Electronic supplementary information (ESI)

A Highly Efficient Microwave-Assisted Synthesis of an LED-Curable Methacrylated Gelatin for Bio Applications

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Table S1- Formulations and process conditions for the synthesis of GelMAs.

| No.	Code	Methacrylation reagent	Methacrylation reagent concentration	Methacrylation time (min)	MW power (W)	Appearance of GelMA solution after 10 min
1	MW-G-5-1-100	GMA	5 x	1 (30 s×2 cycles)	100	One phase
2	MW-G-5-1-500	GMA	5 x	1 (30 s×2 cycles)	500	One phase
3	MW-G-5-1-1000	GMA	5 x	1 (30 s×2 cycles)	1000	One phase
4	MW-G-5-5-100	GMA	5 x	5 (30 s×10 cycles)	100	One phase
5	MW-G-5-5-500	GMA	5 x	5 (30 s×10 cycles)	500	One phase
6	MW-G-5-5-1000	GMA	5 x	5 (30 s×10 cycles)	1000	Two phases
7	MW-G-5-10-100	GMA	5 x	10 (30 s×20 cycles)	100	One phase
8	MW-G-5-10-500	GMA	5 x	10 (30 s×20 cycles)	500	Two phases
9	MW-G-5-10-1000	GMA	5 x	10 (30 s×20 cycles)	1000	Two phases
10	MW-G-10-1-100	GMA	10 x	1 (30 s×2 cycles)	100	One phase
11	MW-G-10-1-500	GMA	10 x	1 (30 s×2 cycles)	500	One phase
12	MW-G-10-1-1000	GMA	10 x	1 (30 s×2 cycles)	1000	One phase
13	MW-G-10-5-100	GMA	10 x	5 (30 s×10 cycles)	100	One phase
14	MW-G-10-5-500	GMA	10 x	5 (30 s×10 cycles)	500	Two phases
15	MW-G-10-5-1000	GMA	10 x	5 (30 s×10 cycles)	1000	Two phases
16	MW-G-10-10-100	GMA	10 x	10 (30 s×20 cycles)	100	One phase
17	MW-G-10-10-500	GMA	10 x	10 (30 s×20 cycles)	500	Two phases
18	MW-G-10-10-1000	GMA	10 x	10 (30 s×20 cycles)	1000	Two phases
19	MW-M-5-1-100	MA	5 x	1 (30 s×2 cycles)	100	One phase
20	MW-M-5-1-500	MA	5 x	1 (30 s×2 cycles)	500	One phase
21	MW-M-5-1-1000	MA	5 x	1 (30 s×2 cycles)	1000	One phase
22	MW-M-5-5-100	MA	5 x	5 (30 s×10 cycles)	100	One phase
23	MW-M-5-5-500	MA	5 x	5 (30 s×10 cycles)	500	Two phases
24	MW-M-5-5-1000	MA	5 x	5 (30 s×10 cycles)	1000	Two phases
25	MW- M-5-10-100	MA	5 x	10 (30 s×20 cycles)	100	One phase
26	MW-M-5-10-500	MA	5 x	10 (30 s×20 cycles)	500	Two phases
27	MW-M-5-10-1000	MA	5 x	10 (30 s×20 cycles)	1000	Two phases
28	MW-M-10-1-100	MA	10 x	1 (30 s×2 cycles)	100	One phase
29	MW-M-10-1-500	MA	10 x	1 (30 s×2 cycles)	500	One phase
30	MW-M-10-1-1000	MA	10 x	1 (30 s×2 cycles)	1000	Two phases
31	MW-M-10-5-100	MA	10 x	5 (30 s×10 cycles)	100	One phase
32	MW-M-10-5-500	MA	10 x	5 (30 s×10 cycles)	500	Two phases
33	MW-M-10-5-1000	MA	10 x	5 (30 s×10 cycles)	1000	Two phases
34	MW-M-10-10-100	MA	10 x	10 (30 s×20 cycles)	100	One phase
35	MW-M-10-10-500	MA	10 x	10 (30 s×20 cycles)	500	Two phases
36	MW-M-10-10-1000	MA	10 x	10 (30 s×20 cycles)	1000	Two phases
37	C-G-5	GMA	5 x	240	NA*	One phase
38	C-G-10	GMA	10 x	240	NA	One phase
39	C-M-5	MA	5 x	240	NA	One phase
40	C-M-10	MA	10 x	240	NA	One phase

