

Supplementary Materials: UVA-Degradable Collagenase Nanocapsules as a Potential Treatment for Fibrotic Diseases

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Characterization Of Compounds

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1. Double-Fmoc Protected Amide (Product 1)

¹H NMR spectrum

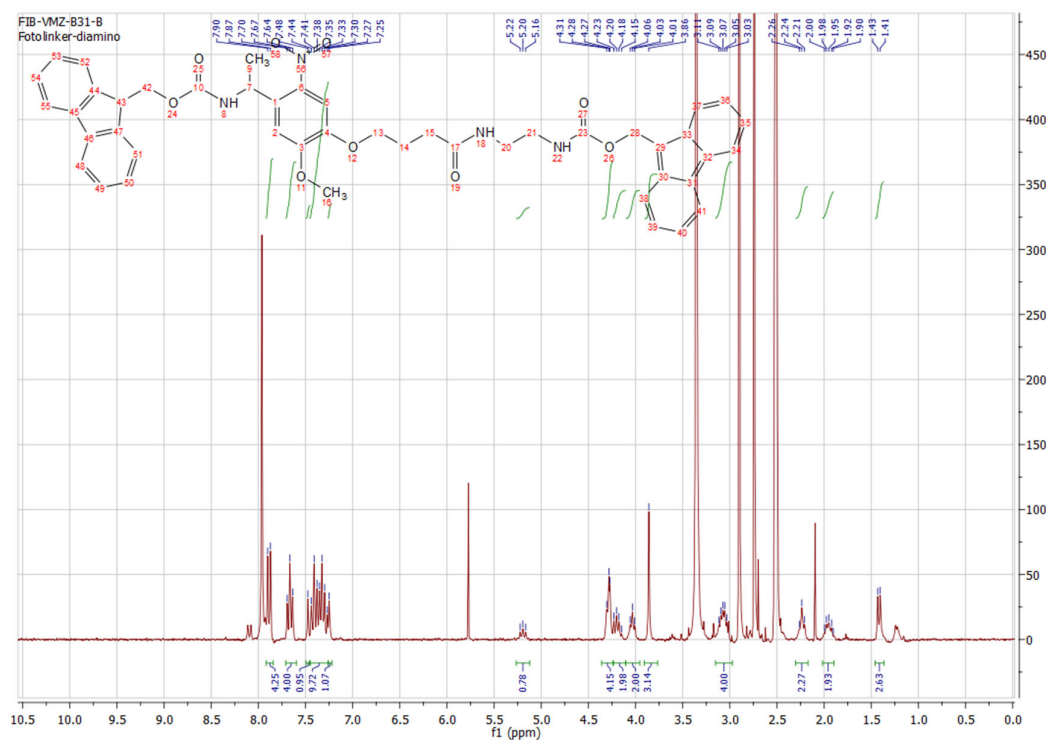


Figure S1. ¹H NMR (250 MHz, MeOD) spectrum of Fmoc-PL-NH-Fmoc (1). Solvent residual peaks observed for DCM (5.76 ppm), Acetone (2.09 ppm) and DMF (7.95 ppm, 2.89 ppm, 2.73 ppm).

