear strength reached 2.2 Mpa. (b) Left: adhesive sample is enough to hold 20 pound kettlebell. Right: zoom in photo of 20 pound kettle bell.

14. Monomer Characterization



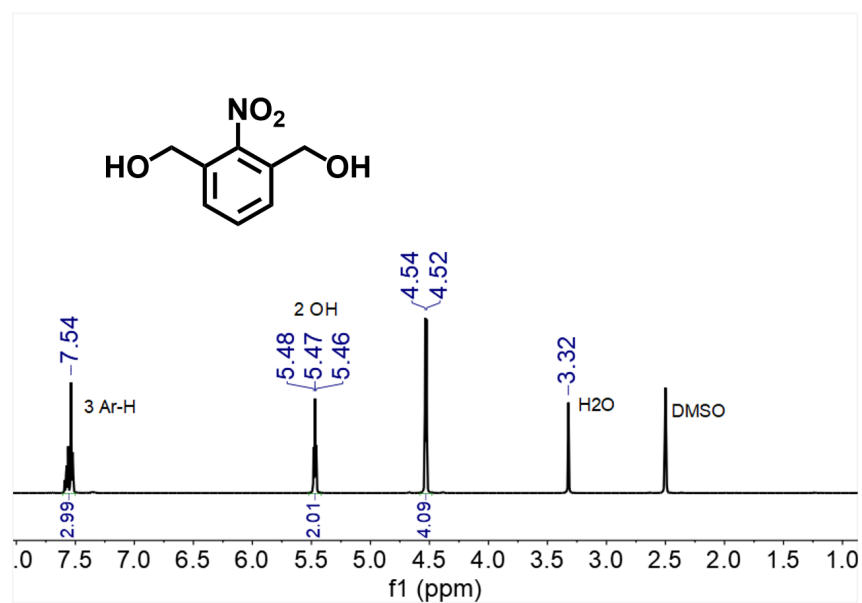


Fig. S24 ^1H NMR spectrum of monomer **2** in $\text{DMSO-}d_6$.

