Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Modular photo-induced RAFT polymerised hydrogel *via* thiol-ene click chemistry for 3D cell culturing

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Experimental

Synthesis of pentafluorophenol acrylate (PFPA). Pentafluorophenol (30.0g, 0.06 mol), dichloromethane (100 mL), and triethylamine (27.8 mL) were measured into a round bottom flask. After which acryloyl chloride (16.2 mL) in excess dichloromethane was slowly added dropwise to the reaction mixture in an ice bath. The reaction was stirred at room temperature for 24 h. The solution was filtered and the orange filtrate was washed with water, HCl (0.1 M, 10 mL x 3), brine solution (10 mL x 3) and water (10 mL x 3). The solution was dried with magnesium sulfate and solvent was removed by rotary evaporation. The orange solution was further purified by vacuum distillation (0.9 Torr, 60 °C) and a clear solution was obtained and the PFPA was confirmed by ^{19}F NMR and ^{1}H NMR spectroscopy.

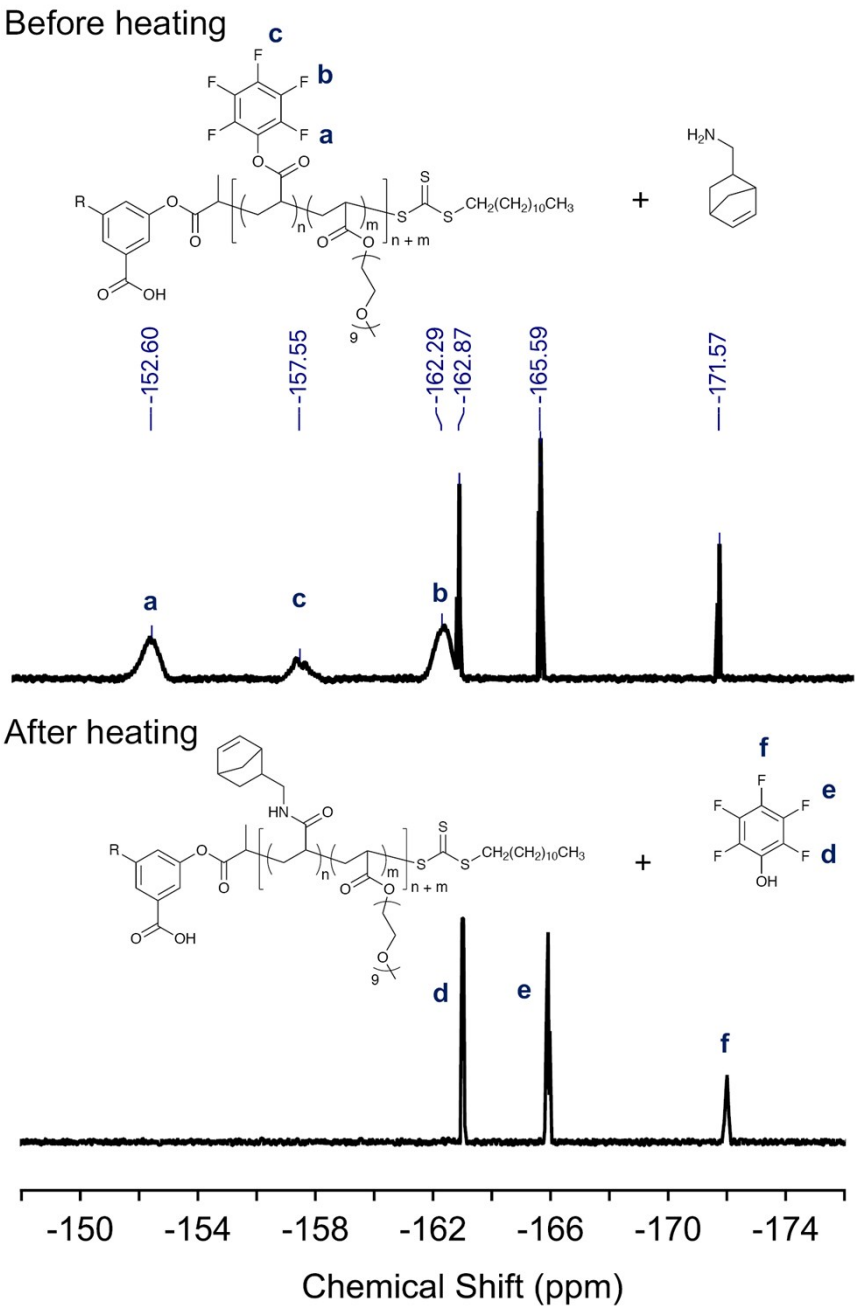

Figure S1. ^{19}F NMR spectra (300 MHz in $CDCl_3$) of the reaction between poly(PEGMEA-*stat*-PFPA) and norbornene in the presence of triethylamine, before and after the completion of the reaction, showing the disappearance of the PFPA characteristic fluorine peaks at -152.60 (ortho), -157.55 (para) and -162.29 (meta) ppm.

