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Multi-Material Hydrogel with Widely Tunable Elasticity by Selective Photo-Polymerization of PEG Diacrylate and Epoxy Monomers

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Multi-material structures with variation in chemical, physical and mechanical properties offer numerous possibilities to make unique devices. Biomaterials for in vitro disease models and in vivo tissue engineering [1,2] pose particular mechanical challenges since they need to match the compliance of soft tissue while remaining mechanically stable as an operational device. Here, we show how selective photo-polymerization of a mixture of epoxy and acrylate monomers can be used to make functionally graded multi-material structures, with unique freedom to tune the mechanical properties from <100 kPa to >10 MPa by initiating each

monomer individually at separate wavelengths and with a defined light dose (Figure 1). Functionally graded materials, with a gradient variation of physical or chemical properties, have been made in several types of materials including polymers.[3] Such materials are typically made by first curing one monomer followed by immersion into a second monomer solution to initiate diffusion-limited swelling of the first polymer gel network. Before diffusion equilibrium is reached the second monomer is cross-linked, typically initiated by light illumination, thereby creating a gradient of the second polymer within the material.[4–6] Important limitations of this approach is that a) the second monomer has to be able to diffuse into the cross-linked first monomer gel together with a photoinitiator, b) the gradient profile can only be defined by the diffusion process, c) light must be able to penetrate the structure, and d) the final gel must be transferred between different monomer solutions in the process. This restricts the application to relative small structures and places a high demand on extensive test or very precise modeling of the diffusion of the monomer and photoinitiator into the material.

Higher control over the spatial distribution of material can be achieved with stereolithography where 3D structures can be made layer by layer with patterned light illumination and has been used to make many different types of devices.[7–11] However, currently all commercial stereolithography printers can only make mono-material structures. This limits the application especially within tissue engineering: Soft hydrogel devices can be made, but these devices are extremely fragile, and for many applications stiff support structures are required.[12–14] This also applies to in vitro 3D tissue models where medium perfusion of soft scaffold constructs requires stiff stable connection points to external pumping systems.[15] Therefore, it would be advantageous to be able to produce multi-material structures containing both soft and stiff

material in a single repeatable process flow. There are only a few examples of multi-material structures made by stereolithography where typically the structure of two different materials is made by washing and exchanging the monomer liquid between exposures of each layer.[16–18] Hence, each layer will contain identical material, which limits the range of applications. Additionally, the process is time consuming and complex to automate.

Multi-material structure can be made from a resin solution that cures into different materials when exposed to different light sources. To make this type of solution it has to contain two different monomers that each has to be initiated individually and polymerize independently. The combination of acrylate and epoxy monomers together with radical and cationic photoinitiators, respectively, offers the possibility to initiate the monomers selectively. When the free radical photoinitiator is excited it initiates the acrylate groups without initiating the epoxy group [19,20]. The cationic photoinitiator produces a Brønsted acid upon excitation, and this super acid initiates polymerization of epoxy groups. [21,22] However, the cationic photoinitiator also produces free radical species, and consequently initiates the acrylate monomers as well. As the two monomers polymerize by independent mechanisms, an interpenetrating polymer network (IPN) is created where the two polymers are interlaced but not covalently linked. [21,23]

To our knowledge, only two former reports have described the separate polymerization of an epoxy and acrylate monomer component. [19,20] Ruiter *et al.* synthesized a monomer with an acrylate and an oxetane functional group, and selectively polymerized each functional group [20]. The acrylate was polymerized with a radical photoinitiator illuminated with filtered light above 385 nm and the epoxy monomer were polymerized by a cationic photoinitiator

with light below 385 nm. In a prior study, Decker made a mixture of an acrylate and an epoxy and first cured the acrylates by a photoinitiator illuminated with light above 350 nm followed by excitation of a cationic photoinitiator illuminated with light below 350 nm. [19] For both systems, acrylate was shown to cure independently of the epoxy. However, no material specific properties were examined in either report and this idea has not been pursued further to our knowledge.

Here, we show that polyethylene glycol diacrylate (PEGDA) monomer via a photoinitiator can be cured to a soft hydrogel by visible blue light (450 nm) without epoxy polymerization, whereas epoxy monomer is cured to a hard material when exposing the same liquid to UV light (365 nm). This results in an epoxy material that can be several hundred times stiffer than the PEGDA material. Chemical analysis with FT-IR confirmed that only the PEGDA was polymerized under blue light. Moreover, the compressive elastic properties of the material was shown to depend on the light exposure time, resulting in a functionally graded material. The use of widely separated wavelengths is in itself technically beneficial as unfiltered light from commercially available high power LED sources may be used instead of filtering of conventional broad-band light sources. Restorative dentistry researchers have long utilized spectrally matched, compact, power efficient, fast switchable, long-lived LED sources for curing of photoinitiated acrylates and epoxies.[24] Recent years have also seen a surge in research into new photoinitiator systems taking advantage of the spectral freedom of LEDs. [25] For experimental convenience, we have used a filtered mercury vapor lamp system for UV excitation in the current work to provide homogeneous illumination across a microtiter plate. However, fully equivalent results will result from exposure using commercially available 365 nm LEDs.
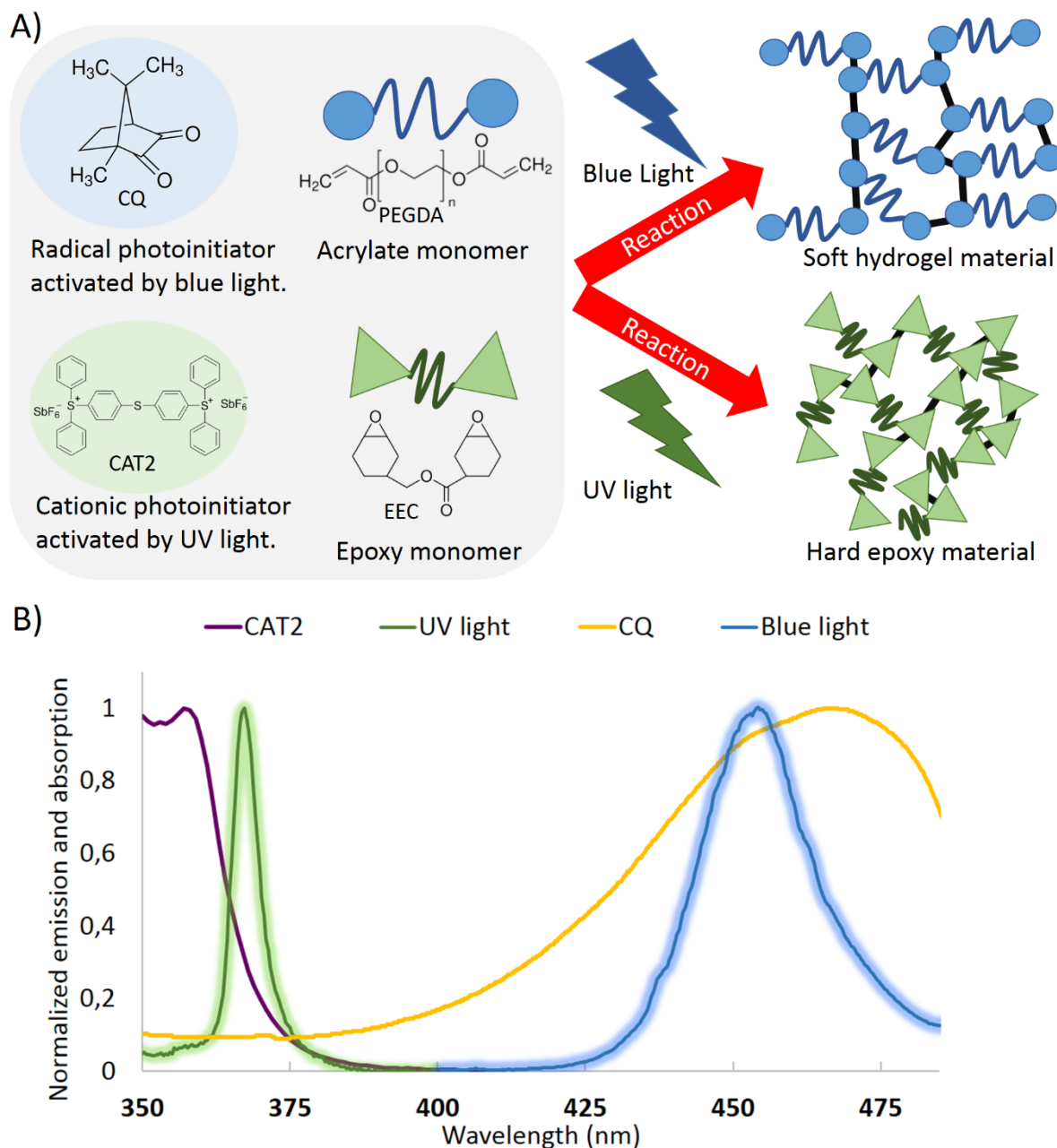
Figure 1 A) Reaction scheme for CQ and CAT2 photo-initiation of the free radical polymerization of the acrylate component and cationic polymerization of the epoxy component, respectively. B) Normalized absorption of the CQ and CAT2 photoinitiators, and normalized emission spectra of the blue (450 nm) and UV (365 nm) light sources.