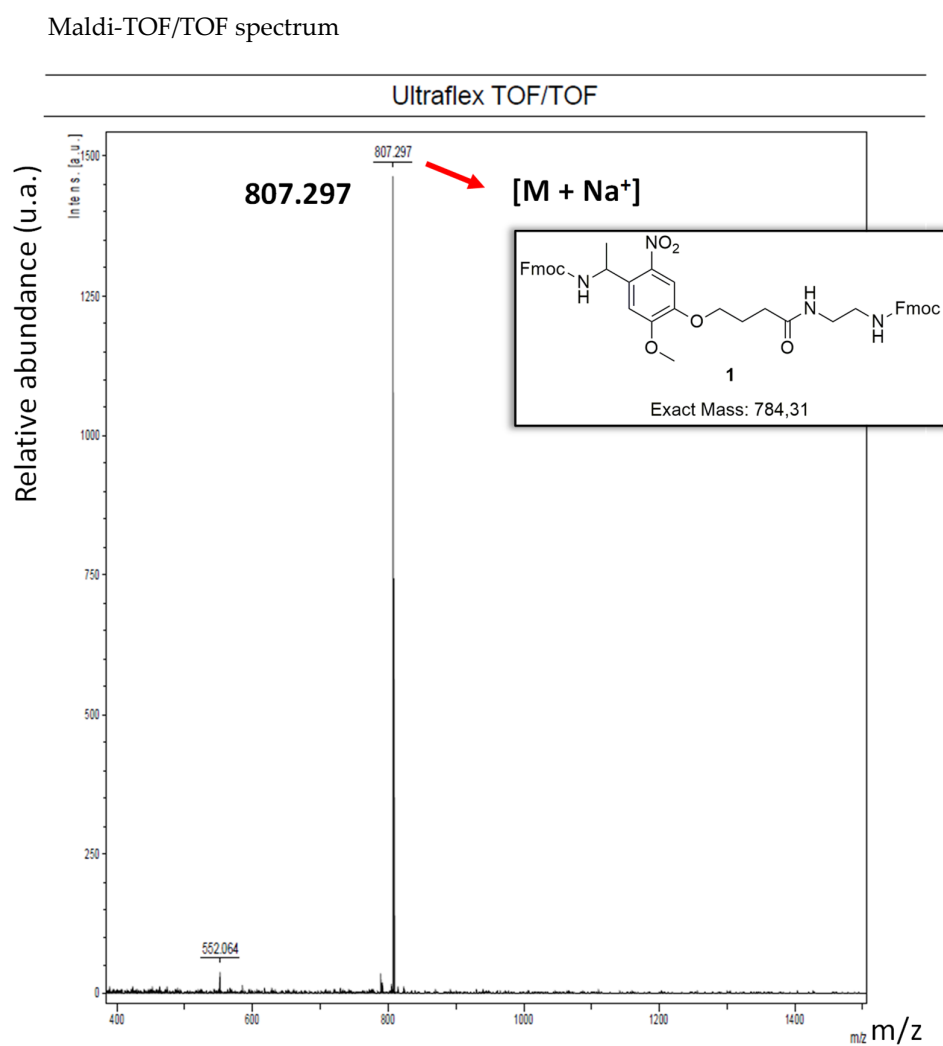


Figure S2. Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight (Maldi-TOF/TOF) MS analysis of Fmoc-PL-NHFmoc (**1**). Chemical Formula: $C_{45}H_{44}N_4O_9$. Exact Mass (m/z): 784,31.