*Not applicable
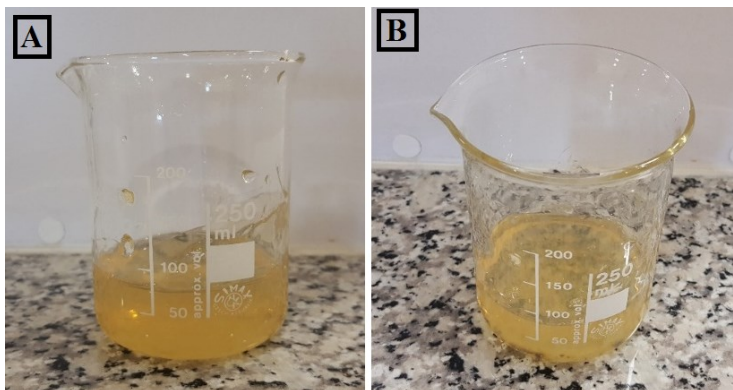
Figure S1- Clear yellowish viscous dialyzed GelMA solutions, A: GMA-GelMA and B: MA-GelMA.
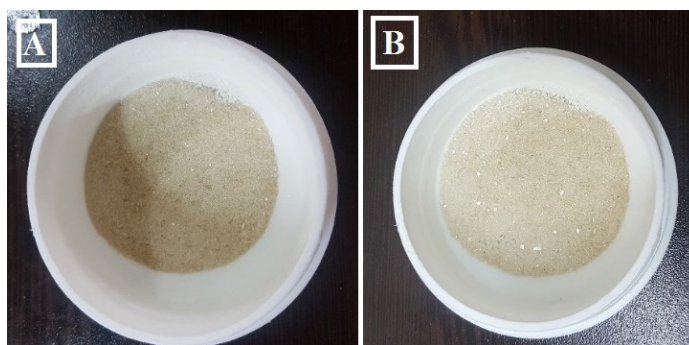

Figure S2- MWA-synthesized GelMA powder after freeze-dry, A: GMA-GelMA and B: MA-GelMA.
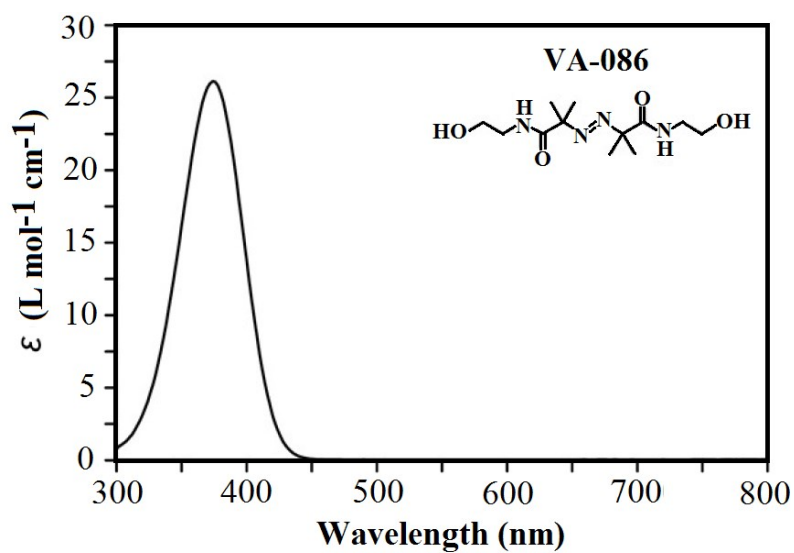
Figure S3- UV-Vis spectrum and molar absorptivity of the VA-086 (ε_{374} = 26.12 L mol^{-1}cm^{-1}) in DMSO solvent (0.1 mol/L).
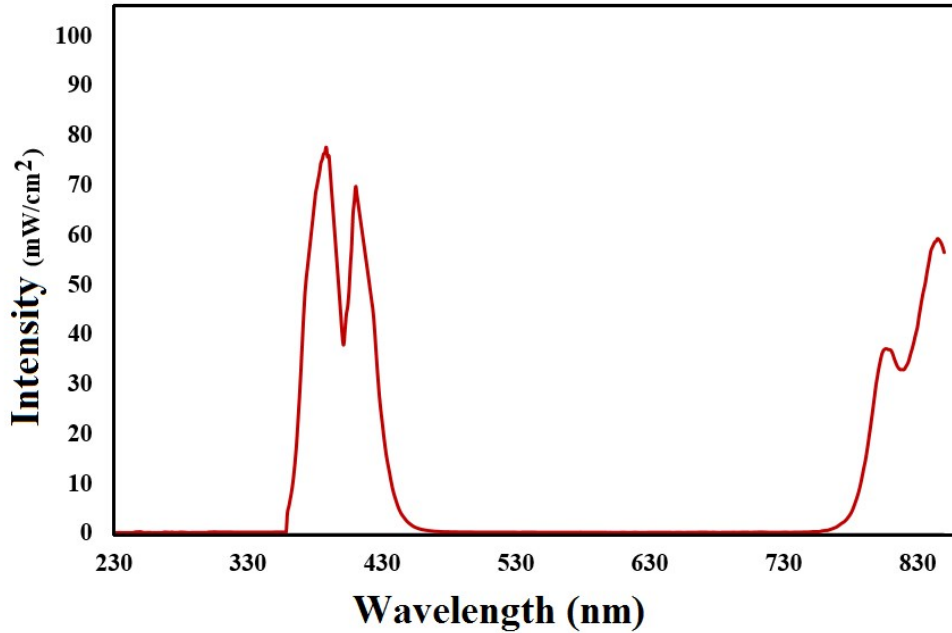
Figure S4- Spectral power distribution of custom-made blue LED light source.

