

## Supporting Information

### 3D printing hydrogel network regulation based on macroinitiator induced rapid photoATRP

Menghan Si,<sup>a#</sup> Mengjie Zhou,<sup>a#</sup> Zhang Wenjie,<sup>a</sup> Ge Shi,<sup>a</sup> Yanjie He,<sup>a</sup> Xiaoguang Qiao,<sup>a,b\*</sup> Weihua Fan,<sup>a\*</sup> Xinchang Pang<sup>a,c\*</sup>

<sup>a</sup> Henan Joint International Research Laboratory of Living Polymerizations and Functional Nanomaterials, Henan Key Laboratory of Advanced Nylon Materials and Application, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

<sup>b</sup> College of Materials Engineering, Henan International Joint Laboratory of Rare Earth Composite Materials, Henan Engineering Technology Research Center for Fiber Preparation and Modification, Henan University of Engineering, Zhengzhou 451191, China

<sup>c</sup> School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471023, PR China

\*Corresponding authors

E-mail:joexiaoguang@hotmail.com

fanweihua@zzu.edu.cn

Pangxinchang1980@163.com

## ***Materials***

Hydroxyethyl acrylate (HEA, 96%, Aladdin), 2-Hydroxyethyl methacrylate (HEMA, 96%, Aladdin) were passed over a column of basic alumina prior before using. Poly(ethylene glycol) diacrylate (PEGDA, 600 g mol<sup>-1</sup>, Aladdin), N-Isopropylacrylamide (NIPAM, 98%, Aladdin), N,N'-Methylenebis (acrylamide) (MBA, 99%, Aladdin), Copper(II) bromide (CuBr<sub>2</sub>, 99%, Aladdin), Tris(pyridin-2-ylmethyl)amine (TPMA, >98%, Aladdin), Ethylenediaminetetraacetic acid disodium salt dehydrate (Na<sub>2</sub>EDTA, 98%, Aladdin), 2-Hydroxyethyl 2-bromoisobutyrate (HEBiB, 95%, Bidepharm), o-phenylenediamine (98%, Macklin) were used as received.

## ***Characterization***

The morphology of CDs was observed with transmission electron microscopy (TEM) (JEM-2100). Monomer conversion was measured using <sup>1</sup>H NMR spectroscopy in D<sub>2</sub>O using a Bruker Avance 500 MHz spectrometer at room temperature. Gel permeation chromatography (Agilent 1260 Infinity II system) was used to determine the number average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}$ ) values with two PL gel 10 MIXED-B 300 x 7.5 mm columns, a column temperature of 45°C, an RI detector and N,N-Dimethylformamide (DMF, containing 18 mM) LiBr as an eluent at a flow rate of 1 mL/min. The column system was calibrated with linear poly(methyl methacrylate) standards. UV–Vis characterization was performed on a Thermo Fisher Scientific Evolution 300 UV–Vis spectrophotometer. ATR-FTIR spectroscopy was obtained using a Thermo Nicolet-is5 transform infrared spectrometer. Tensile properties of standard dumbbell-type samples (170 mm × 10 mm × 4 mm) were tested using a universal mechanical tester (CMT5104, Meters Industrial Systems, Inc., USA) with a 200N stress sensor, and the stretching rate was 10 mm/min.

## ***Synthesis of N-doped carbon quantum dots (CDs).***

1g of o-phenylenediamine was first dissolved in 100 mL deionized water. The solution was then transferred to a polytetrafluoroethylene high-pressure reactor and kept for 8 hours under 200°C. After cooling, the solution was filtrated and solid powder of CDs was obtained after freeze-drying.

### ***Synthesis of PHEA macroinitiator***

HEA (9 mL, 86.0 mmol), HEBiB (124.2  $\mu$ L, 0.86 mmol), CuBr<sub>2</sub> (192  $\mu$ L, 10 mg/mL CuBr<sub>2</sub> stock solution in water, 8.6  $\mu$ mol), TPMA (14.94 mg, 51.6  $\mu$ mol), 4.5 mg CDs and 8.81 mL deionized water were mixed and introduced to a 20 mL glass bottle. The bottle was placed in a photo-reactor for 25 min (6W,  $\lambda_{\text{max}}=465$  nm, 2 mW cm<sup>-2</sup>) to achieve high monomer conversion (>97%). PHEA macroinitiators with different degree (Dp=100, 200, 300) of polymerization were synthesized by changing molar ratios of HEA and HEBiB, and the samples were named as PHEA<sub>n</sub>.