2. Diamine-Photolinker (Product 2)

^1H NMR spectrum

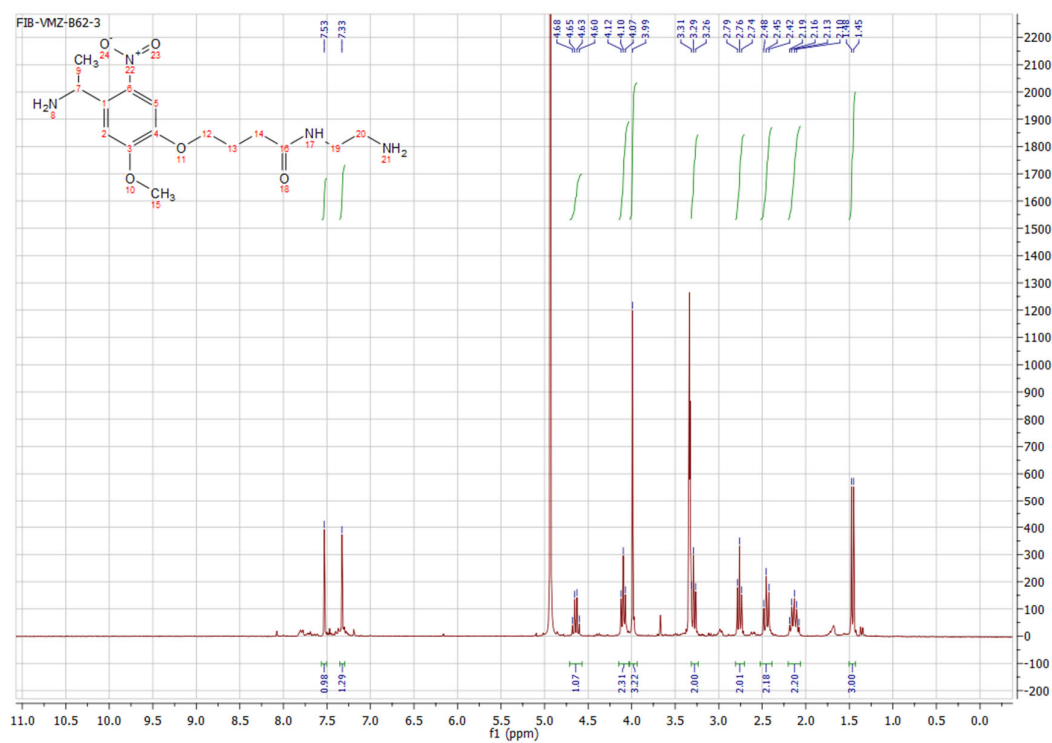


Figure S3. ^1H NMR (250 MHz, MeOD) spectrum of Diamine-Photolinker (2).

3. Bisacrylamide Photolinker, PL (Product 3)

^1H NMR spectrum

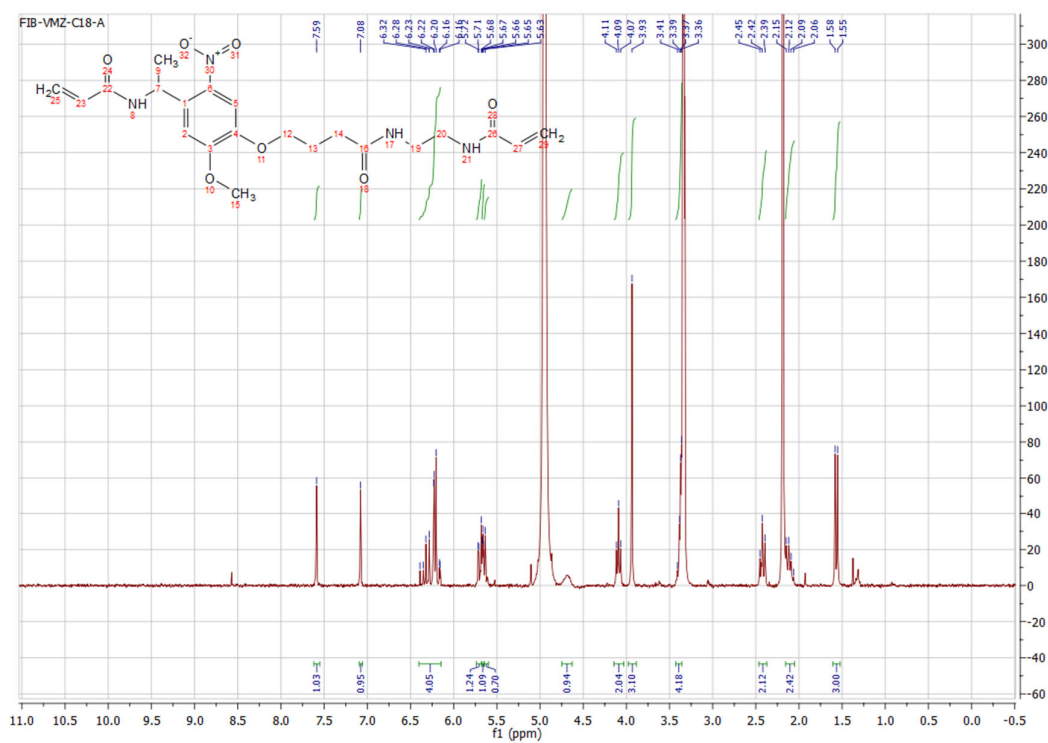


Figure S4. ^1H NMR (250 MHz, MeOD) spectrum of Bisacrylamide-Photolinker (3).

