Supporting Information

Photo-Reactive Nanogel as a Means to Tune Properties during Polymer Network Formation

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Characterization

FT-IR Spectroscopy. A FT-IR spectrometer (Nicolet 6700, ThermoFisher Scientific) was used for sample conversion and real-time kinetics measurements. Nanogel-initiated photopolymerization kinetics of methacrylate group was monitored by either near-IR[1] (6160 cm^{-1}) or mid-IR (1640 cm^{-1}).

Polymerization Stress Analysis. A tensometer (American Dental Association Foundation) was used to measure polymerization stress in real-time with simultaneous near-IR (NIR) experiments to correlate stress generation with conversion[2]. The deflection of a horizontal steel cantilever beam during polymerization was monitored with a linear variable differential transducer. Two aligned quartz rods (6 mm diameter) were mounted vertically between cantilever beam and the base after they were polished and cleaned using acetone and DI water followed by surface treatment with a silane agent (Fusion bonding system, George Taub Products and Fusion Co., Jersey City, NJ, USA) to introduce methacrylate groups. The distance between rods was adjusted to 1 mm and the gap was filled with the monomeric resin samples. The bottom rod was connected to a mercury arc light source (Acticure 400, EXFO) through a light guide. A 320 – 500 nm filter was used for polymerization with an irradiation duration of 30 min and intensities of 28 mW/cm^2 for the control and 85 mW/cm^2 for the less reactive nanogel-filled systems. These incident irradiance levels were measured at the exit of the quartz rod by a radiometer (Model: ILT1400A – 6255, InternationalLight Technologies, Peabody, MA). Conversion data was monitored with IR spectroscopy by aligning two fiber optic cables (1 mm diameter) horizontally with the sample (n=3). Real-time NIR scans were started 30 s before beginning data collection with the tensometer and 1 min before triggering the curing light.

Rheology Measurement. A photo-rheometer (ARES, TA Instruments) was utilized to measure the dynamic storage and loss moduli (G' and G", respectively) data. Quartz plates (8 mm diameter) were used with a frequency of 30 Hz and starting strain rate of 100 %. Torque-based automatic strain rate reduction was applied to prevent overloading as modulus increased during polymerization, especially as the material becomes glassy. A custom-designed optical accessory[3] allowed NIR and UV light access to quartz plates in the rheometer for real-time conversion profile measurement simultaneously with

modulus evolution. Samples were degassed by application of three evacuation-thaw cycles before loading the rheometer plates and N_2 purging was also carried out before and throughout the reaction with a chamber surrounding the plates to avoid edge effects due to oxygen inhibition. A UV light source (Acticure 400; Exfo) and a $320 - 390$ nm bandpass filter with a incident light intensity of 0.35 mW/cm^2 were applied to the nanogel-free control system, while 10 mW/cm^2 light intensity for nanogel-filled systems. Both IR signal collection and rheometer measurement started 2 min before light irradiation. Three replicates of each sample were averaged.

Viscosity data of nanogel-filled resins was measured with plate-plate setting in rheometer. 20 mm plates and 0.2 mm gap was applied.

Flexural Properties. A universal testing system (858 Mini Bionix, MTS System Corporation, Eden Prairie, MN, USA) was used to measure ambient temperature flexural strength and flexural modulus. Samples were prepared between glass slides with Teflon spacers with a geometry of 2 mm × 2mm × 25 mm. All systems were cured with a UV source (Acticure 400) and a $320 - 390$ nm filter with 60 mW/cm^2 light intensity for control system for 15 min and 120 mW/cm^2 for nanogel-filled system for 30 min to achieve matched final conversions. A span width of 10 mm and a crosshead speed of 1 mm/min were applied during three-point bending tests. Three replicates were performed for all samples.

Gel Permeation Chromatography (GPC). The molecular weights and polydispersities of nanogel together with hydrodynamic radii were analyzed by triple-detection GPC (Viscotek, Houston, TX) including reflective index detector (VE 3580), a viscometer and light-scattering detector (Viscotek 270 dual detectors). THF was used as eluent at a 1 ml/min flow rate.