For the soft part of the material the radical initiated poly(ethylene glycol) diacrylate (PEGDA) (700 Da) was used, as this is known to form soft hydrogels useful in tissue engineering.[7,26,27] For the stiff part, the epoxy monomer, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC) turned out to polymerize the fastest compared to other cationic initiated monomers (Table S1, Supporting Information). A panel of different radical photoinitiators were tested with blue light exposure. Camphorquinone (CQ) was found to induce the shortest cure time at 450 nm (data not shown). Further optimization showed that 10 mg/ml CQ and ≥10% v/v PEGDA are required for gelation within a useful time window of 10 min. (Table S2, Supporting Information). A number of cationic photoinitiators were tested, and initiators based on triarylsulfonium hexafluoroantimonate salts (called CAT2) were found to be most efficient in polymerizing monomers using 365 nm illumination (Table S1, Supporting Information). The aim is to produce hydrogel structures, but water could not be used as solvent since the epoxy monomer is water insoluble and since water interferes in the cation-initiated polymerization by chain transfer. Diethylene glycol diethyl ether (DGDE), essentially a very short PEG molecule, was found to dissolve the different components without interfering with the polymerization processes.

Cure speed is one of the most important parameter for selective production of multi-material structures. Table 1 show the time to gelation as a function of light source wavelength (365 nm and 450 nm), photoinitiators (CQ and CAT2), and monomers (PEGDA and EEC). For the samples exposed to 450 nm blue light, only the samples containing both CQ and PEGDA cured. The time to gelation was almost independent of CAT2 and EEC concentration, and no EEC polymerization was observed. At 365 nm illumination, CAT2 initiated crosslinking of both PEGDA and EEC monomer, and the time to gelation decreased with increasing CAT2

concentration. The samples with only CQ did not cure, indicating that only CAT2 is excited at 365 nm as expected from the absorption spectra of the two photoinitiators (Figure 1B). Moreover, the addition of CQ to CAT2 did not change the time to gelation. This shows that PEGDA is only polymerized at 450 nm via CQ whereas both EEC and PEGDA can be polymerized at 365 nm via CAT2. Some sulfonium salts may be photosensitized by camphorquinone but triarylsulfonium salts like CAT2 were previously reported to be insensitive to photoinitiated CQ due to the high reduction potential of the triarylsulfonium group [28].

Exposed at 450 nm

CQ (mg/ml)	CAT2 (mg/ml)	EEC (0%), PEGDA (20%)	EEC (20%), PEGDA (20%)	EEC (40%), PEGDA (20%)	EEC (0%)	EEC (20%)	EEC (40%)
0	0	>600	>600	>600	>600	>600	>600
0	2	>600	>600	>600	>600	>600	>600
0	6	>600	>600	>600	>600	>600	>600
0	17	>600	>600	>600	>600	>600	>600
0	50	>600	>600	>600	>600	>600	>600
10	0	120	60	90	>600	>600	>600
10	1	120	60	90	>600	>600	>600
10	6	90	60	60	>600	>600	>600
10	17	60	60	60	>600	>600	>600
10	50	360	90	60	>600	>600	>600

Exposed at 365 nm

CQ (mg/ml)	CAT2 (mg/ml)	EEC (0%), PEGDA (20%)	EEC (20%), PEGDA (20%)	EEC (40%), PEGDA (20%)	EEC (0%)	EEC (20%)	EEC (40%)
0	0	>600	>600	>600	>600	>600	>600
0	1	>600	>600	>600	>600	>600	420
0	6	180	180	180	>600	360	240
0	17	120	120	120	>600	300	240
0	50	120	120	60	>600	240	180
10	0	>600	>600	>600	>600	>600	>600
10	1	>600	>600	300	>600	>600	420
10	6	240	180	120	>600	420	300
10	17	120	120	60	>600	360	240
10	50	120	120	60	>600	300	180