SS1- Dielectric Constant (ε_r) calculation method

ε_r, the ability of materials to absorb and store the electrical potential energy, is defined as the ratio of the electric permeability of the material to the vacuum electric permeability. Also, ε_r can be calculated according to Equation S1.[1]

$$\varepsilon_r = 1 + [1/(3\,V\,K_B\,T\,\varepsilon_0)]\,(\langle\mu^2\rangle - \langle\mu\rangle^2) \qquad\qquad \textbf{Equation S1}$$

V, T, k_B, ε_o, $\langle\mu^2\rangle$ and $\langle\mu\rangle^2$ are volume, temperature (K), Boltzmann's constant, vacuum dielectric constant, the average value of dipole moment squared, and the square of the mean dipole moment values, respectively.

SS2- Dipole moment calculation procedures

The BIOVIA Material Studio 2017 software (2017.1.0.48, Accelrys Inc., USA) was run to simulate the molecular structures and calculate the total energy to estimate the dipole moment (μ) of GMA and MA as the quantum properties. Steps:

1) Drawing the GMA and MA molecular structures in the 3D atomistic media.

2) Optimizing the molecular structure geometrically (Module: Forcite/ task: Geometry Optimization/ Forcefield: COMPASS/ Quality: Ultra-fine).

3) Identifying all of the possible molecule conformers and their total energy (Module: Conformer/ task: conformer Calculation/ Forcefield: COMPASS).

4) Calculating the μ average value of all of these possible conformers.

SS3- Dipole moment calculation of GMA
SS3-1- Geometric optimization of GMA
---- Energy parameters ----
Forcefield   : COMPASS
Charges   : Forcefield assigned
Electrostatic terms:
 Summation method   : Atom based
 Truncation method   : Cubic spline
 Cutoff distance   : 18.5 A
 Spline width   : 1 A
 Buffer width   : 0.5 A
van der Waals terms:
 Summation method   : Atom based
 Truncation method   : Cubic spline
 Cutoff distance   : 18.5 A
 Spline width   : 1 A
 Buffer width   : 0.5 A

Geometry optimization status
Total energy   :   99.420520 kcal/mol
Contributions to total energy (kcal/mol):
 Valence energy (diag. terms) :   80.002
  Bond   :   2.019
  Angle   :   117.209
  Torsion   :   -39.227
  Inversion   :   0.000
 Valence energy (cross terms) :   -8.818
  Stretch-Stretch   :   -0.025
  Stretch-Bend-Stretch   :   -0.737
  Stretch-Torsion-Stretch   :   -0.241

Separated-Stretch-Stretch	:	0.000
Torsion-Stretch	:	-0.831
Bend-Bend	:	-0.498
Torsion-Bend-Bend	:	-6.508
Bend-Torsion-Bend	:	0.022
Non-bond energy	**:**	**28.237**
van der Waals	:	3.212
Electrostatic	:	25.024