### ***Photocuring with PHEA macroinitiator***

An aqueous solution of PEGDA was directly added to the previous glass bottle reactor (one pot) for the synthesis of PHEA macroinitiator. The bottle was then reirradiated in a photo-reactor for 5min. The weight fraction of PEGDA in the system was changed from 4% to 21%, to discuss the effect of fraction of crosslinker (PEGDA) on the formation of hydrogel.

### ***3D printing***

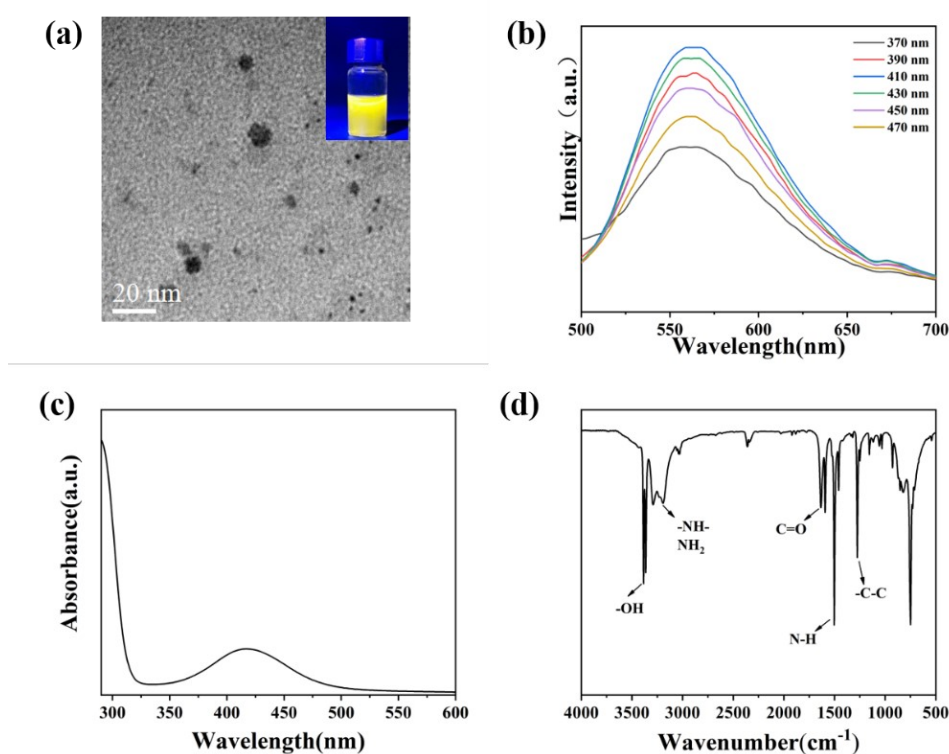
A 3D object was designed using Tinkercad 3D modelling software and the object was exported as an .stl file. The .stl file was opened using Photon Workshop where the Z lift speed and Z retract speed were set to 0.25 mm/s, and the Z lift distance was set to 1.50 mm. The first two bottom layers were printed at 2× the standard layer exposure time to ensure adequate adhesion to the build

stage. The .stl file was then sliced in Photon workshop and copied to a flash drive for use with a masked DLP 3D printer (Anycubic Mono X) with a violet ( $\lambda_{\max} = 405$  nm) light LED array.

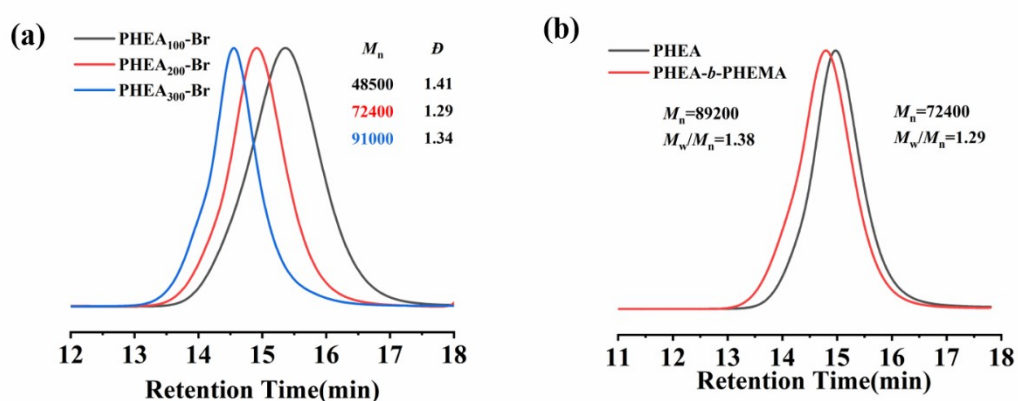
### Swelling Experiments

The hydrogel was immersed in water for 48h, removed and weighed to obtain  $W_s$ , freeze-dried for 24h and weighed to obtain  $W_d$ .