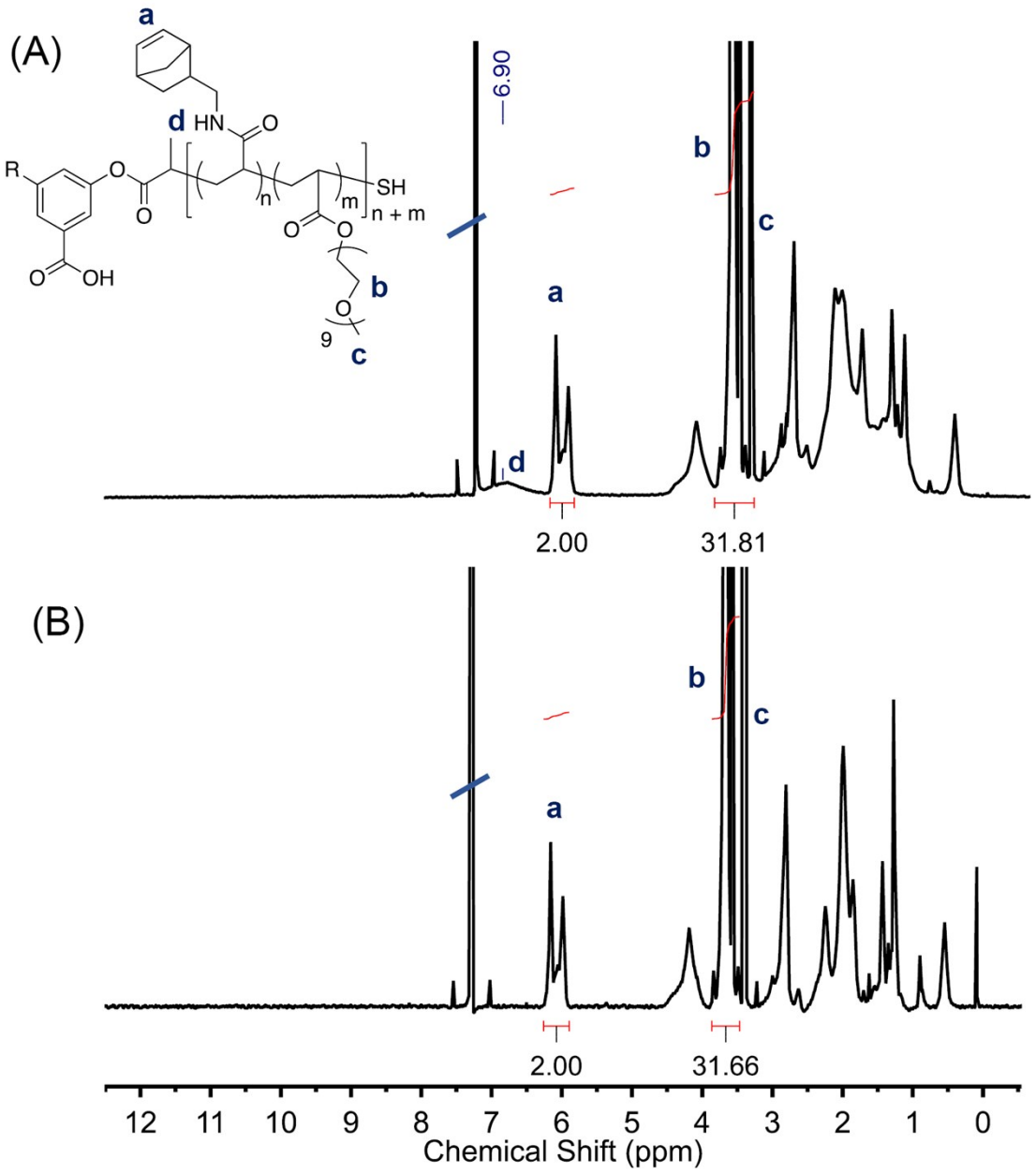

Figure S2. Representative ^{1}H NMR spectra (400 MHz in $CDCl_3$) of poly(PEGMEA-*stat*-5N2MA) **(A)** and ^{1}H NMR spectrum of D_2O proton exchange of poly(PEGMEA-*stat*-5N2MA) **(B)**. Characteristic peaks of PEGMEA (at 3.66 ppm) and the characteristic peak of alkene of the norbornene (at 5.90-6.26 ppm) are shown. A broad singlet (at 6.90 ppm) is representative of the amide proton **(A)**, the disappearance of this signal in D_2O proton exchange **(B)** confirms the amide proton of the norbornene-functionalised polymer.