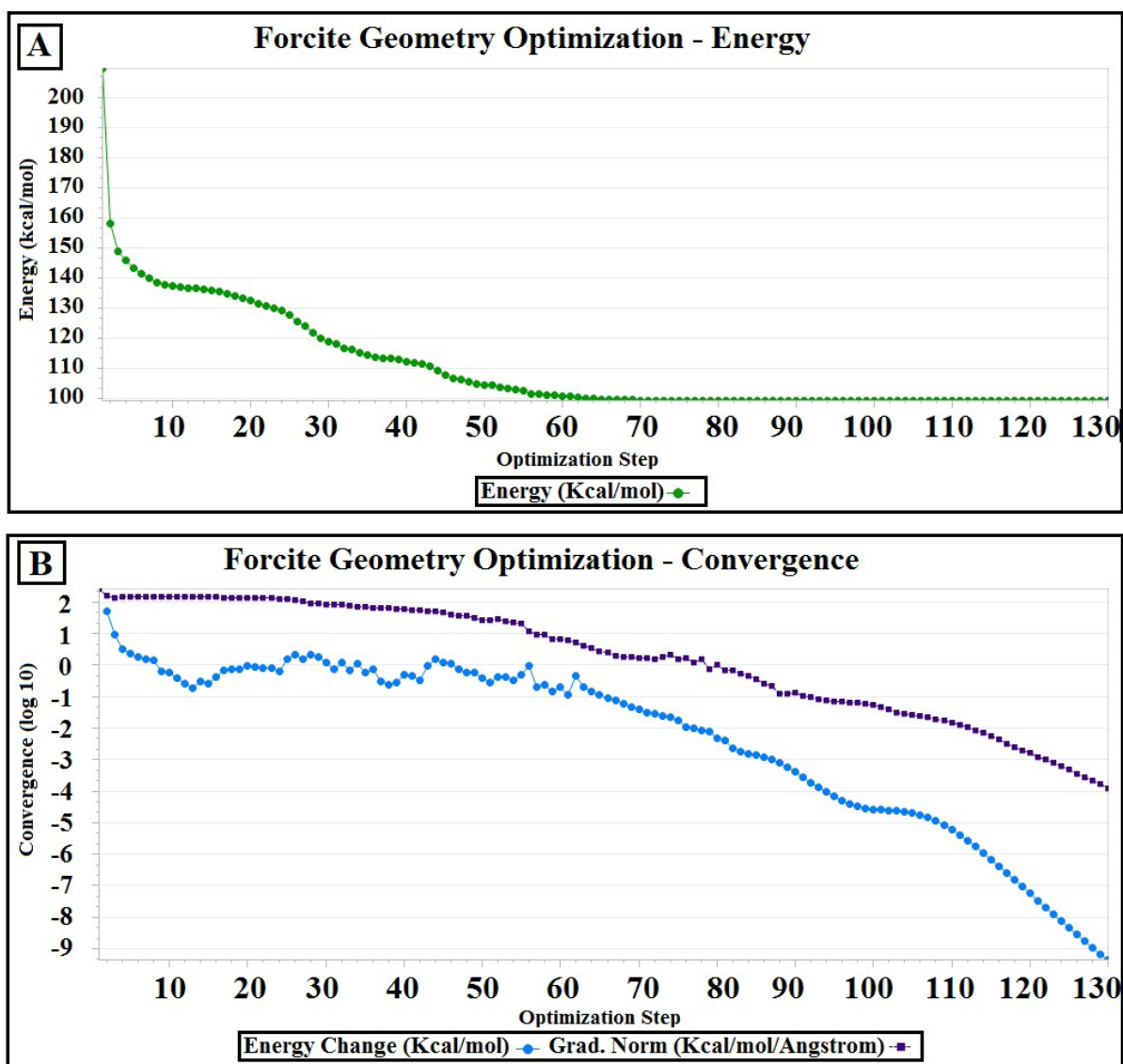rms force : 1.246E-004 kcal/mol/A
max force : 3.678E-004 kcal/mol/A