Table 1. Time to gelation (seconds) as a function of CAT2 and EEC concentration, with or without the presence of 20% v/v PEGDA. Samples were examined for up to 600 s. Samples remaining liquid at that time point are shown as ">600". EEC and PEGDA concentrations are specified as % v/v.
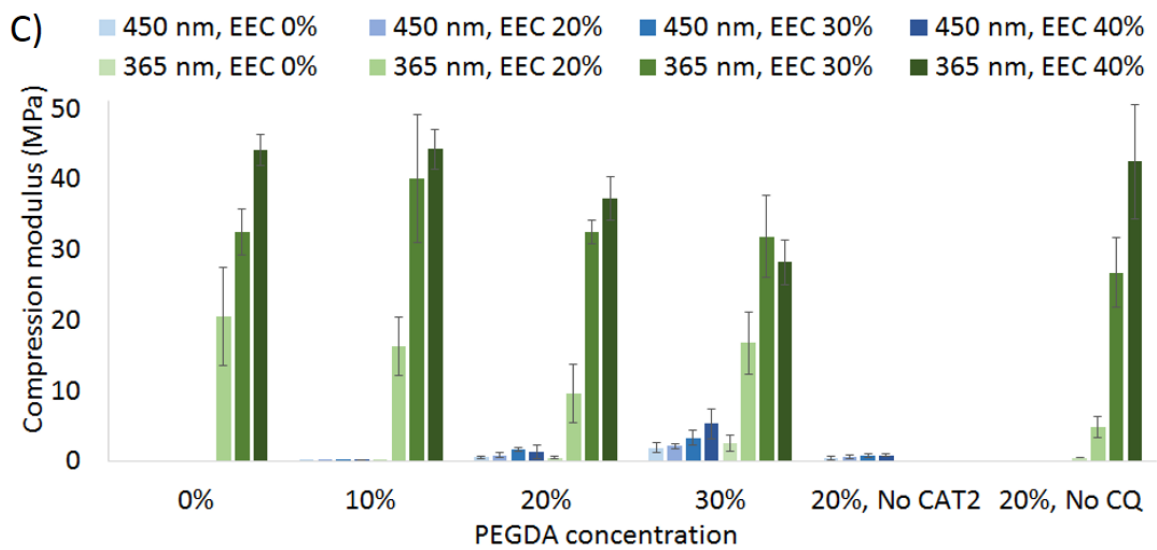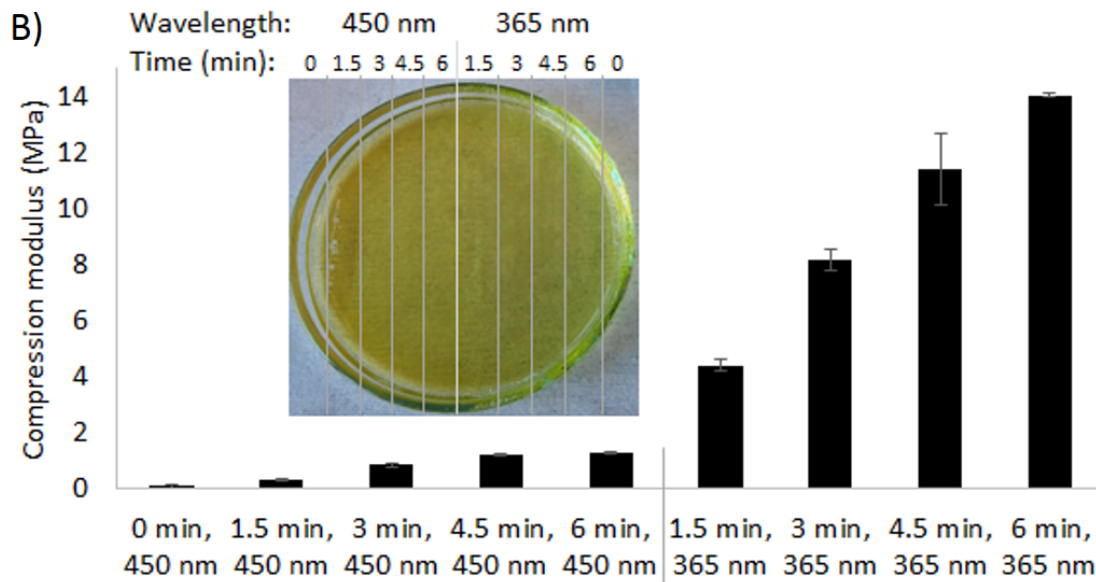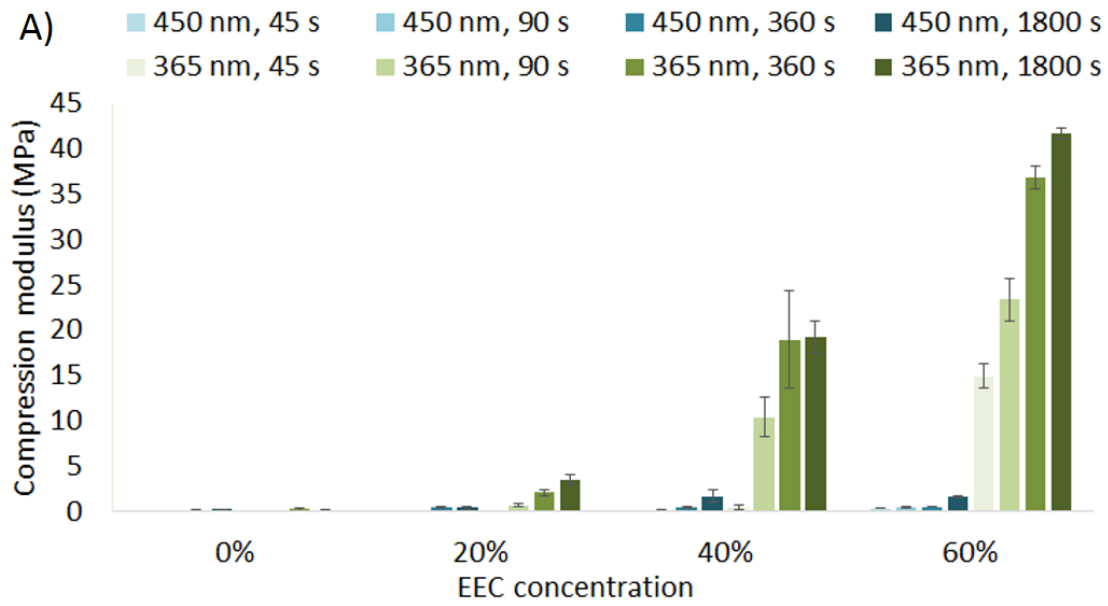
The compression modulus of both materials is strongly dependent on the exposure dose and the amount of EEC (Figure 2A). Samples with varying concentrations of EEC (0 - 60% v/v) and fixed concentrations of PEGDA (20% v/v), CAT2 (15 mg/ml), and CQ (10 mg/ml) were

exposed at 450 nm or 365 nm for different time periods. The epoxy-containing samples cured with 365 nm light were significantly stiffer than identical sample compositions cured at 450 nm, where most likely only the PEGDA cured. Moreover, the stiffness increased strongly with illumination time up to 360 s. A much longer exposure of 1800 s only lead to slightly stiffer materials, indicating that the samples are close to fully cured at 360 s. As expected, higher epoxy concentrations resulted in larger compression moduli. For samples without epoxy the stiffness resulting from exposure at 450 nm or 365 nm was almost the same, supporting that both CQ and CAT2 can initiate crosslinking of PEGDA.