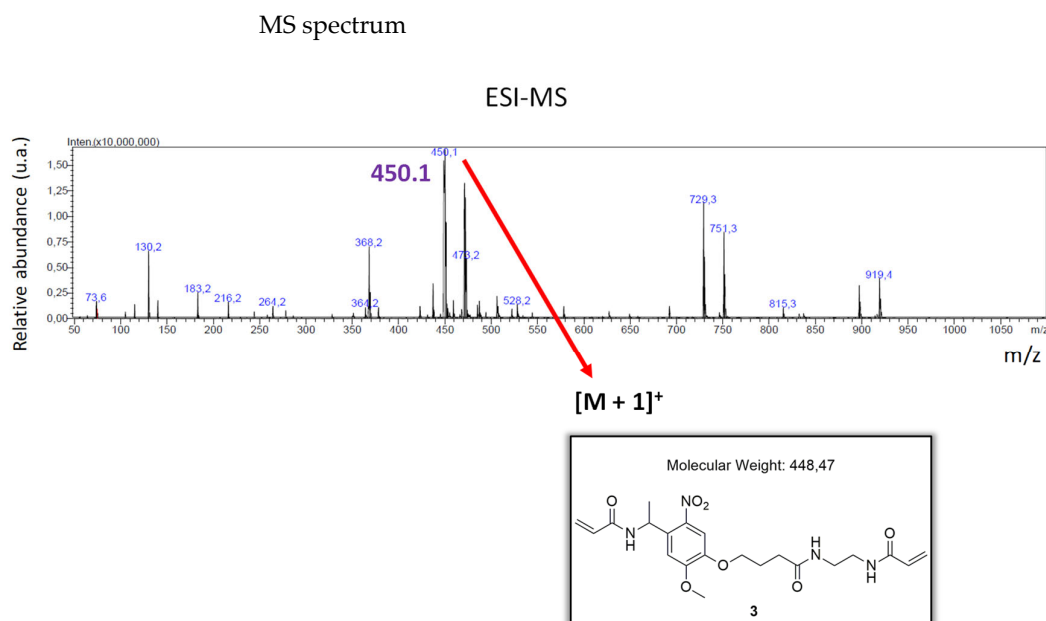


Figure S5. Electrospray Ionization (ESI-MS) MS analysis of Bisacrylamide-Photolinker (**3**). Chemical Formula: $C_{21}H_{28}N_4O_7$. Exact Mass (m/z): 448,47.