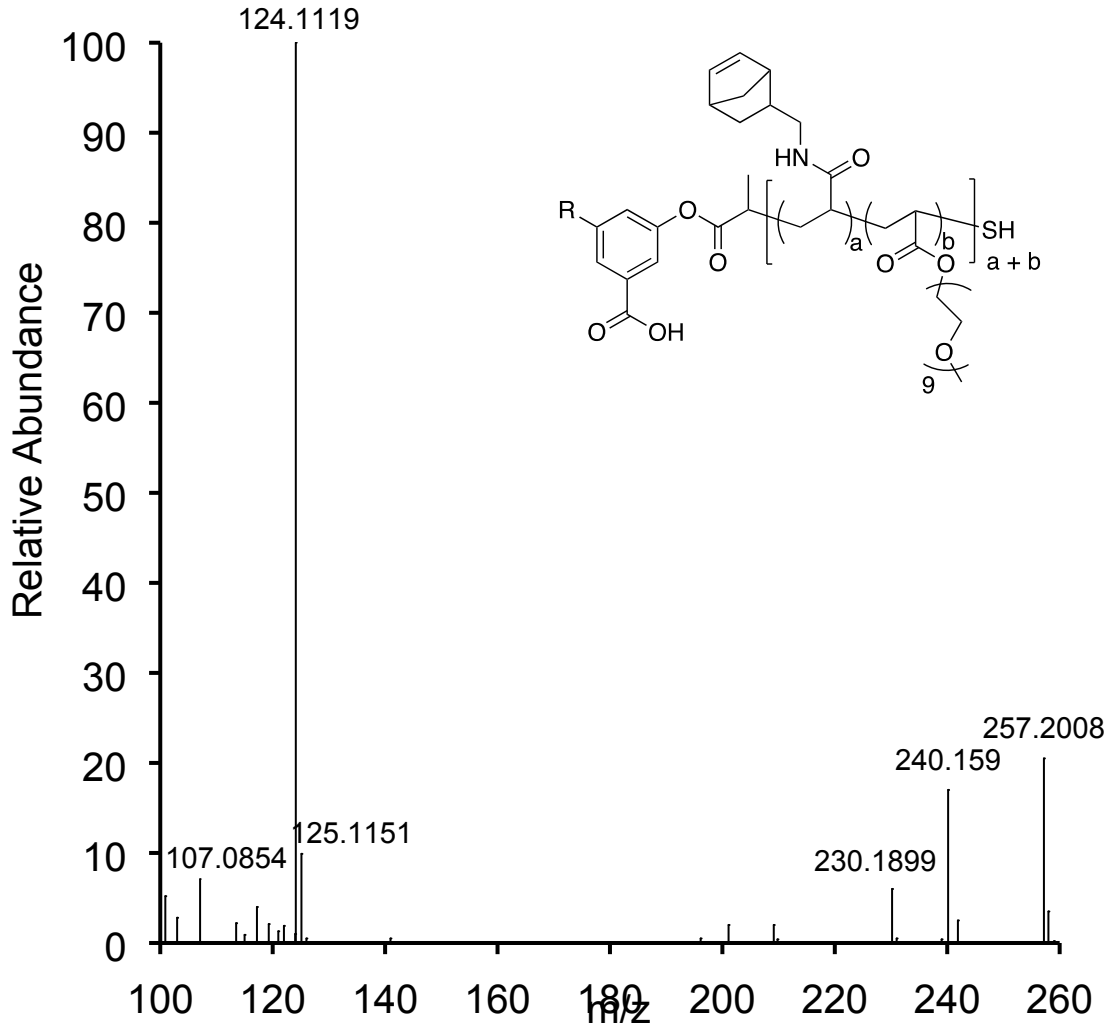

Figure S3. Mass spectrum of purified poly(PEGMEA-*stat*-5N2MA) showing the lack of the 184 m/z peak, which corresponds to the pentafluorophenol group.