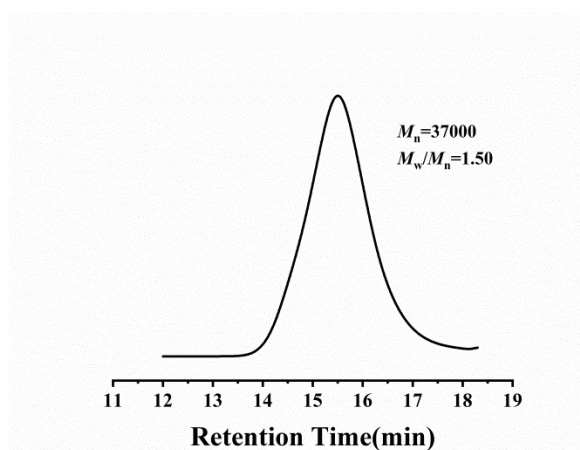
$$\text{Swelling ratio} = \frac{W_s - W_d}{W_d}$$



**Figure S1.** (a) TEM image of CQDs (scale bar = 20 nm), (inset, Digital image of carbon quantum dot aqueous solution at 365 nm UV light). (b) Fluorescence spectra of CDs at different excitation wavelengths. (c) UV-vis absorption spectrum of CQDs. (d) The Fourier-transform infrared (FTIR) spectrum of CQDs with air as background.



**Figure S2.** (a) GPC traces of different target polymerization degree(100, 200, 300) of PHEA-Br. (b) GPC traces of chain extension of PHEA-Br macroinitiator with HEMA.

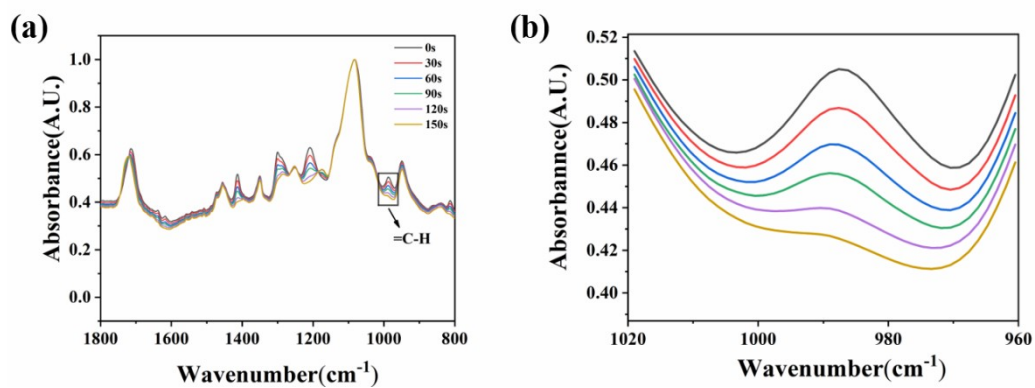


**Figure S3.** GPC traces of PNIPAM macroinitiator.

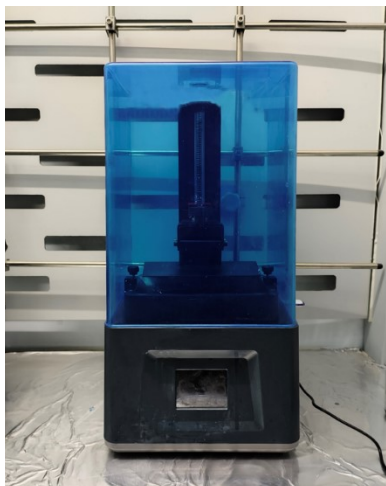
**Table S1.** Characterizations of PHEA-Br synthesized by photo-ATRP mediated polymerization.

Macroinitiator	Conversion(%) <sup>a</sup>	$M_{n,GPC}$ <sup>b</sup>	$\bar{D}$	Repeating units( <sup>1</sup> H NMR) <sup>c</sup>
PHEA <sub>100</sub> -Br	97	48500	1.41	97
PHEA <sub>200</sub> -Br	98	72400	1.29	196
PHEA <sub>300</sub> -Br	98	91000	1.34	294
PNIPAM	77	37000	1.50	77

<sup>a</sup> Monomer conversion were determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> Molecular weight and polydispersity were determined by gel permeation chromatography (GPC), using DMF as eluent.



**Figure S4.** Absorbance of reaction mixtures at different reaction times as measured by ATR-FTIR spectroscopy. (a) spectra from 1800-800 cm<sup>-1</sup> showing the C=O stretching mode, C-N stretching more, and =C-H out of plane bending mode. (b) disappearance of the peak in the range of 970-1005 cm<sup>-1</sup> after increasing irradiation times.