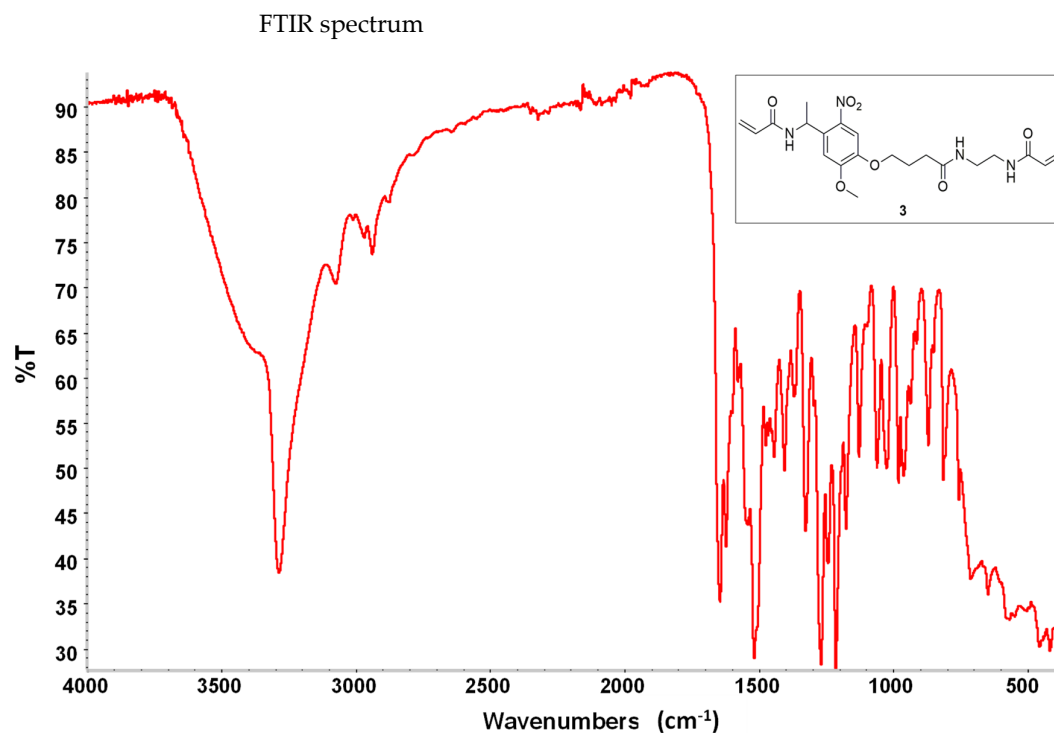


Figure S6. FTIR spectrum of Bisacrylamide-Photolinker (**3**). Intense peaks for C-O stretching at $\sim 1210\text{ cm}^{-1}$ and $\sim 1280\text{ cm}^{-1}$ were assigned to aryl alkyl ethers. Peaks for N=O stretching at $\sim 1550\text{ cm}^{-1}$ (asymmetric) and $\sim 1330\text{ cm}^{-1}$ (symmetric) were attributed to aromatic nitro group. Intense peak for aromatic C=C stretching at $\sim 1500\text{--}1520\text{ cm}^{-1}$ were attributed to aromatic ring. Intense peak for C=C stretching at $\sim 1630\text{ cm}^{-1}$ corresponded to vinyl groups. Strong C=O peak at $\sim 1650\text{ cm}^{-1}$ relative to C=O from amides. C-H stretching peaks at $\sim 2800\text{--}3100\text{ cm}^{-1}$ related to vinyl groups and aromatic ring. Strong N-H stretching peak at 3300 cm^{-1} related to amides. Broad O-H stretching band at $\sim 3300\text{--}3700\text{ cm}^{-1}$ was assigned to water traces present in the sample.