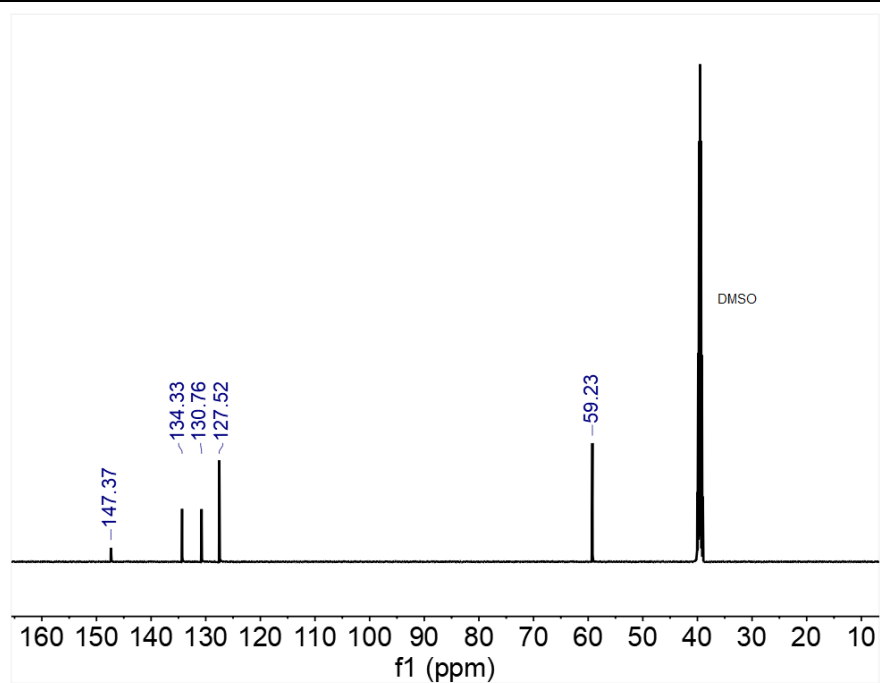
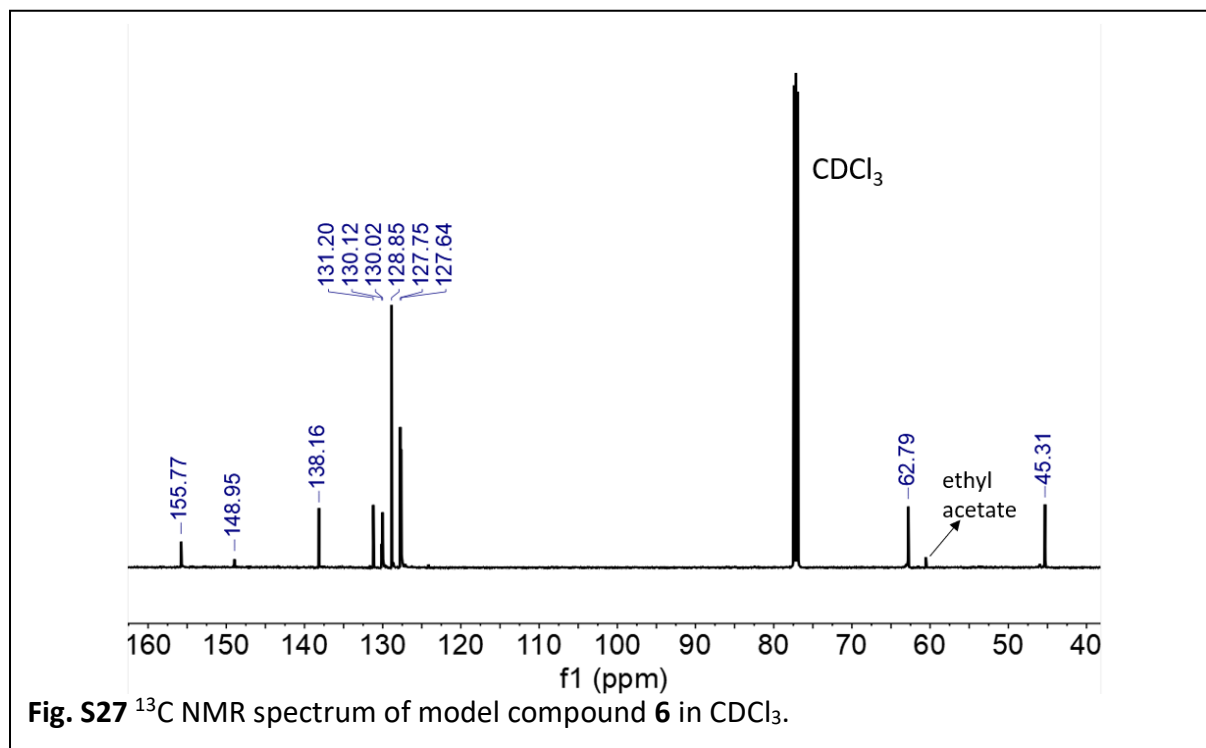
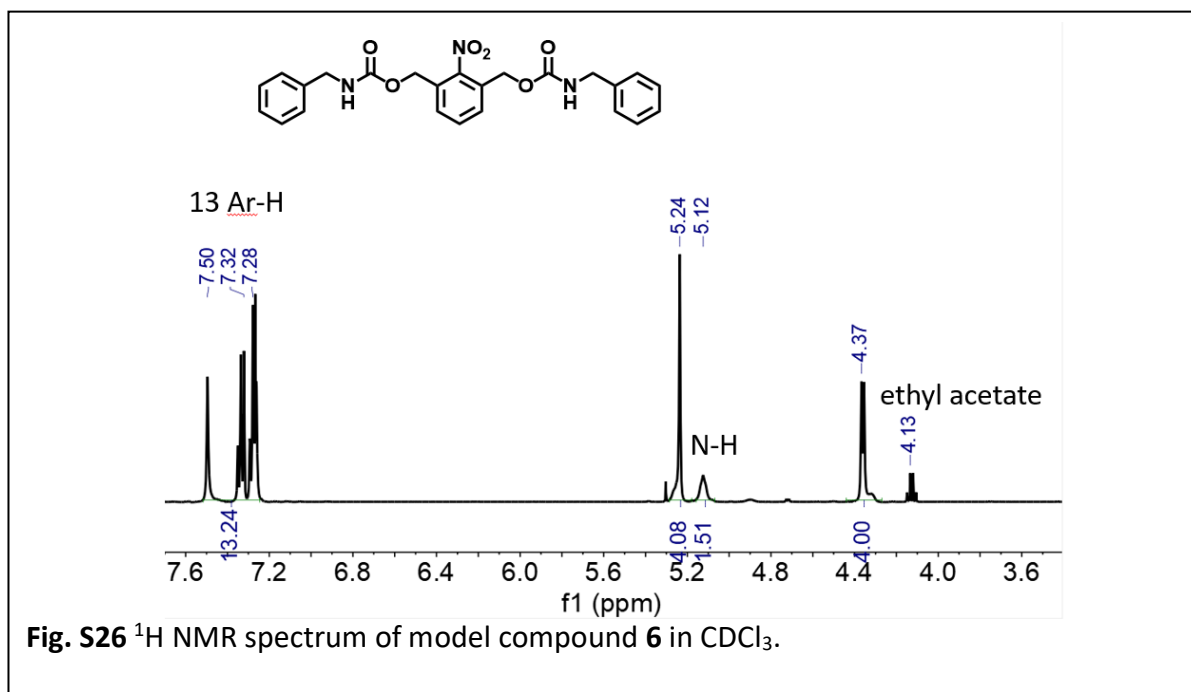


Fig. S25 ^{13}C NMR spectrum of monomer **2** in $\text{DMSO-}d_6$.



15. References

1. S. Rajendran, R. Raghunathan, I. Hevus, R. Krishnan, A. Ugrinov, M. P. Sibi, D. C. Webster and J. Sivaguru, *Angew. Chem., Int. Ed.*, 2015, **54**, 1159-1163.
2. Y. Xu, S. Sen, Q. Wu, X. Zhong, R. H. Ewoldt and S. C. Zimmerman, *Chem. Sci.*, 2020, **11**, 3326-3331.