A functionally graded material resulted from exposing a solution at different positions in a petri dish using increasing exposure times from 0 to 6 minutes of first 450 nm and then 365 nm light (Figure 2B insert). The solution consisted of 40% v/v EEC, 20% v/v PEGDA, and both the CQ and CAT2 photoinitiators. Examination of the compression modulus showed that a graded material was made where the compression modulus increases with exposure time at both light wavelengths (Figure 2B). As seen in the previous experiments the sample areas illuminated with blue light were much softer than UV exposed areas, where the epoxy crosslinked. The mechanical measurements showed that simple variation of the actinic light wavelength and dose resulted in a material with more than 100-fold variation in elasticity. The dose dependence at each wavelength is consistent with reports in the literature, as increased initiation rates lead to higher degrees of monomer conversion. [29,30]

The organic solvent as well as remaining monomers and photoinitiators must be removed after polymerization to make the materials compatible with living cells. This was accomplished through first a solvent exchange to ethanol and a second exchange to water. The gradual

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exchange of compounds could visually be monitored by a decreasing intensity of the yellow color of the CQ photoinitiator in the gels (data not shown). The influence of solvent exchange on the mechanical properties was investigated using variable PEGDA and EEC concentrations exposed to 450 nm or 365 nm light for a fixed time (360 s) followed by step-wise exchange of the solvent to water. Analysis of the compression modulus showed that the epoxy-containing samples exposed with 365 nm light were op to 400 times stiffer than identical samples exposed with blue light (Figure 2C). Moreover, the epoxy samples became softer with increasing PEGDA concentration, whereas samples exposed with 450 nm light became harder. We speculate that for samples with epoxy exposed to 365 nm light, the additional PEGDA makes the material softer as there is a lower total percentage of epoxy compared to PEGDA in these samples. For samples exposed to 450 nm light the uncured epoxy is extracted during solvent exchange, leaving only crosslinked PEGDA in the gel. It was observed that the modulus increases with the amount of PEGDA, most likely because higher amount of PEGDA gives a more crosslinked gel. The compression moduli of the samples were also measured before solvent exchange, which showed in general softer material as the solvent was still present (Figure S1, Supporting Information). As expected, the cure time was shorter for samples containing higher amounts of monomer (Table S3, Supporting Information).

A) Compression modulus (MPa) vs EEC concentration, with legend: 450 nm, 45 s; 450 nm, 90 s; 450 nm, 360 s; 450 nm, 1800 s; 365 nm, 45 s; 365 nm, 90 s; 365 nm, 360 s; 365 nm, 1800 s.

B) Compression modulus (MPa) vs time and wavelength. Wavelength: 450 nm, 365 nm. Time (min): 0 1.5 3 4.5 6 1.5 3 4.5 6 0. Categories: 0 min, 450 nm; 1.5 min, 450 nm; 3 min, 450 nm; 4.5 min, 450 nm; 6 min, 450 nm; 1.5 min, 365 nm; 3 min, 365 nm; 4.5 min, 365 nm; 6 min, 365 nm.

C) Compression modulus (MPa) vs PEGDA concentration, with legend: 450 nm, EEC 0%; 450 nm, EEC 20%; 450 nm, EEC 30%; 450 nm, EEC 40%; 365 nm, EEC 0%; 365 nm, EEC 20%; 365 nm, EEC 30%; 365 nm, EEC 40%. Categories: 0%, 10%, 20%, 30%, 20%, No CAT2, 20%, No CQ.

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Figure 2. A) Compression modulus as a function of light exposure and epoxy concentration of samples in a 96-well plate. All solutions contained 20% v/v PEGDA as well as CQ and CAT2 photoinitiators. Error bars show the standard deviation (n=3). B) Compression modulus of a solution of 40% v/v EEC, 20% v/v PEGDA, CQ, and CAT2 exposed with gradually increasing doses of either 450 nm or 365 nm light in a petri dish (Ø6 cm). The insert shows a picture of a sample in a petri dish with the gradient of light duration and wavelength indicated. Error bars show the standard deviation of replicate measurements within the dish (n = 3). C) Compression modulus **after** solvent exchange to water as a function of EEC and PEGDA concentration after 360 seconds light exposure of the samples in a 96-well plate. Both photoinitiators are present unless stated otherwise. All concentrations are specified as % v/v. Error bars show the standard deviation (n = 4).

The degree of swelling is important for structural stability and as a measure of the average pore size of the crosslinked polymer networks. Swelling was measured after solvent exchange, and revealed large swelling of samples prepared using low PEGDA concentrations with a decreasing degree of swelling with increasing PEGDA concentration (Figure 3A). This is consistent with literature, as the swelling decreases with the higher density of crosslinks in hydrogels with higher initial PEGDA concentration[31]. Samples containing EEC and exposed with 365 nm light exhibited very low swelling, since the epoxy is hydrophobic (Figure 3B). The degree of swelling for samples with only PEGDA was very similar and was largely independent on the wavelength of the light exposure. The dry weight of the samples exposed with 365 nm light showed an increasing mass with increasing monomer concentration (Figure 3C-D). For samples containing both PEGDA and EEC exposed to 450 nm light, the mass was identical to the mass of the samples without EEC exposed to 365 nm light, again supporting

that the non-cured EEC was completely removed from the cured PEGDA gel during solvent exchange. For samples exposed to 365 nm light, the dry weight increased with either increasing EEC or PEGDA concentration.
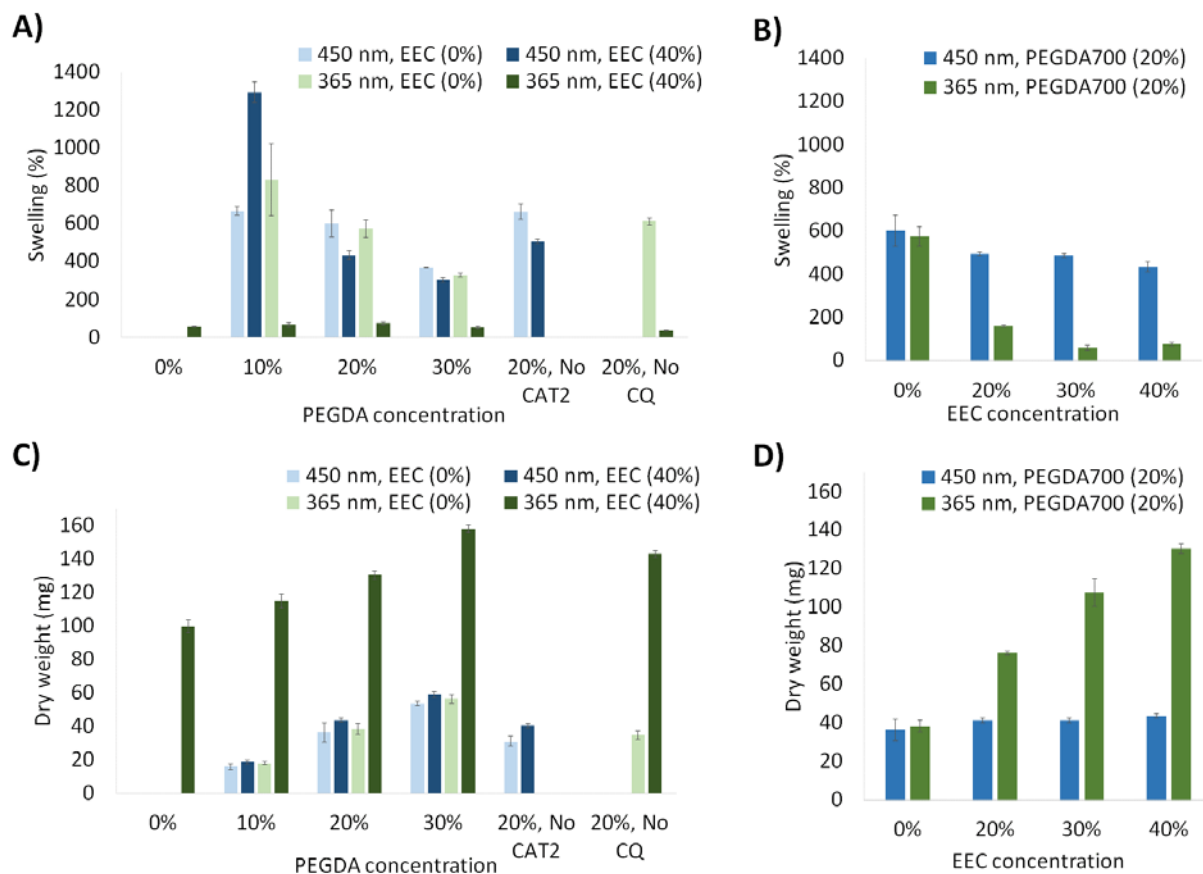
Figure 3. (A+B) Swelling and (C+D) dry weight after solvent exchange as a function of EEC and acrylate concentration and of the presence of the photoinitiators. Both photoinitiators are present unless stated otherwise. Error bars show the standard deviation (n = 4).