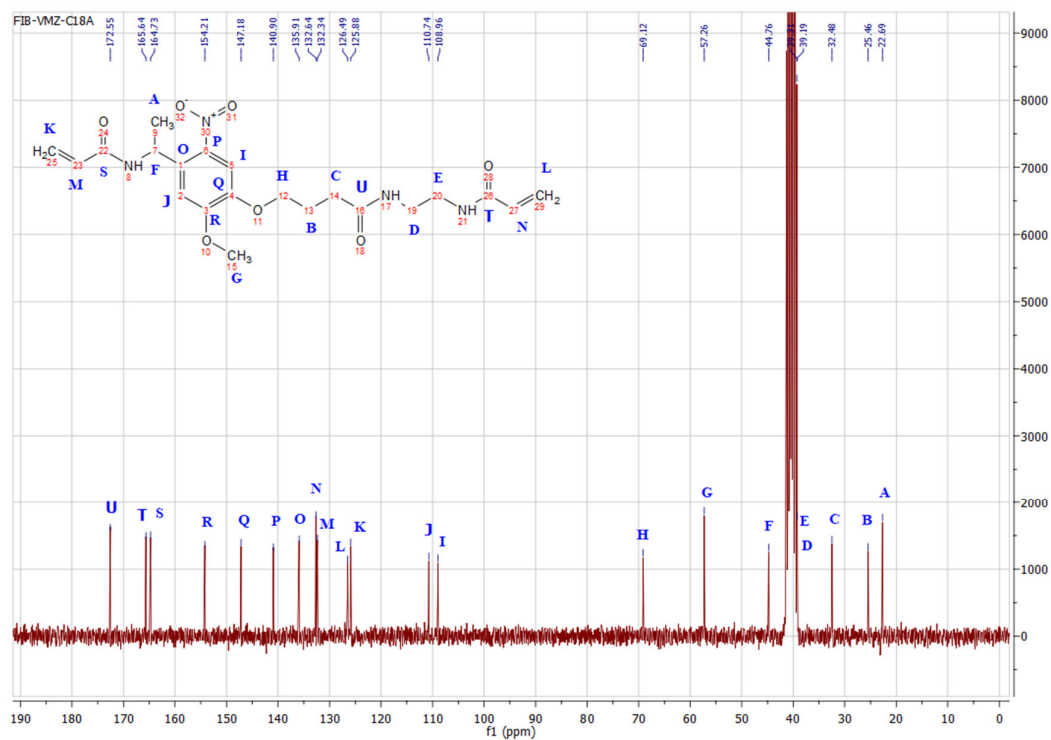
^{13}C NMR spectrum

Figure S7. ^{13}C -NMR spectrum of Bisacrylamide-Photolinker (3). ^{13}C -NMR (63 MHz, DMSO) δ 172.55, 165.64, 164.73, 154.21, 147.18, 140.90, 135.91, 132.64, 132.34, 126.49, 125.88, 110.74, 108.96, 69.12, 57.26, 44.76, 39.31, 39.19, 32.48, 25.46, 22.69.

COSY 2D-NMR spectrum

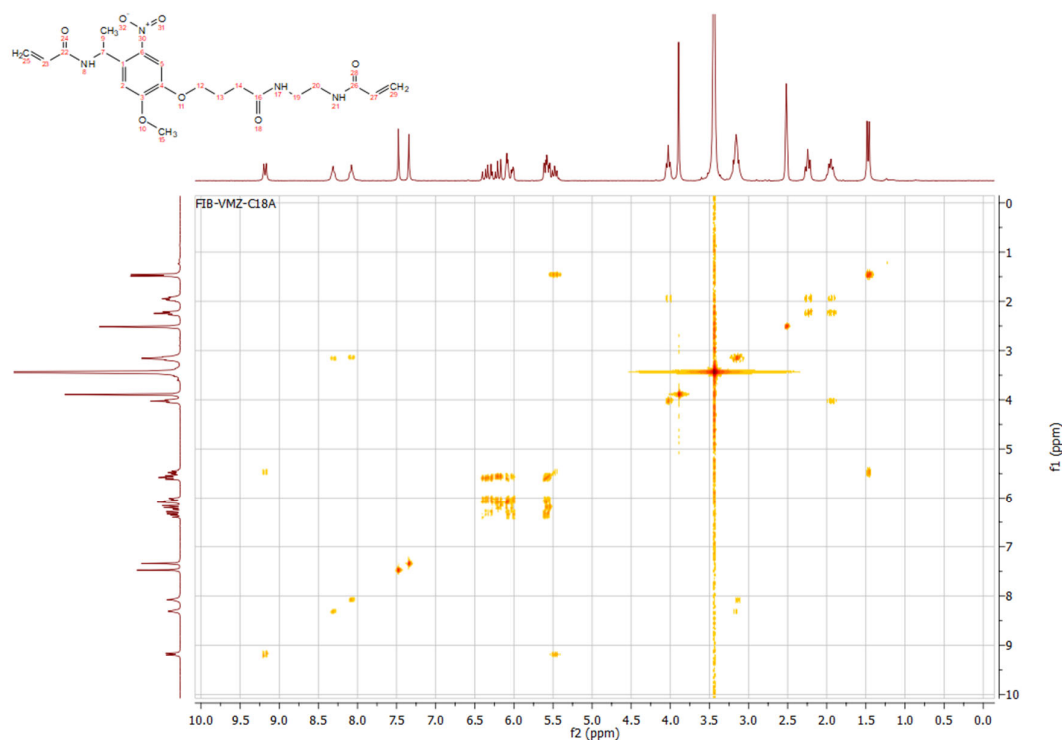


Figure S8. COSY 2D-NMR spectrum of Bisacrylamide-Photolinker (3).