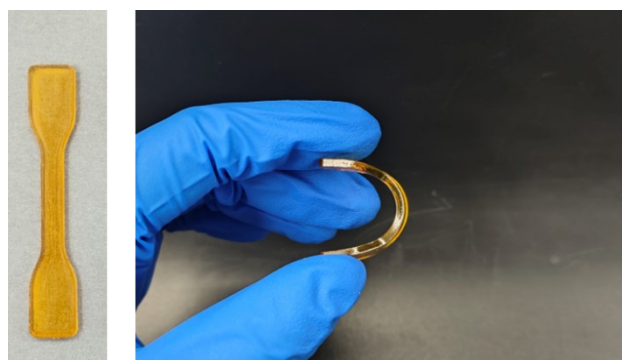


**Figure S5.** The picture of the 3D printer used in this article.

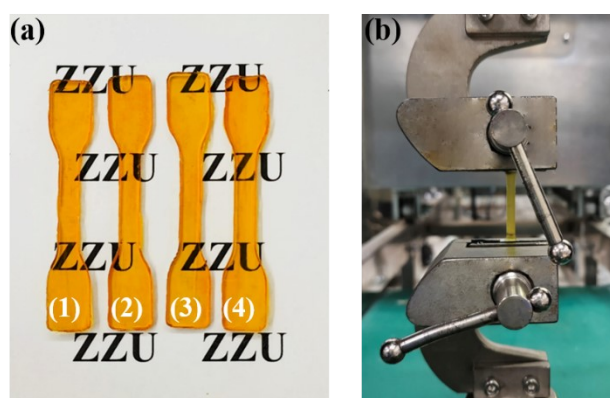
**Table S2.** The hydrogels synthesized under the conditions of different crosslinking agent content and macromolecular initiator with different polymerization degree <sup>a</sup>.

		PHEA <sub>100</sub>	PHEA <sub>200</sub>	PHEA <sub>300</sub>
PEGDA <sub>600</sub>	4%			
	5%			
	6%			
	7%			
	9%			
	12%			
PEGDA <sub>600</sub>	15%			
	18%			
	21%			

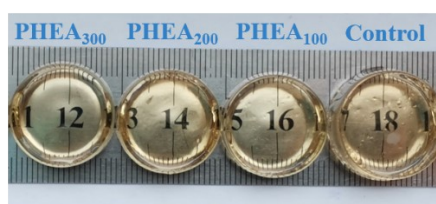
<sup>a</sup> Polymerization conditions: [PEGDA]:[PHEA]=x:(100-x), 50%(w/w) deionized water. Then pour the liquid into the polytetrafluoroethylene mold and shine it under purple light for the same time.



**Figure S7.** (a) Optical images of splines prepared by different systems. (b) Bending picture of dumbbell stretch spline.



**Figure S8.** (a) Dumbbell-shaped samples, Control: [PEGMA]:[PEGDA]:[HEA]:HEBiB:[CuBr<sub>2</sub>]:[TPMA]=90:30:100:1:0.03:0.18 and [PEGMA]:[PEGDA]:[PHEA<sub>n</sub>]=90:30:1 (n=100, 200, 300), from left to right. (b) Picture of the dumbbell spline stretching process.



**Figure S9.** Images of gel prepared by different systems (48 h after full swelling in water). Control: [PEGMA]:[PEGDA]:[HEA]:HEBiB:[CuBr<sub>2</sub>]:[TPMA]=90:30:100:1:0.03:0.18 and [PEGMA]:[PEGDA]:[PHEA<sub>n</sub>]=90:30:1 (n=100, 200, 300).

**Table S3.** Printing parameters of different systems

Macroinitiator	Formulations	Layer thickness	Layer cure
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<b>r</b>			<b>time</b>
<b>PHEA<sub>100</sub></b>		200 $\mu\text{m}$	100 s
<b>PHEA<sub>200</sub></b>	[PEGDA]:[PHEA <sub>n</sub> ]=30:1 (n=100, 200, 300)	250 $\mu\text{m}$	100 s
<b>PHEA<sub>300</sub></b>		300 $\mu\text{m}$	100 s
<b>Control</b>	[PEGDA]:[HEA]:[HEBiB]:[Cu Br <sub>2</sub> ]:[TPMA]=30:100:1:0.03:0.1 8	300 $\mu\text{m}$	80 s
<b>PNIPAM</b>	[PEGDA]:[PNIPAM]=30:1	200 $\mu\text{m}$	120 s



Figure S9. 3D printing resolution comparison for hydrogel when changing the layer cure time (Layer Thickness=300  $\mu\text{m}$ ).