Infrared spectrometry (FT-IR in ATR mode) was used to analyze the conversion of the monomer as a function of light exposure (Figure 4). Samples with 20% v/v PEGDA and 40% v/v EEC was exposed to 450 nm or 365 nm light for different times. Exposure to 450 nm light resulted in a decreasing intensity of the peaks from acrylate (810, 1190, 1410 cm^{-1}) [32] with

exposure time (Figure 4A). The peak intensity from the epoxy monomer (790 cm^{-1} and 1165 cm^{-1})[33] did not change with 450 nm light exposure. This supports that only the acrylate is cured at 450 nm. Identical samples exposed to 365 nm showed a rapid decrease in the signal from epoxy at 790 cm^{-1} and 1165 cm^{-1} (Figure 4B). Moreover, a peak from the newly formed ether appeared at 1075 cm^{-1} as previously observed. [33] Unfortunately this signal is slightly overlapping with peaks from the EtOH used to clean the samples from residual reagents. The FT-IR results strongly support that both the epoxy and acrylate is converted under 365 nm light. Solutions containing either EEC or PEGDA together with both CQ and CAT2 were exposed to either 365 nm or 450 nm light, respectively (Figure S3, Supporting Information). FT-IR analysis of the resulting samples supported that the epoxy monomer could only be polymerized using 365 nm light, whereas the acrylate monomer was polymerized using either light source.
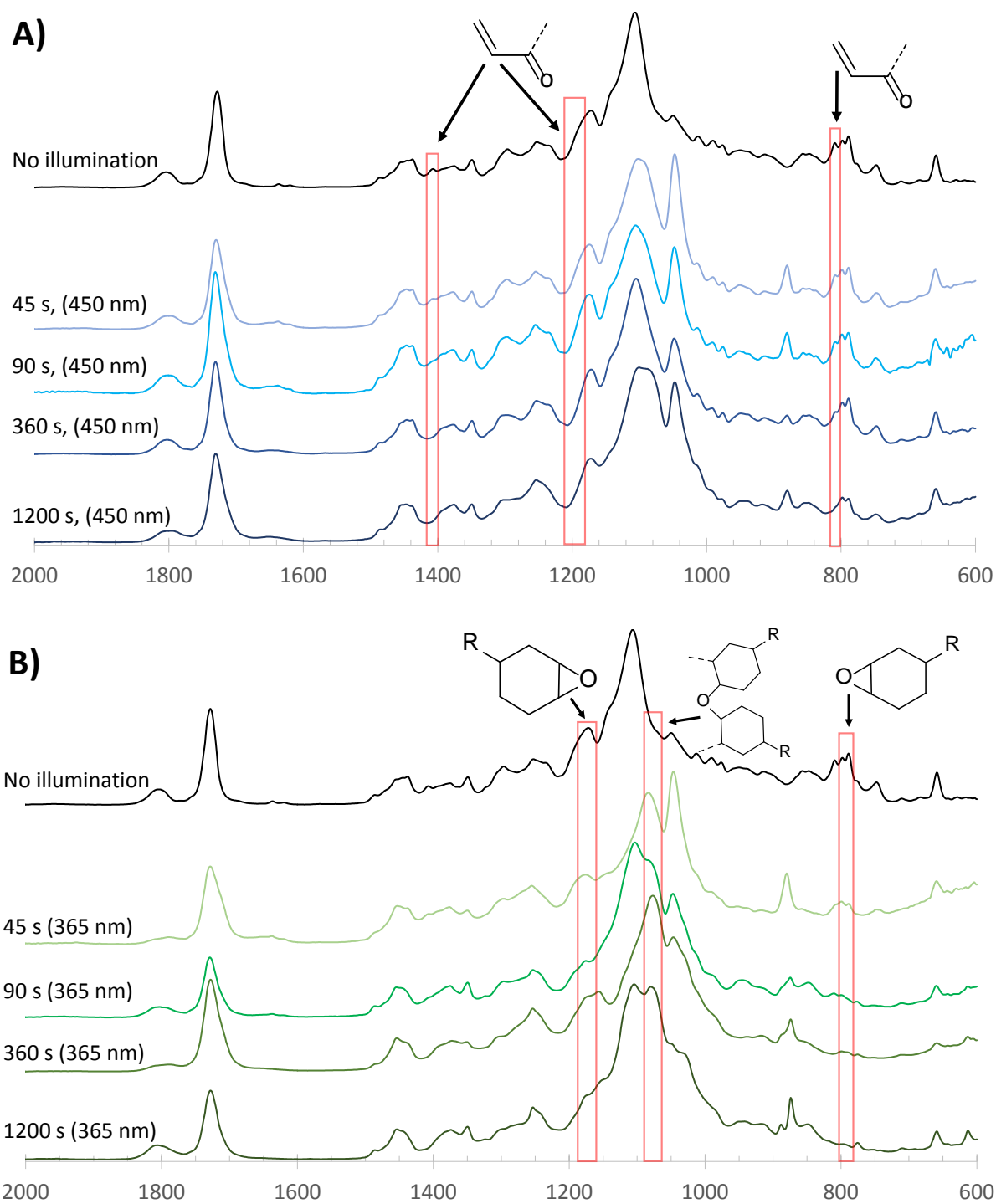
Figure 4. FT-IR of samples of 20% v/v PEGDA and 40% v/v EEC with added CQ and CAT2 photoinitiators exposed for varying times to light with a wavelength of (A) 450 nm or (B) 365 nm.

