Polymer Chemistry

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Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-05-2020-000779.R1
Article Type:	Paper
Date Submitted by the Author:	23-Jul-2020
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PAPER

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

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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 continous 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 hexylmethylene diisocyanate. 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 ^{1}H NMR and gel permeation chromatography (GPC) suggest that initial UV irradiation tirggers 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.

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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.
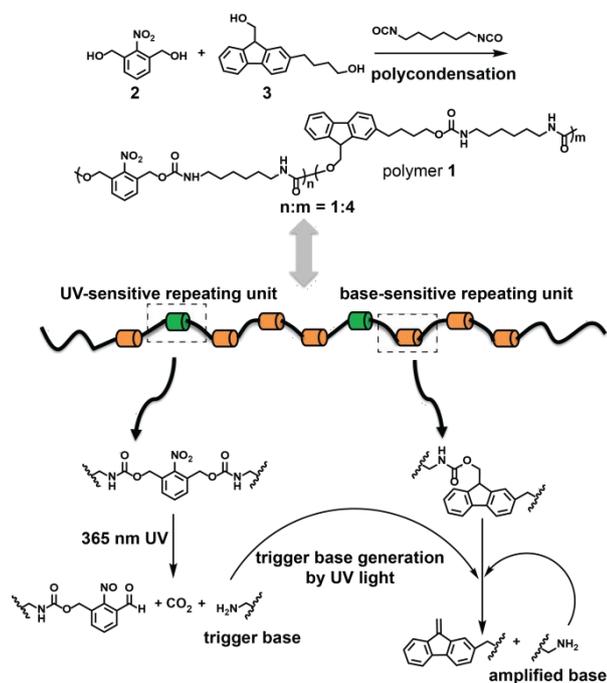
Results and discussion

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), hexylmethylene diisocyanate, and 0.1 eq of dibutyltindilaurate (DBTDL) as catalyst with *N*-methylpyrolidone (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.
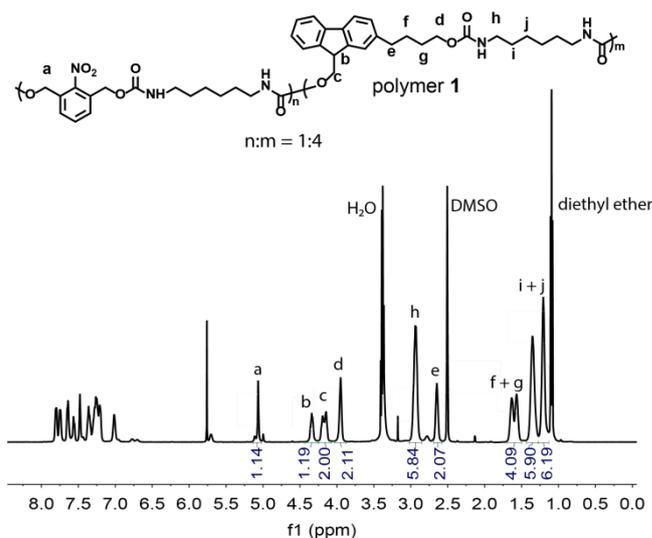

Fig. 2 ^{1}H NMR spectrum of polymer **1**.

Polymer **1** was characterized using ^{1}H 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 ^{1}H NMR spectra (Fig. S10).

The degradation of polymer **1** was studied using ^{1}H 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 ^{1}H NMR spectra were taken at regular intervals for 25 h (Fig. 3b and Fig. S5). The ^{1}H 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 ^{1}H 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.