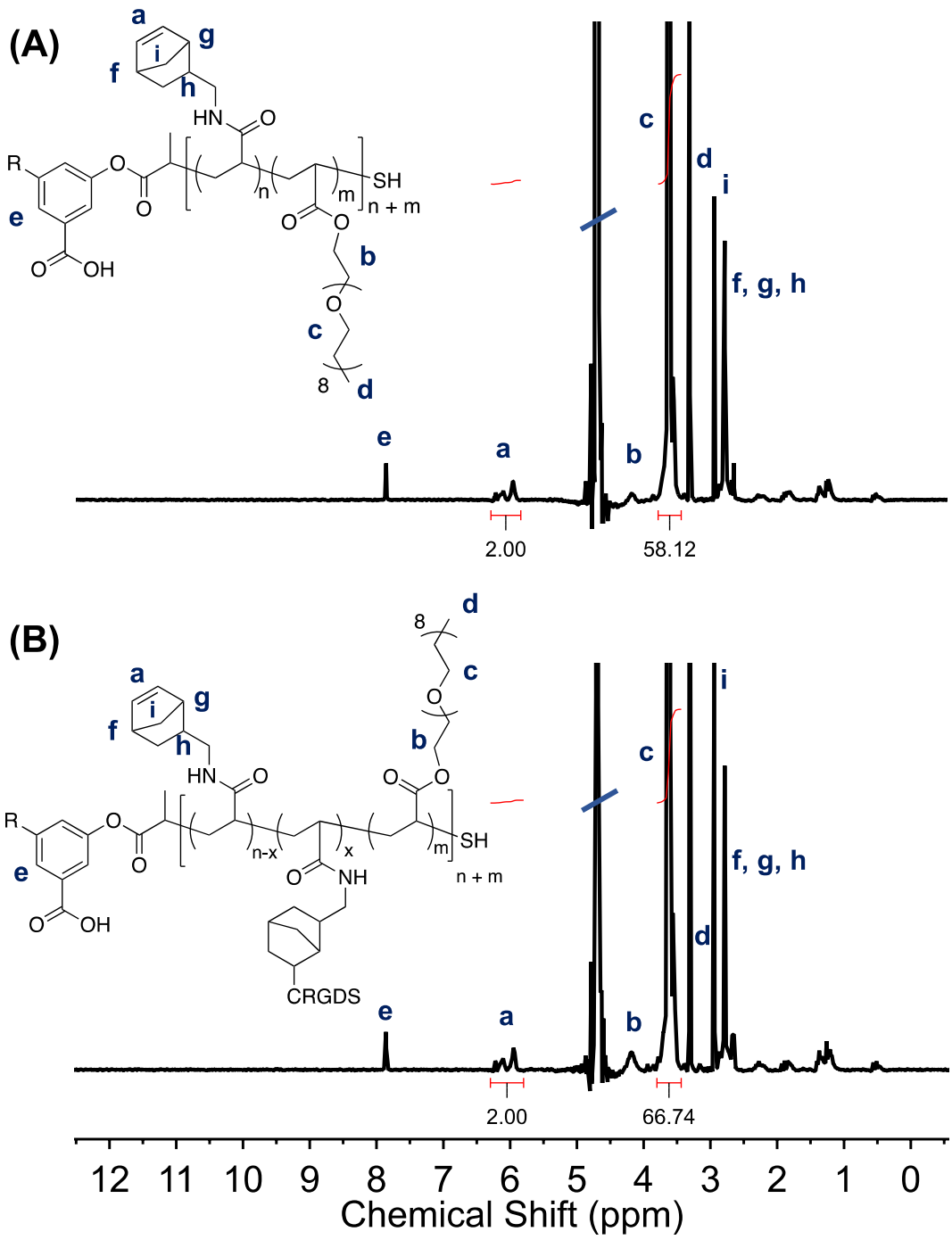

Figure S4. Representative ^{1}H NMR spectra (300 MHz in D_2O) of poly(PEGMEA-*stat*-5N2MA) **(A)** and poly(PEGMEA-*stat*-(5N2MA-*stat*-CRGDS)) **(B)**, showing the peaks characteristic to PEGMEA (at 3.66 ppm) and the characteristic peak of norbornene (at 5.93-6.24 ppm). The integration of the methylene proton of PEGMEA from 66.74 before aminolysis **(A)** to 58.12 after aminolysis **(B)**. This increase in the integration values of PEGMEA suggest the attachment of CRGDS on the polymer.