HMQC 2D-NMR spectrum

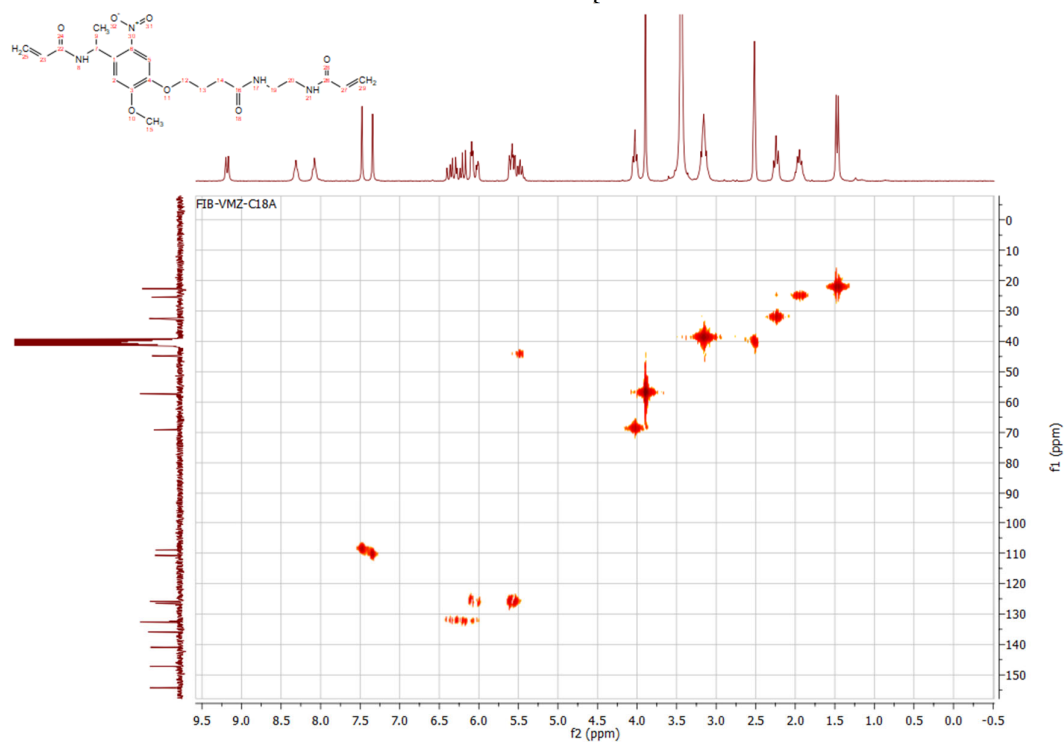


Figure S9. HMQC 2D-NMR spectrum of Bisacrylamide-Photolinker (3).

4. UVA-Induced Degradation of PL to dPL

¹H-NMR calculated yield: The integral area of a ¹H peak corresponding to Photolinker (PL) and a ¹H peak corresponding to degraded Photolinker (dPL) was calculated after each irradiation pulse of 10 min of UVA. They were compared with the ¹H signal of an internal standard (considered integral of CH₂ at 1.95 ppm). Comparing the equivalents obtained from integral area of both products, it was calculated the molar ratio between both compounds. The molar ratio for each compound was obtained as: % = (¹H area of compound X / total ¹H area of PL and dPL) × 100.