In conclusion, we have demonstrated how a multi-material can be made using selective photo-polymerization of acrylate and epoxy monomers. This is the first example of selective polymerization of an acrylate by blue light together with an epoxy monomer. We showed that curing rate, stiffness, and swelling can be controlled by varying the monomer composition, photoinitiators, and illumination conditions. The use of dual color stereolithography will allow for 3D printing of multi-material structure with spatially freely tunable mechanical properties, thereby producing unique materials for many application areas including tissue engineering.

Experimental Section
Materials:

Poly(ethylene glycol) diacrylate 700 g/mol (PEGDA), 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC), Diethylene glycol diethyl ether (DGDE), Triarylsulfonium hexafluoroantimonate salts, mixed (CAT2), (4-Methylthiophenyl)methyl phenyl sulfonium triflate (CAT4), 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (CAT6), Camphorquinone (CQ), Trimethylolpropane triglycidyl ether (TTC), Poly(ethylene glycol) diglycidyl ether 6000 g/mol (PEGDE), and Glycidyl methacrylate (GMA) were purchased from Sigma-Aldrich (St. Louis, MO). All water used was from a Millipore MilliQ purification system (Boston, MA). Polypropylene 96 well microplates were bought from Greiner-bio.

Curing of monomer:

Solutions consisted of acrylate and epoxy monomers together with photoinitiator(s) dissolved in DGDE in various concentration (Figure 1 and Table 1). 100 µl solution was pipetted into 96 well polypropylene (PP) well plates and exposed with either blue light (450 nm LED, 10 mW/cm^2, LightCrafter 4500, Texas Instrument) or UV light (365 nm filtered Hg lamp, 4

mW/cm^2, MA4 mask aligner, Karl Süss). The spectra of the light sources are shown in Figure 1. The time to gelation is the time it takes for the liquid resin to solidify. This parameter was judged by visual observation of whether the sample volumes could flow by gently swirling the sample.

Solvent exchange:

In some of the experiments, the cured samples were purified by solvent exchange through immersing the sample in 96 % EtOH for 2 days, with exchange of the EtOH two times, followed by immersion in H$_2$O for 2 days with exchange of H$_2$O two times.

Swelling and dry weight measurements:

Eppendorf tubes (2 ml; polypropylene) were weighed before addition of 200 µl monomer solutions. After exposure to 450 nm or 365 nm light for 360 seconds, the samples were purified by solvent exchange, followed by removal of any remaining water and weighing of the samples. The samples were left to dry for 5 days and then weighed again. Swelling in % was calculated according to equation (1) from the increase in weight for the swollen sample (W$_S$) over the dry sample (W$_D$).

$$Swelling = 100\% * \frac{W_S - W_D}{W_D} \tag{1}$$

Compression:

Mechanical properties of the gels were examined using a Stable Micro Systems Texture Analyzer (Texture Technologies, Scarsdale, NY). A 2 mm diameter stainless steel cylinder probe was pressed into the gels located in 96-well plates with a speed of 0.1 mm/s and the required position-dependent force was recorded. Values of the compression modulus of elasticity were calculated as a ratio of the stress and strain in the linear region of the curves from 0.1 mm to 0.3 mm (Figure S2, Supporting Information). After solvent exchange new

heights were calculated from the swelling analyses. The corrected compression moduli are reported in figure S1B.

Fourier transform infrared spectroscopy (FT-IR):

FT-IR spectra in attenuated total reflectance (ATR) mode was recorded on a Perkin Elmer Spectrum 100 instrument. The samples were slightly compressed on the ATR crystal to get a good signal. For many of the samples a small amount of uncured material was first removed, followed by brief rinsing with EtOH and drying with tissue paper before measurement.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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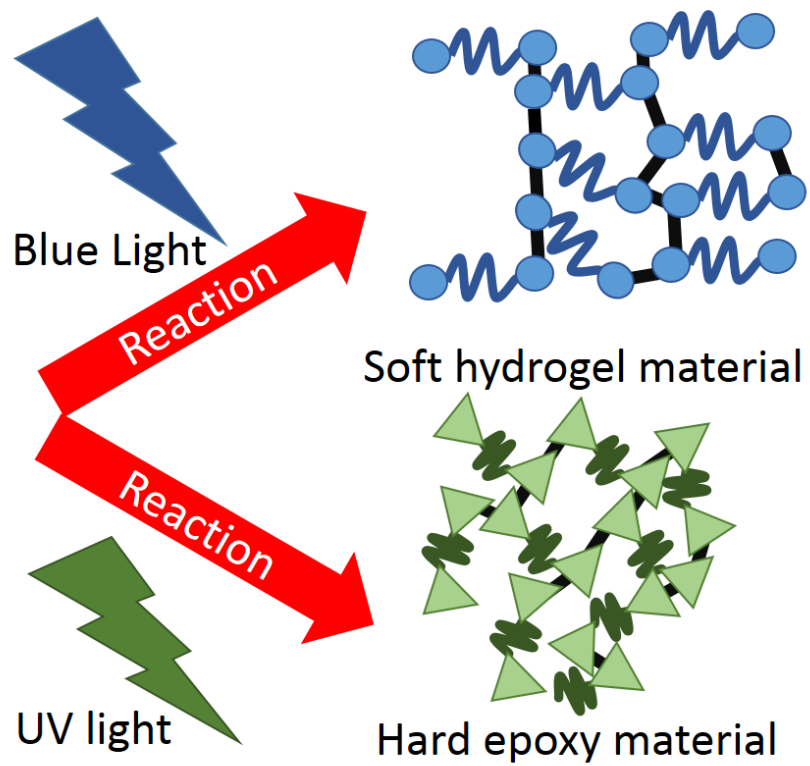
The table of contents entry:

Multi-material structures made from a poly(ethylene glycol) diacrylate and epoxy resin solution becomes selectively either a soft hydrogel or a stiff polymer when exposed to blue or UV light. Materials with graded mechanical properties spanning >2 orders of magnitude result from varying the wavelength and time of the exposure.

Keyword: UV and visible curing; epoxy and acrylate monomers; functionally graded materials; multi-material hydrogels; tissue engineering scaffolds

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Multi-Material Hydrogel with Widely Tunable Elasticity by Selective Photo-Polymerization of PEG Diacrylate and Epoxy Monomers

ToC figure

Blue Light

Reaction

Soft hydrogel material

UV light

Reaction

Hard epoxy material

ToC figure

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Supporting Information

Functionally Graded Multi-Material Hydrogel with Variable Elasticity by Selectively Photo-Polymerization of PEG Diacrylate and Epoxy Monomer

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Time to gelation studies as a function of different cationic photoinitiators (CAT2, 4 and 6) and epoxy monomers after exposure with 365 nm light show a) that CAT2 is the most efficient photoinitiator, and b) that EEC has the fastest cure speed of the epoxy monomers (Table S1).

	CAT2	CAT4	CAT6
PEGDA (20%)	10	>600	>600
EEC (50%)	120	>600	>600
EEC (20%)	120	>600	>600
GMA (20%)	600	>600	>600
TTE (50%)	600	>600	>600
TTE (20%)	>600	>600	>600
PEGDE (50%)	>600	>600	>600
PEGDE (20%)	>600	>600	>600
Only solvent	>600	>600	>600

Table S1. Time to gelation (seconds) as a function of type of photoinitiator (CAT2, 4, or 6) and epoxy monomer. Samples were examined for up to 600 s. Samples remaining liquid at that time point are shown as ">600". All concentrations are specified as % v/v.