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 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 $k_2 c_0$ 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
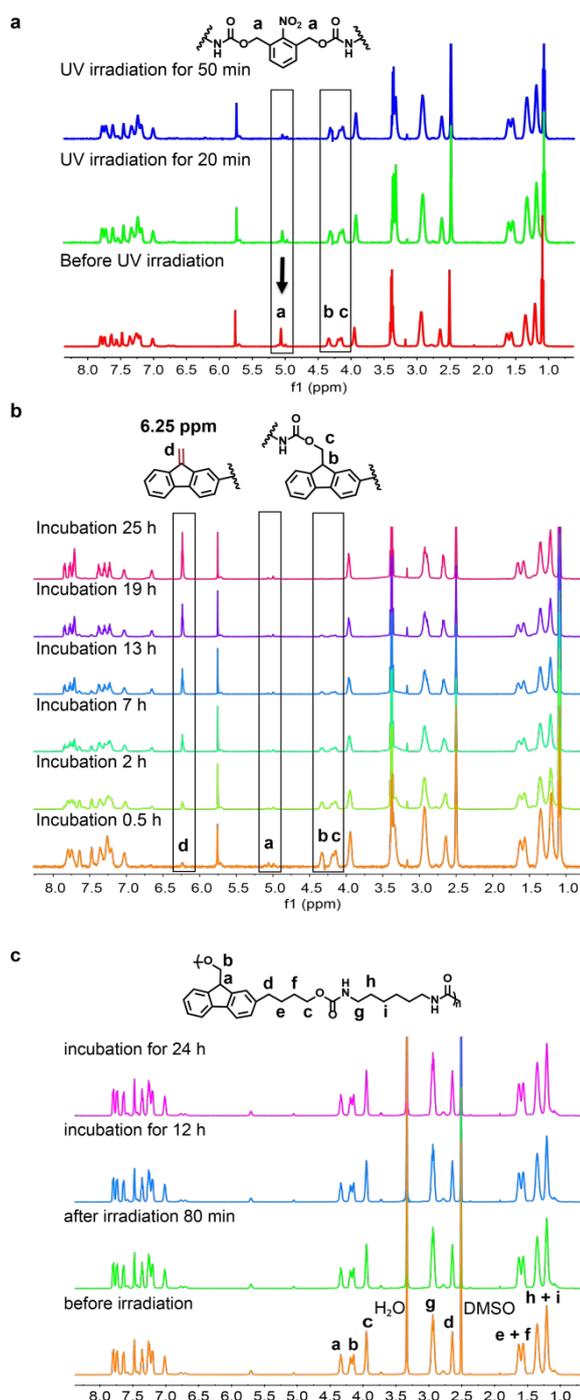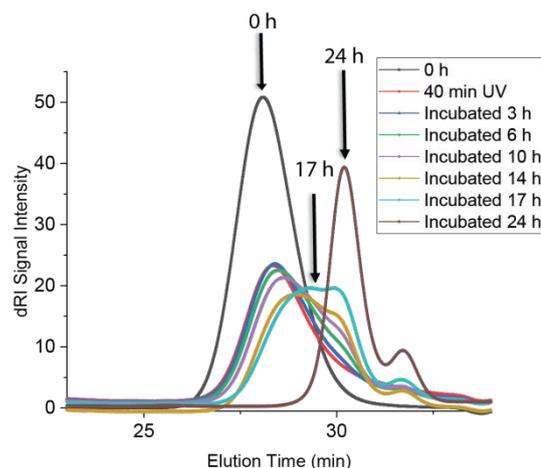

Fig. 4 GPC monitor of polymer **1** degradation overtime after being irradiated by UV light for 40 min.

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 μm 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).