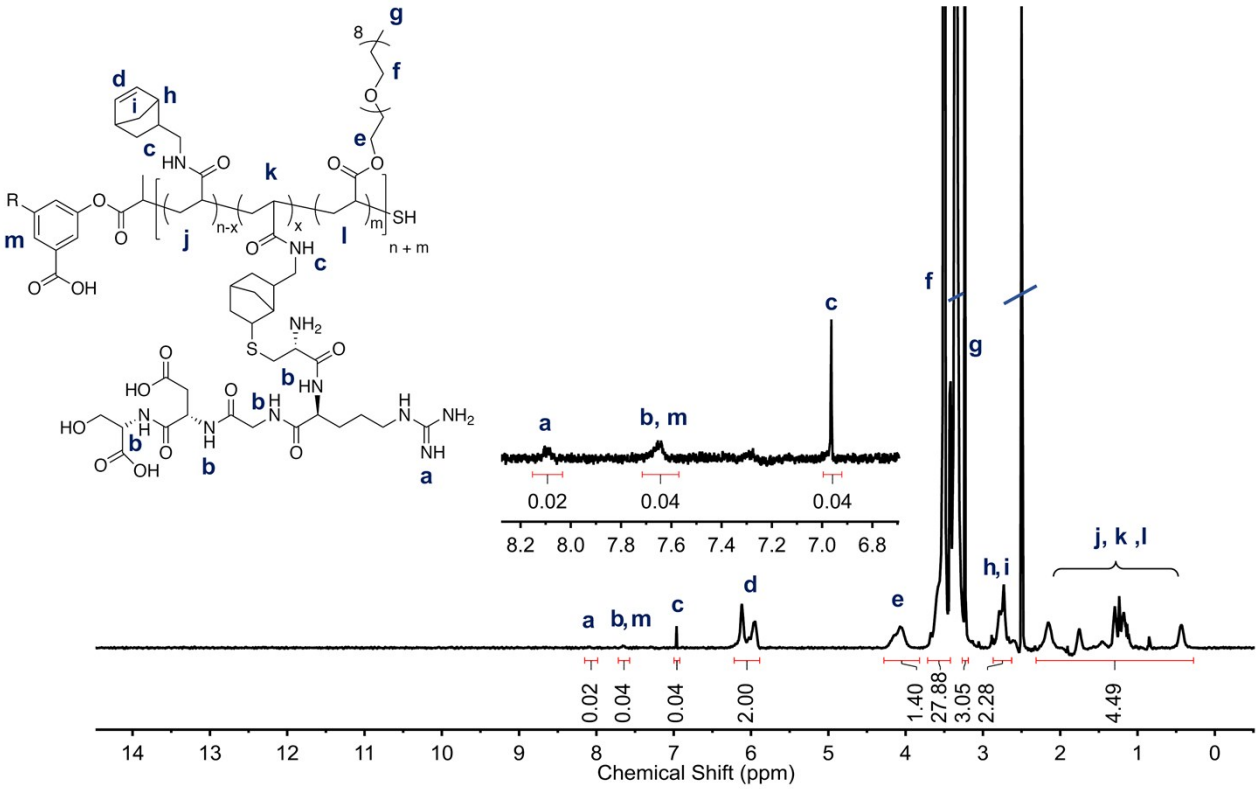

Figure S5: Representative ^{1}H NMR spectra (400 MHz in DMSO) of poly(PEGMEA-*stat*-(5N2MA-*stat*-CRGDS)).

Table S1. Eosin-Y concentration and their respective gelation time.

Eosin-Y concentration / mM	Gelation time / min
0.1	8.24
0.3	5.03