Time to gelation studies as a function of PEGDA and CQ concentrations show that at least 10% v/v PEGDA is required for gelation within 10 min, and that increased CQ concentrations lead to shorter cure times (Table S2).

450 nm	PEGDA (5%)	PEGDA (10%)	PEGDA (15%)	PEGDA (20%)
CQ (0 mg/ml)	>600	>600	>600	>600
CQ (5 mg/ml)	>600	600	240	240
CQ (7.5 mg/ml)	>600	600	240	90
CQ (10 mg/ml)	>600	600	90	90
CQ (15 mg/ml)	>600	240	90	90
CQ (20 mg/ml)	>600	600	90	90

Table S2. Time to gelation (seconds) as a function of CQ and PEGDA concentrations using 450 nm illumination. Samples were examined for up to 600 s. Samples remaining liquid at that time point are shown as ">600". PEGDA concentrations are specified as % v/v.

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Time to gelation studies as a function of EEC and acrylate concentration show that the cure speed increases with EEC and PEGDA concentration (Table S3).

450 nm	EEC (0%)	EEC (20%)	EEC (30%)	EEC (40%)
PEGDA (0%)	>600	>600	>600	>600
PEGDA (10%)	270	240	120	75
PEGDA (20%)	180	105	60	30
PEGDA (30%)	180	105	30	30
PEGDA (20%), No CAT2	240	135	90	60
PEGDA (20%), No CQ	>600	>600	>600	>600
PEGDA (20%), No CAT2 and CQ	>600	>600	>600	>600

365 nm	EEC (0%)	EEC (20%)	EEC (30%)	EEC (40%)
PEGDA (0%)		345	300	240
PEGDA (10%)	360	330	240	172.5
PEGDA (20%)	360	210	127.5	75
PEGDA (30%)	285	187.5	60	40
PEGDA (20%), No CAT2	>600	>600	>600	>600
PEGDA (20%), No CQ	360	255	165	90
PEGDA (20%), No CAT2 and CQ	>600	>600	>600	>600

Table S3. Time to gelation (seconds) as a function of EEC and acrylate concentrations, as well as the illumination wavelength and the presence of the two photoinitiators. Both photoinitiators were present unless stated otherwise. Samples were examined for up to 600 s. Samples remaining liquid at that time point are shown as ">600". All concentrations are specified as % v/v.

Compression modulus was also measured before solvent exchange (Figure S1). The samples were in general softer than the samples after solvent exchange. Especially the samples containing 20% EEC and exposed to 365 nm light were much softer than the samples after solvent exchange. This could be explained by the inability of alcohol and water to replace the volume occupied by the DGDE solvent, leading to sample shrinkage during the solvent exchange. The final samples contain more epoxy and have higher compression moduli.
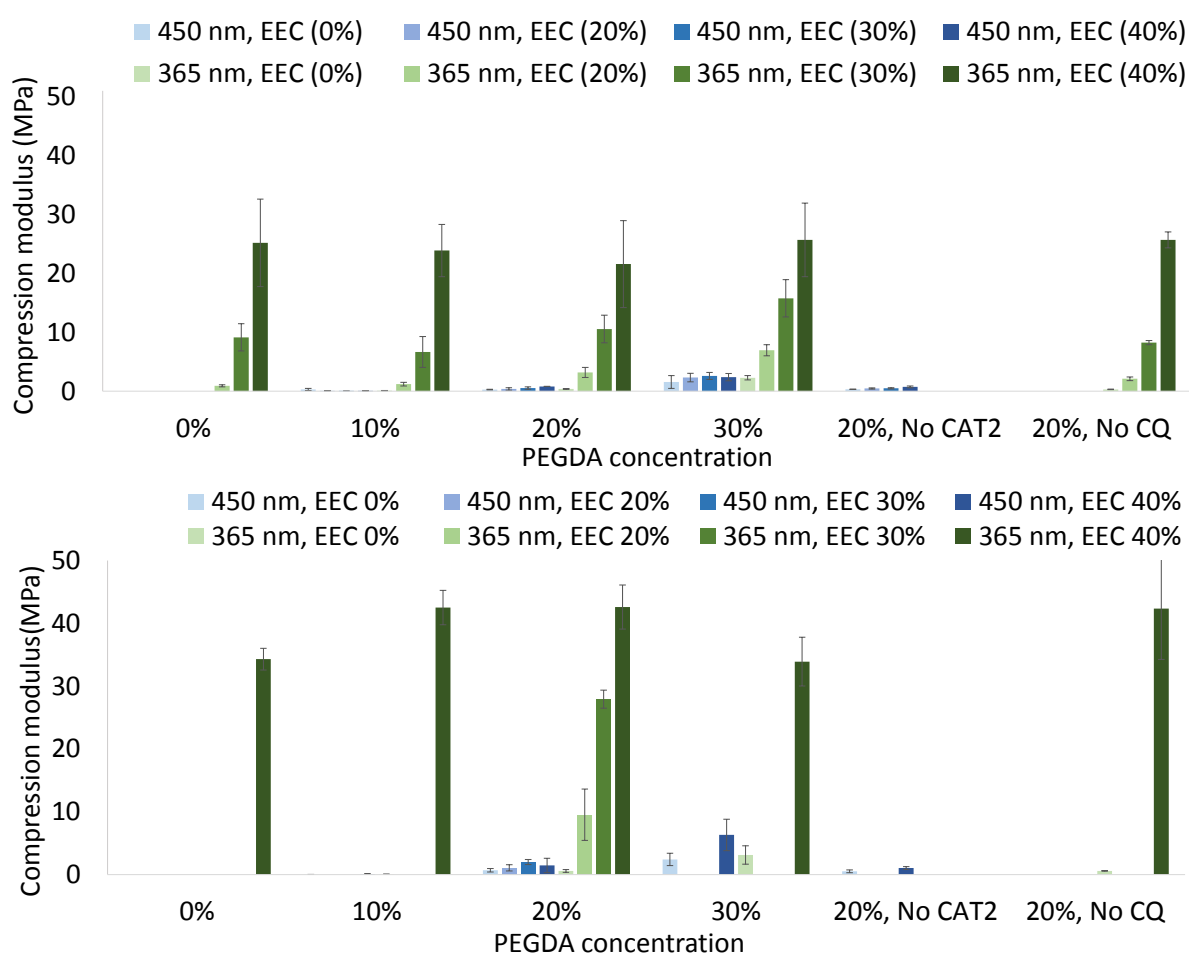