Figure S5- Forcite geometry optimization A: Energy and B: Convergence of GMA.
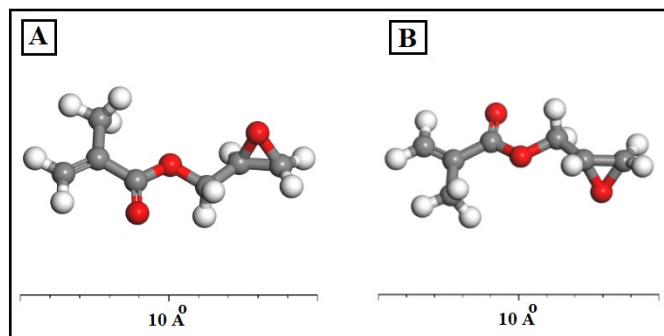
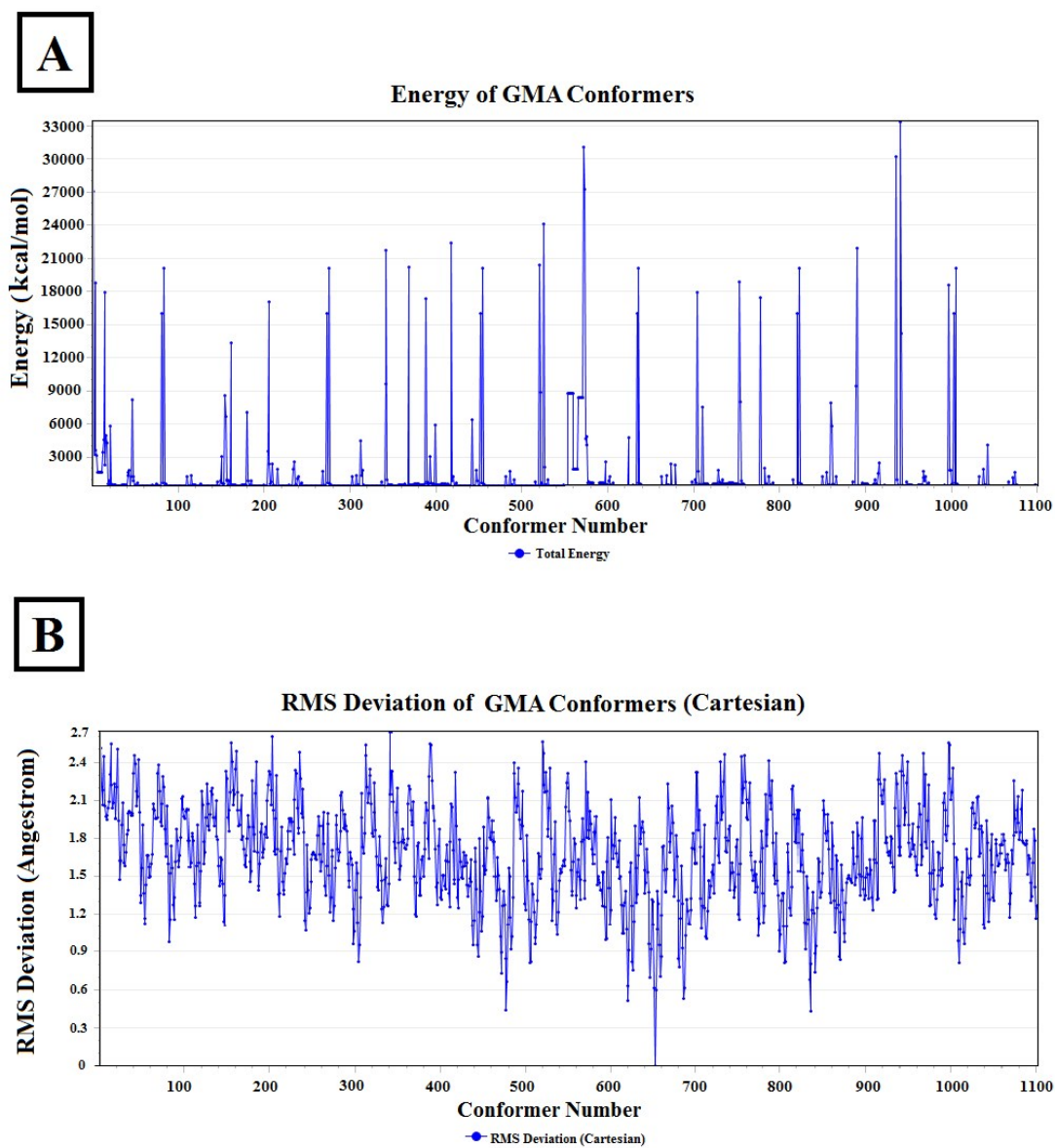**Figure S6- Geometry optimized molecular structures of GMA.**

A

B

Figure S7- A: Energy and B: RMS deviation of all of the possible spatial conformers of GMA.

SS3-2- Conformers and dipole moment of GMA

---- Conformer Search Status ----

Progress: 100%   (1296/1296 conformers)
1296 conformers are sterically allowed.
Number accepted: 85%   (1101 conformers)
Module   : Conformers

                    ---- Search Parameters ----

Search method   : Systematic grid scan
H-bond scale factor   : 0.4
Anchor atom ID   : -1
Perturb from   : Perturb reference
VdW radii scale factor   : 0.4
Vicinal radii scale factor   : 0.4

---- Energy parameters ----
Forcefield   : COMPASS
Charges   : Use current
Electrostatic terms:
  Summation method   : Atom based
  Truncation method   : Cubic spline
  Cutoff distance   : 18.5 A
  Spline width   : 1 A
  Buffer width   : 0.5 A

van der Waals terms:
  Summation method   : Atom based
  Truncation method   : Cubic spline
  Cutoff distance   : 18.5 A
  Spline width   : 1 A
  Buffer width   : 0.5 A

SS4- Dipole moment calculation of MA

SS4-1- Geometric optimization of MA

---- Energy parameters ----

Forcefield   : COMPASS
Charges   : Use current

Electrostatic terms:

 Summation method   : Atom based
 Truncation method   : Cubic spline
 Cutoff distance   : 18.5 A
 Spline width   : 1 A
 Buffer width   : 0.5 A

van der Waals terms:

 Summation method   : Atom based
 Truncation method   : Cubic spline
 Cutoff distance   : 18.5 A
 Spline width   : 1 A
 Buffer width   : 0.5 A

Geometry optimization status

Total energy   :   18.568365 kcal/mol

Contributions to total energy (kcal/mol):

Valence energy (diag. terms)	:	**6.970**
Bond	:	1.561
Angle	:	4.547
Torsion	:	0.814
Inversion	:	0.048
Valence energy (cross terms)	:	**-8.818**
Stretch-Stretch	:	-0.025
Stretch-Bend-Stretch	:	-0.737
Stretch-Torsion-Stretch	:	-0.241
Separated-Stretch-Stretch	:	0.000
Torsion-Stretch	:	-0.831
Bend-Bend	:	-0.498
Torsion-Bend-Bend	:	-6.508
Bend-Torsion-Bend	:	0.022
Non-bond energy	:	**20.416**
van der Waals	:	20.416
Electrostatic	:	0.000

rms force : 1.350E-004 kcal/mol/A
max force : 6.868E-004 kcal/mol/A

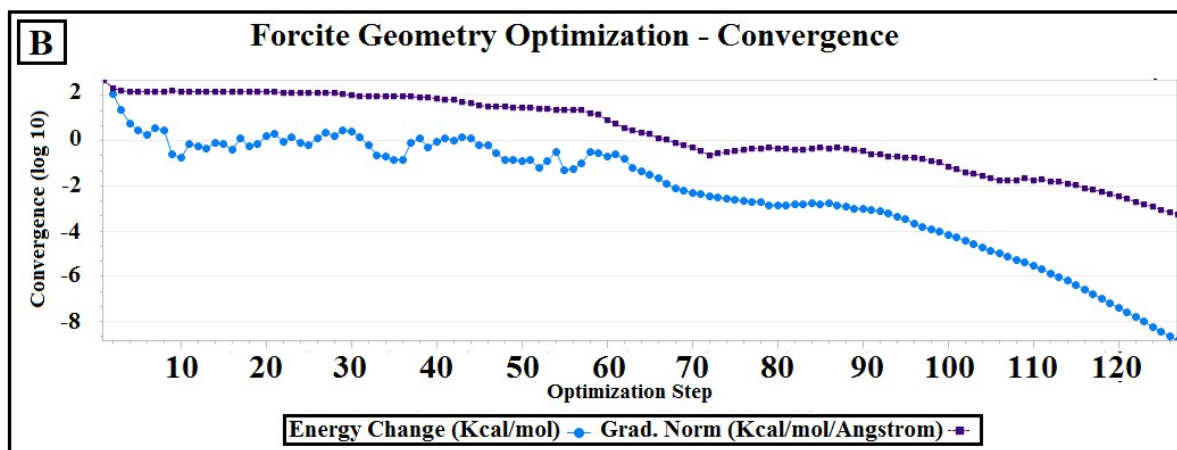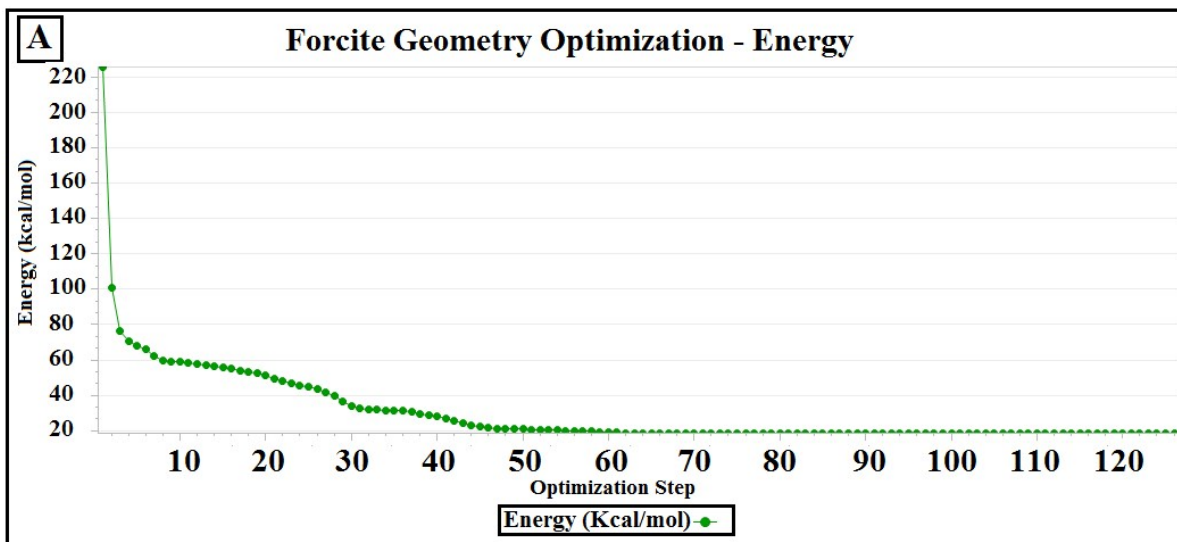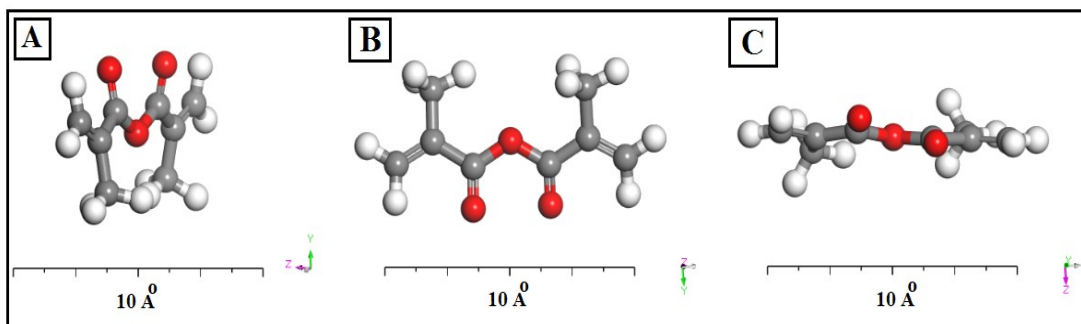**Figure S8- Forcite geometry optimization A: Energy and B: Convergence of MA.**
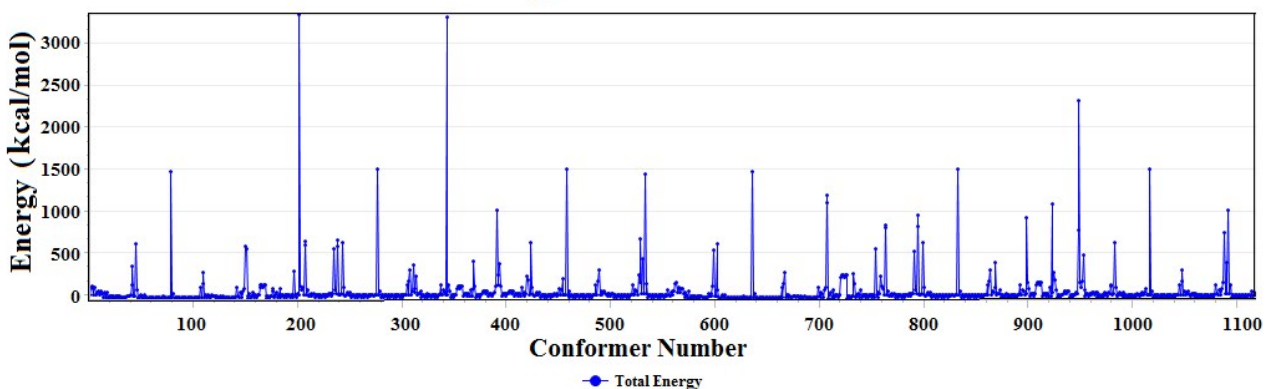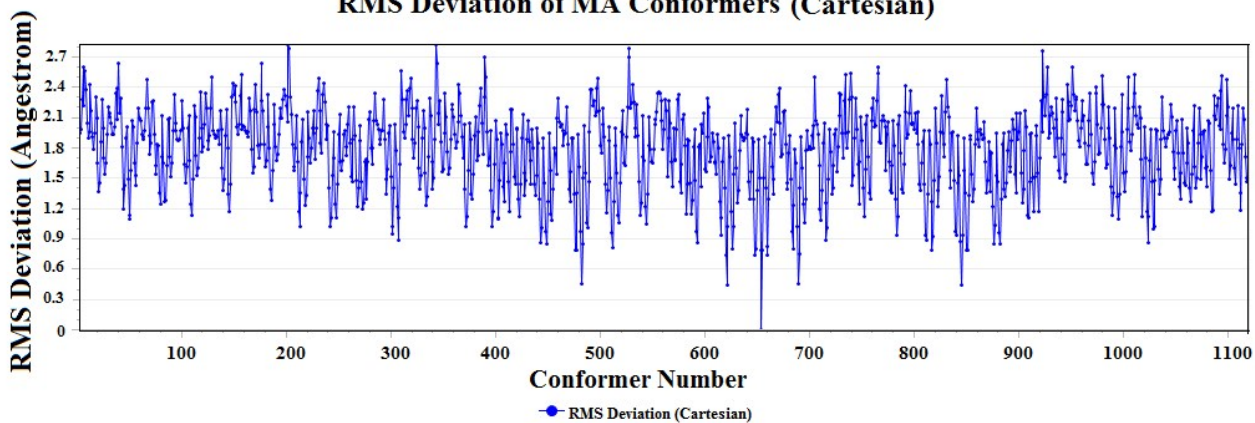