0.5	2.15
0.7	1.5
1	1

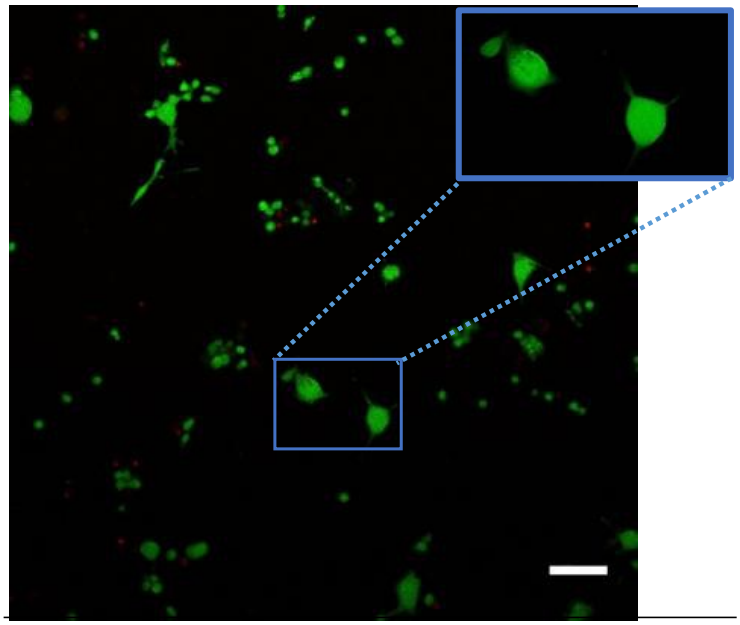

Figure S6. Confocal microscopy images of $Kras^{G12D}$, $p53^{R172H}$ pancreatic cancer cells cultured on the surface of the Matrigel® as the positive control. Zoomed image highlights protrusion of cells. Scale bar: 100 μm.