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**.
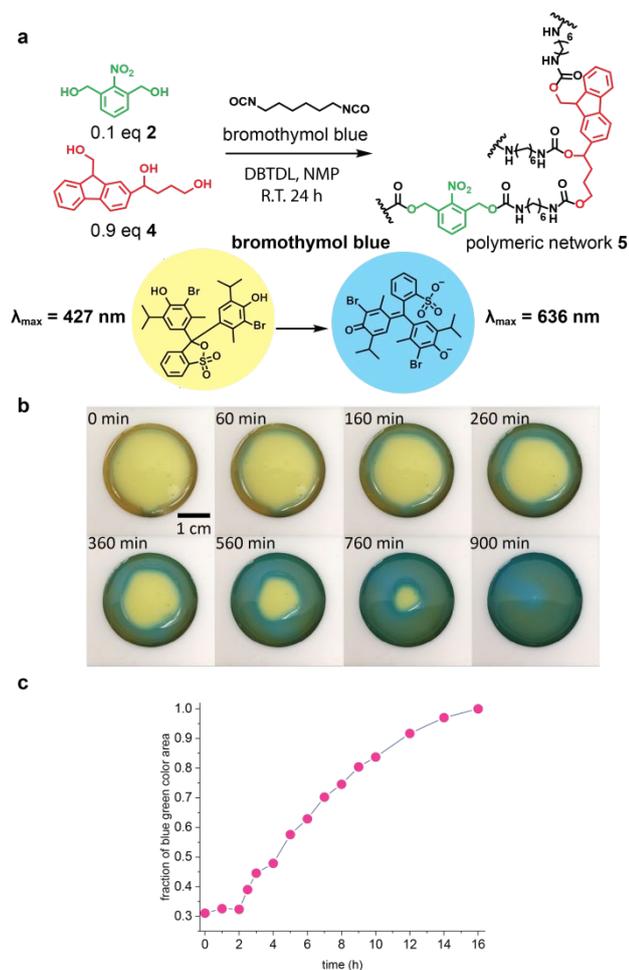
Fig. 5 (a) Synthesis of photo-triggered self-propagating degradable gel **5** with bromothymol blue as pH indicator. (b) Photographs of degradation of polymeric network **5** after a few mm of its outer edge were irradiated by UV light (190 mW, 1.5 mW/cm^2) for 1 h. (c) Quantification of loss of yellow area versus time plot after UV irradiation. Lines added to guide the eye.

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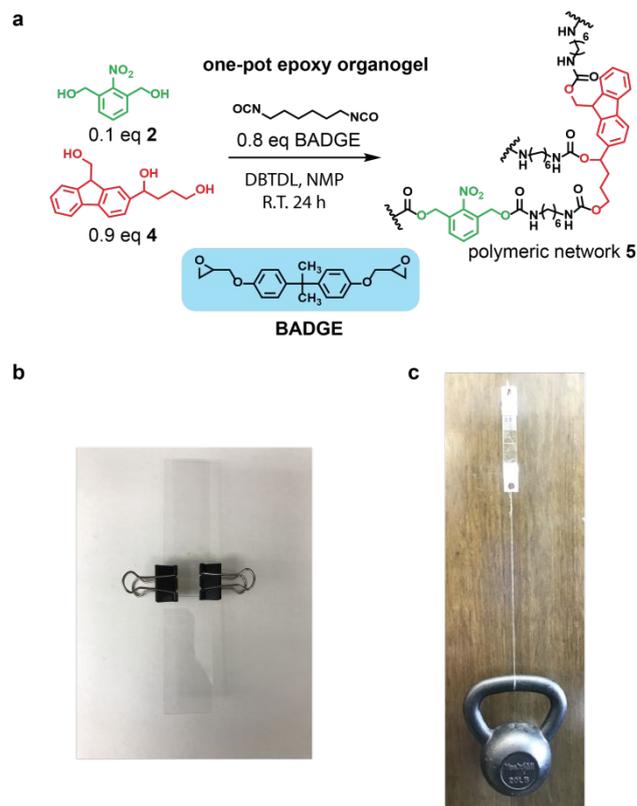

Fig. 6 (a) Synthesis of photo-triggered base-propagating degradable polymeric network **5** with BADGE epoxide monomer encapsulation (one-pot epoxy polyurethane organogel). (b) Preparation of adhesive sample with microscope slides and binder clips. The slices were cured at 95 °C under nitrogen in vacuum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

turned green until finally the whole polymer was consumed by this green color and has fully transitioned into a liquid after 15 h. Despite 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 (λ_{max} = 365 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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