Figure S1. A) Compression modulus before solvent exchange. B) Compression modulus after solvent exchange and with calculated height of the samples from swelling measurements. All samples contained CQ (10 mg/ml) and CAT2 (15 mg/ml) if not indicated otherwise and were illuminated for 360 s using the specified wavelength of light. All concentrations are specified as % v/v.
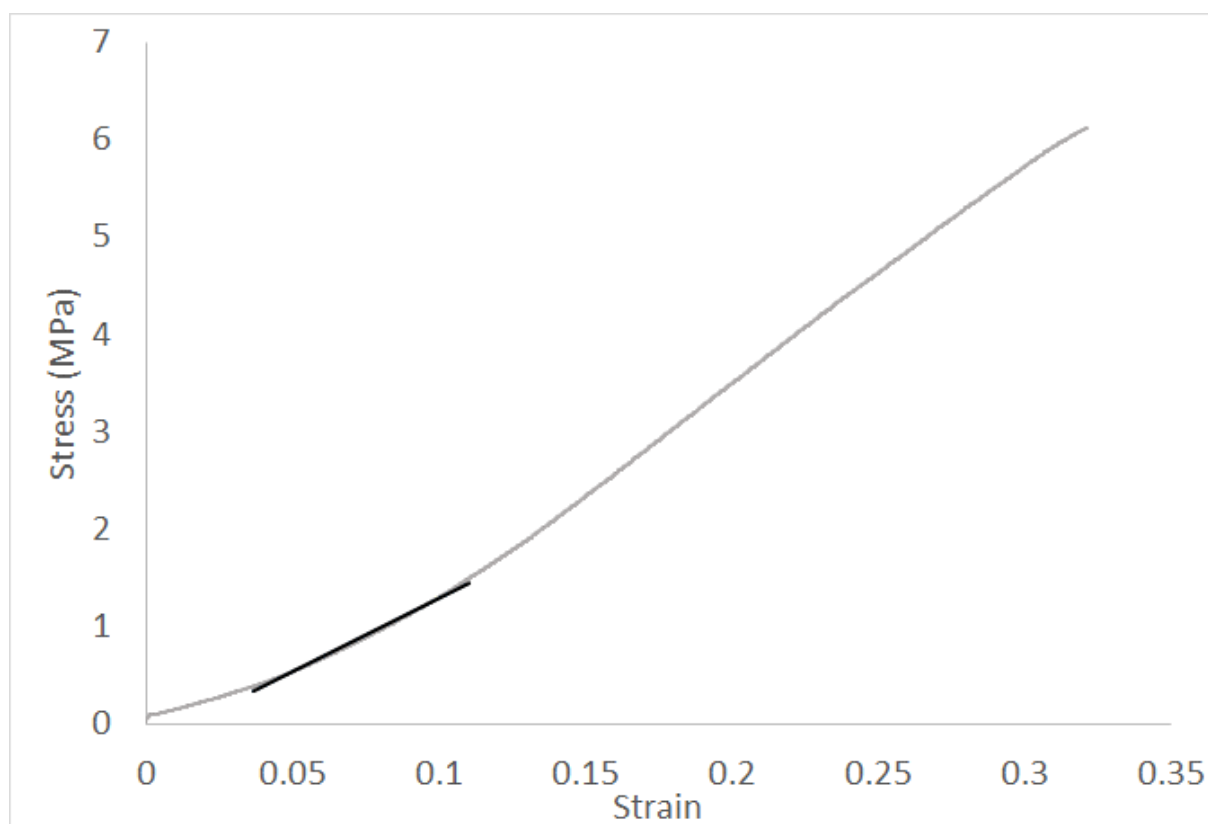
Figure S2. Typical stress/strain curve where the ratio of the compressive stress to the compressive strain in the nearly linear region of the curves from strains of 0.037 to 0.11 was used to calculate the compression modulus for all the samples.

Samples containing either PEGDA (20% v/v) or EEC (40% v/v) in the presence of CAT2 and CQ were exposed at either 365 nm or 450 nm. The resulting samples were analyzed by FT-IR (Figure S3). The EEC (epoxy monomer) peaks at 790 cm^{-1} and 1165 cm^{-1} only disappears when the samples are exposed to 365 nm light. Concurrently, a new peak appears at 1075 cm^{-1} corresponding to the ether group formed during the polymerization. This supports that the epoxy monomer only polymerizes under 365 nm light. The PEGDA (acrylate monomer) exhibits three specific acrylate peaks (810, 1190, 1410 cm^{-1}) that all disappear when exposed to either 365 nm or 450 nm light.
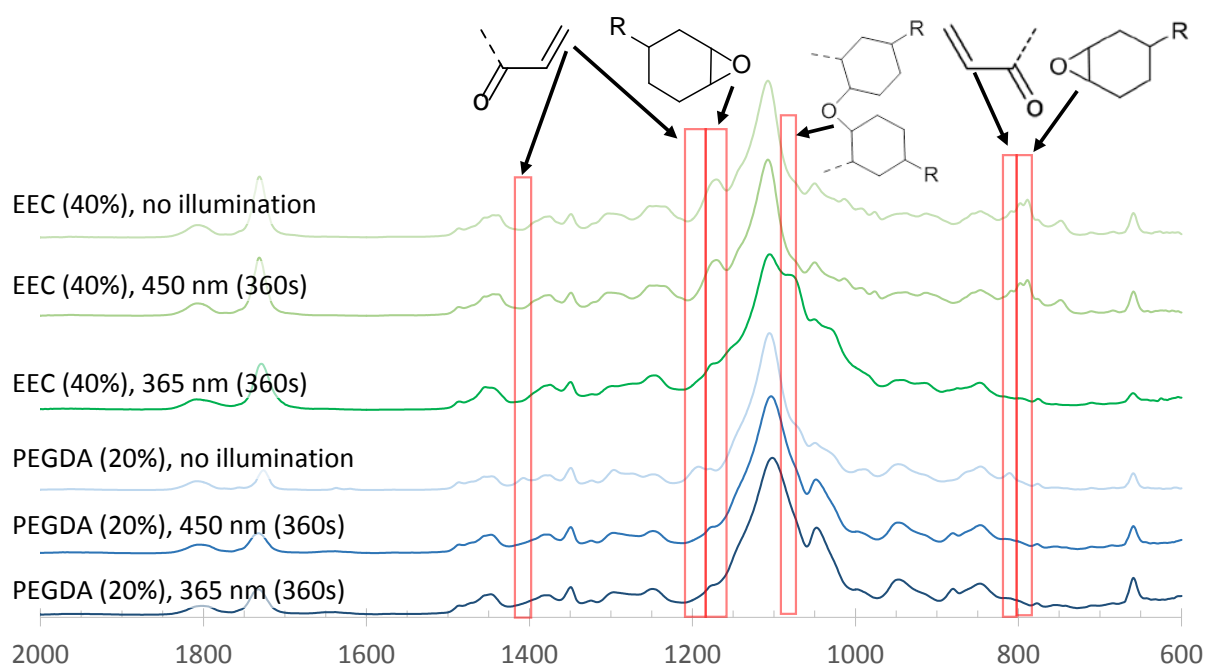
Figure S3. FT-IR of samples of 20% v/v PEGDA or with 40% v/v EEC, both with CAT2 and CQ, as a function of "no illumination", "450 nm" or "365 nm" light.