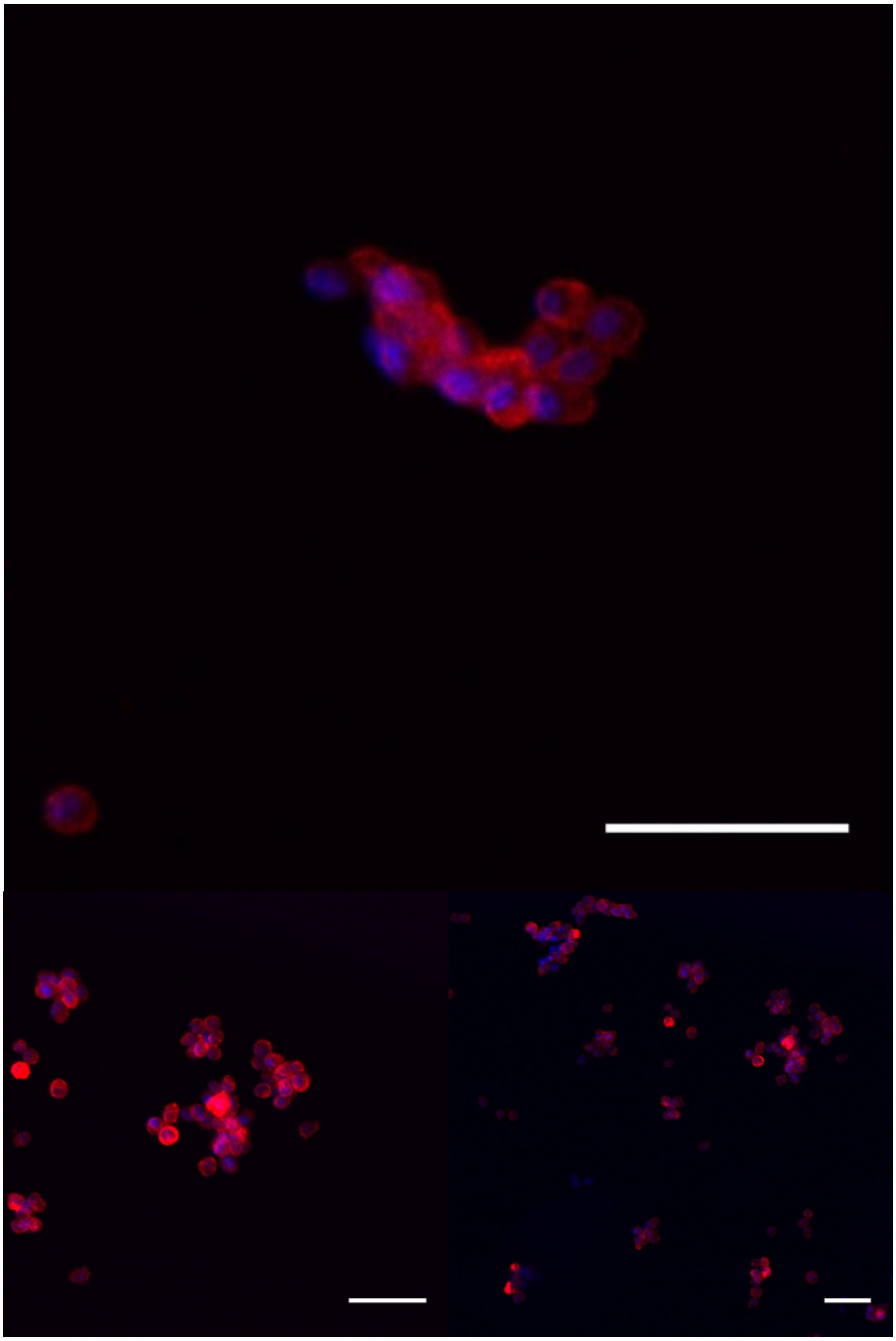

Figure S7. Confocal image of phalloidin stained $Kras^{G12D}$, $p53^{R172H}$ pancreatic cancer cells encapsulated within the hydrogel. The red stain of the image represents the actin component of the cell, while the blue stain represents the nucleus of the cell. Scale bars: 50 μm.

Table S2. Table of two different visible light photoinitators used in replacement of eosin-Y. $PEGMEA_{31}$-*stat*-$5N2MA_{34}$, PEG bis-thiol, and initiator (0.1 mM) were mixed together in PBS. The solution was exposed to light (halogen lamp, 21 V, 150 W, 200 000 Lux, 10 cm above sample) for 5 minutes. Gelation was determined by tube inversion test.

Initiator	Polymer	Result
Riboflavin	$PEGMEA_{31}$-*stat*-$5N2MA_{34}$	No gel formation after 5 minutes of exposure
Camphorquinone	$PEGMEA_{31}$-*stat*-$5N2MA_{34}$	Partial hydrogel formation after 5 minutes with the surrounding polymer blend still fluid.