NMR for UVA-induced degradation of PL to dPL

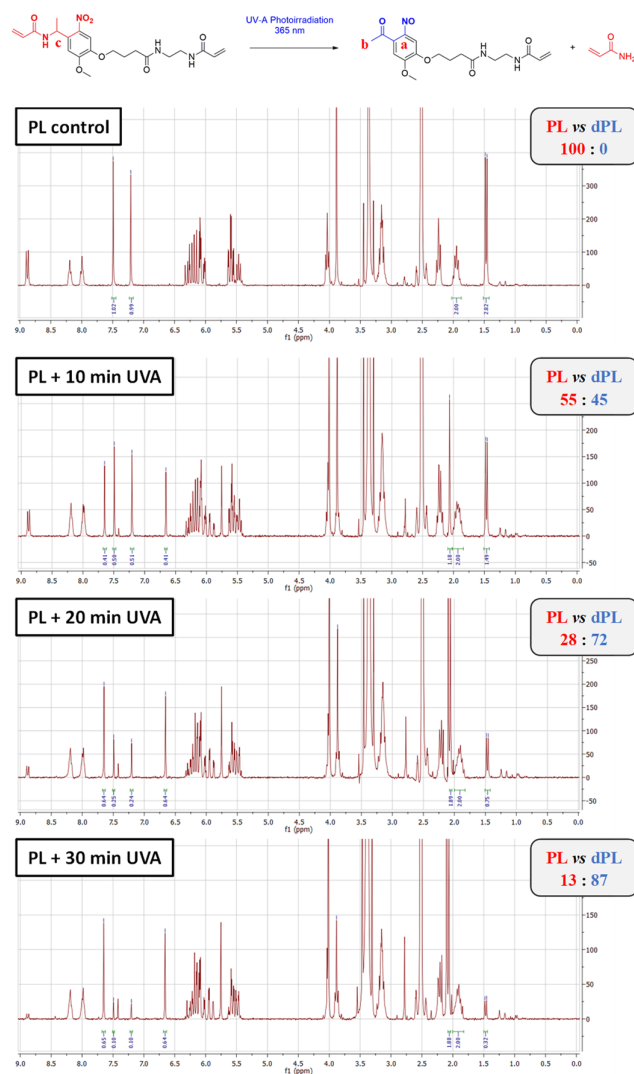


Figure S10. ¹H-NMR spectra for Control PL and for PL irradiated with one pulse of UVA for 10 minutes (PL+10 min UVA), two pulses of 10 + 10 min (PL+20 min UVA), and three pulses of 10 min each (PL + 30 min UVA). Calculated ratio between PL and dPL for each sample is represented in the right boxes.

MS for PL and dPL compounds

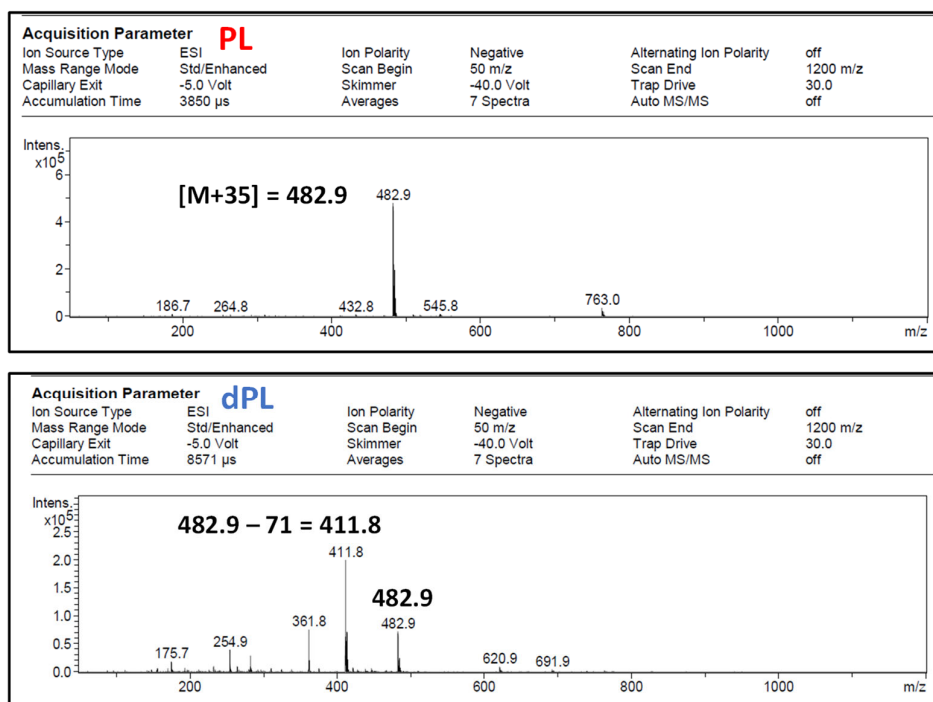
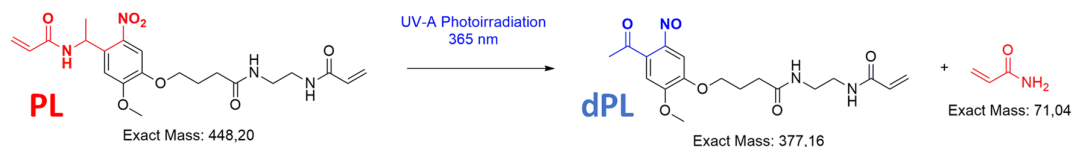


Figure S11. Electrospray Ionization MS (ESI-MS) analysis of Photolinker (PL) before (PL) and after UVA irradiation (dPL). m/z of 482.9 correspond to PL. m/z of 411.8 correspond to degraded PL (dPL). This is consistent with the PL mass–71 (mass of acrylamide degradation subproduct).