Figure S9- Geometry optimized molecular structures of MA.

A

Energy of MA Conformers

B

RMS Deviation of MA Conformers (Cartesian)

Figure S10- A: Energy and B: RMS deviation of all of the possible spatial conformers of MA.

SS4-2- Conformers and dipole moment of MA

---- Conformer Search Status ----
Progress: 100%   (1296/1296 conformers)
1296 conformers are sterically allowed.
Module   : Conformers
---- Search Parameters ----
Search method   : Systematic grid scan
H-bond scale factor   : 0.4
Anchor atom ID   : -1
Perturb from   : Perturb reference
VdW radii scale factor   : 0.4

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Vicinal radii scale factor   : 0.4

---- Energy parameters ----
Forcefield   : COMPASS
Charges   : Forcefield assigned
Electrostatic terms:
  Summation method   : Atom based
  Truncation method   : Cubic spline
  Cutoff distance   : 18.5 A
  Spline width   : 1 A
  Buffer width   : 0.5 A

van der Waals terms:
  Summation method   : Atom based
  Truncation method   : Cubic spline
  Cutoff distance   : 18.5 A
  Spline width   : 1 A
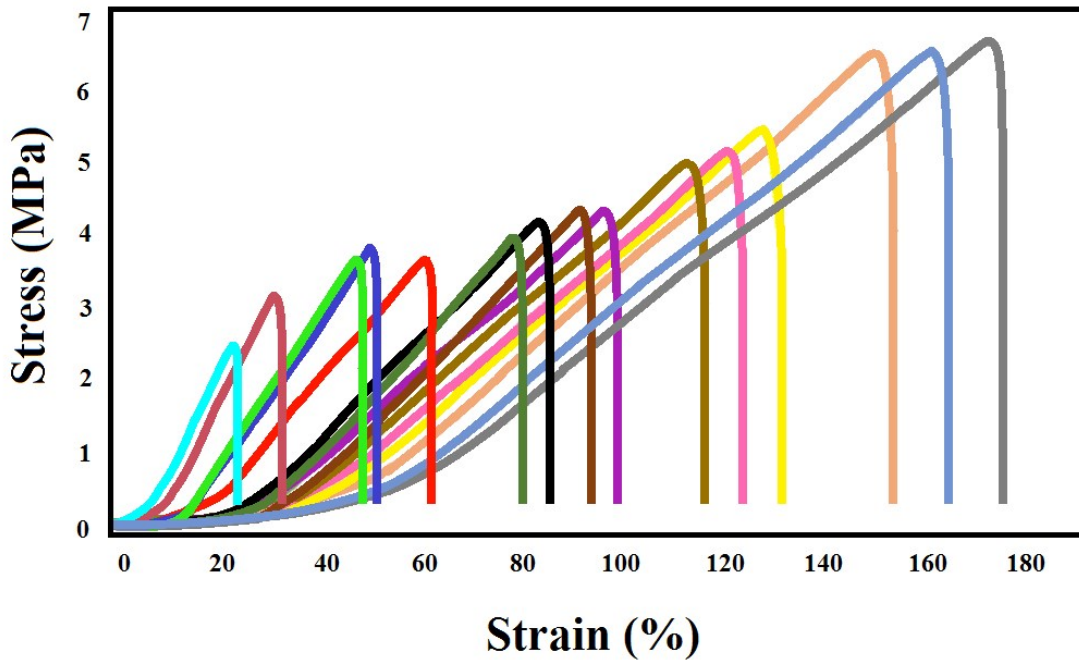 Buffer width   : 0.5 A

Figure S11- Tensile (stress-strain) curves of the LED-cured GelMA hydrogels.

SR- Reference

1   L. Shen, L. Zou, M. Ding, T. Zhao, L. Zhang and Q. Li, Molecular Dynamics Simulation on Dielectric Constant and Thermal Conductivity of Crosslink Epoxy/functionalized graphene Nanocomposites, *Mater. Sci. Eng.*, 2020, **761**, 012009.