Fabrication of Functional Biomaterial Microstructures by *In situ* Photopolymerization and Photodegradation

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Supplemental Information

The following list of ordinary differential equations were solved simultaneously in the model:

$$PI \xrightarrow{h\nu} R^* \quad \text{(E1)}$$

$$R^* + M \rightarrow RM^* \quad \text{(E2)}$$

$$RM_n^* + M \xrightarrow{k_M} RM_{n+1}^* \quad \text{(E3)}$$

$$RM_n^* + RM_m^* \xrightarrow{k_T} RM_nM_m \quad \text{(E4)}$$

$$RM_n^* + O_2 \xrightarrow{k_{O2}} RM_nO \quad \text{(E5)}$$

Where PI in the photoinitiator, R* is the radical formation, M is the monomer unit, and subscripts

n and m represent the number of repeat units. Equation 1 accounts for the consumption or double bond conversion of the monomer species [M] that drives the polymerization reaction. Equation 2 describes the photoinitiator decomposition which is dependent on the UV light intensity [I] (measured using a radiometer) and the sample depth. The sample depth is assumed to be negligible because all features formed were under 100 μm in depth. The conversion efficiency is indicated by the quantum yield. The molar absorptivity of protons (ε) depends on the initiator used as well as the temperature and wavelength. To convert [I] into moles of photons per unit volume the light wavelength (λ), Avogadro's

number (N_A), Plank's constant (h), and speed of light (c) are used. The polymerization reaction is inhibited by oxygen which is consumed by scavenging radicals (Equation 3). For the radical rate terms, complex multispecies termination mechanisms are ignored and all radical species are lumped into a single term, [R]. The balance of radical species is different in the two regions defined. In region 1 radicals are formed by exposure to UV light and can be consumed in either a termination or oxygen inhibition reaction (Equation 4). In region 2 radicals are not being formed only consumed by either monomer termination or oxygen inhibition (Equation 5). The double bond conversion factor, ξ, is used to evaluate hydrogel polymerization or gelation. Full gelation of the hydrogel solution occurs at a double bond conversion fraction of 0.01 or higher.[1,2]

Table S1. Variables used in COSMOL model.

Variable	Definition	Value	Source
r_1	radius of first region	12.5 μm	measured
D_{O2}	diffusion of oxygen through particle	1 x 10^{-10} m^2/s	[3]
D_M	diffusion of monomer into surrounding solution	1 x 10^{-10} m^2/s	[1]
D_{PI}	diffusion of photoinitiator into surrounding solution	2 x 10^{-10} m^2/s	[1]
D_R	diffusion of radical species into surrounding solution	1 x 10^{-10} m^2/s	[1]
k_{O2}	oxygen inhibition consumption rate constant	2 x 10^5 $m^3/(s\ mol)$	[2]

k_M	monomer conversation rate constant	100 $m^3/(s\ mol)$	[1]
k_T	termination rate constant rate constant	2500 $m^3/(s\ mol)$	[1]
φ	quantum yield	0.60	[1]
λ	wavelength	365 nm	lens filter
ε	molar absorptivity of protons at 365 nm	21.8 m^2/mol	[4]
[I]	UV light intensity	200 mW/cm^2	measured
$[M_0]$	initial concentration of monomer	320 mol/m^3	measured
$[PI_0]$	initial concentration of photoinitiator	183.7 mol/m^3	measured
$[O_{20}]$	initial concentration of oxygen	0.50 mol/m^3	measured

Table S2: Light intensities reported in mW cm^{-2} for objectives and wavelengths used.

	365 nm	405 nm
20x	407	355
40x	383	321

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