NMR Spectroscopy. A 400 MHz NMR spectrometer (Bruker Avance-III) was used for ^{1}H NMR and ^{13}C NMR studies of the crosslinker and nanogels. CDCl$_3$ was used as NMR solvent and as internal calibration.

Mass Spectroscopy. An ESI+ analysis was carried out using a Waters SYNAPT G2 high definition mass spectrometry system for the analysis of molecular weight of the crosslinker and detecting residuals impurities. Analyte was dissolved in methanol at a concentration of 10 ppm. The
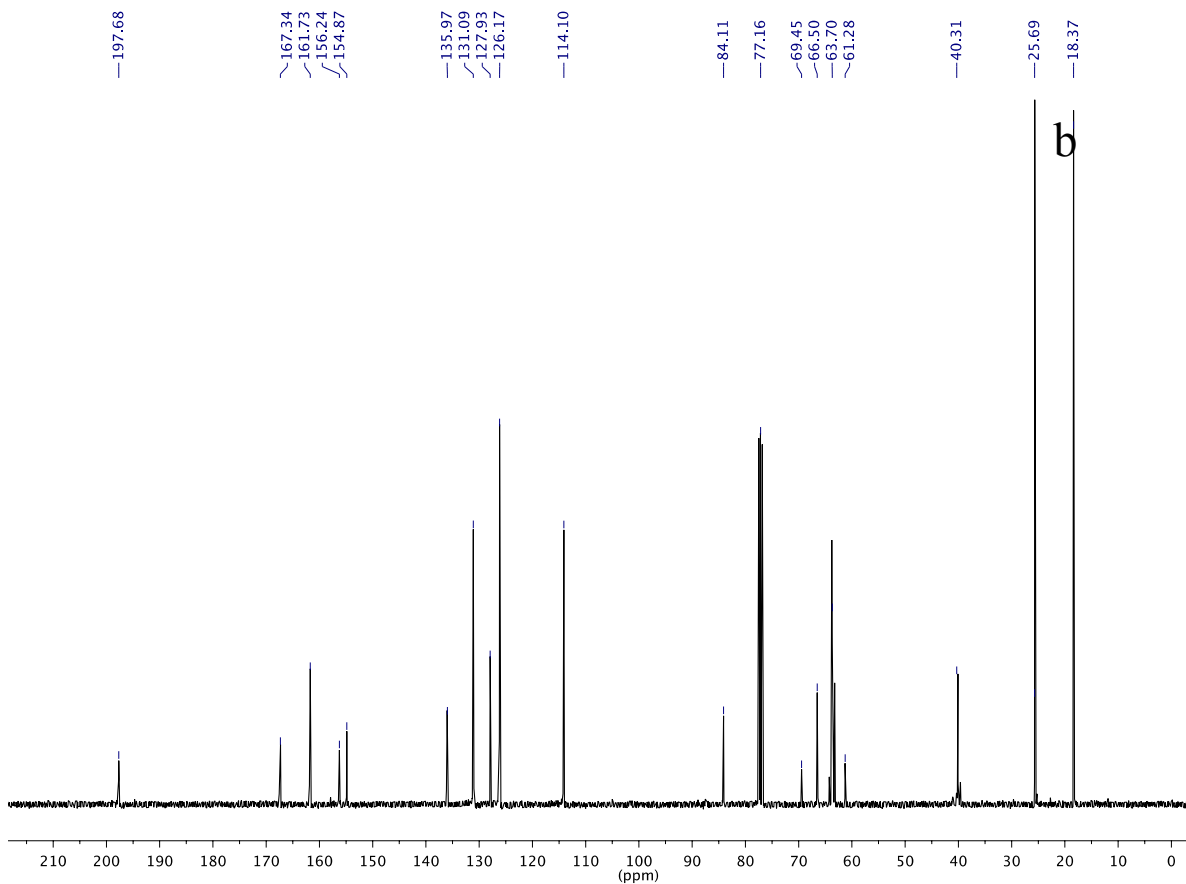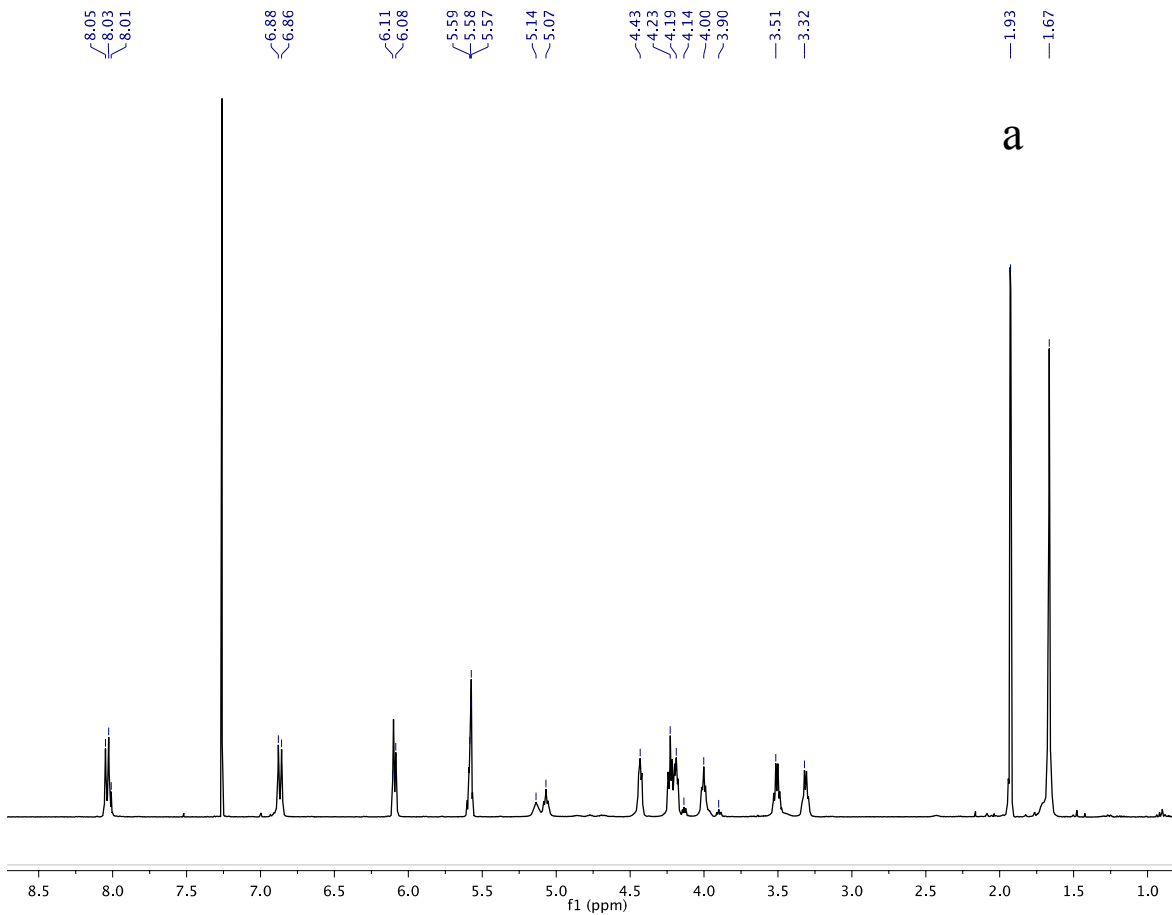
solution was injected into the ESI source at a rate of 5 μL/min. Accurate mass was determined to within 5 ppm of mass accuracy by using the Lock Mass calibration feature with the instrument.

UV/Vis Spectroscopy. Photoinitiation group absorbance was measured with a UV/Vis spectrophotometer (Evolution 300, Thermo Scientific). A set of solutions was prepared from I2959, I2959-IEM-DMA and nanogel with the same effective photoinitiation group concentration in DCM.

Dynamic Mechanical Analysis (DMA). Samples were cured in the same condition with the flexural experiments except for a different dimension of 25×2×1 mm. After reaction, samples were heated to 160 °C overnight to reach at least 98 % conversion to avoid thermally induced post-cure during DMA testing. DMA (Q800, TA Instruments) was applied for the storage modulus and tan δ measurements with a strain of 0.02 %, frequency of 1 Hz and temperature scan from 0 to 220 °C at 2 °C/min (n=3).
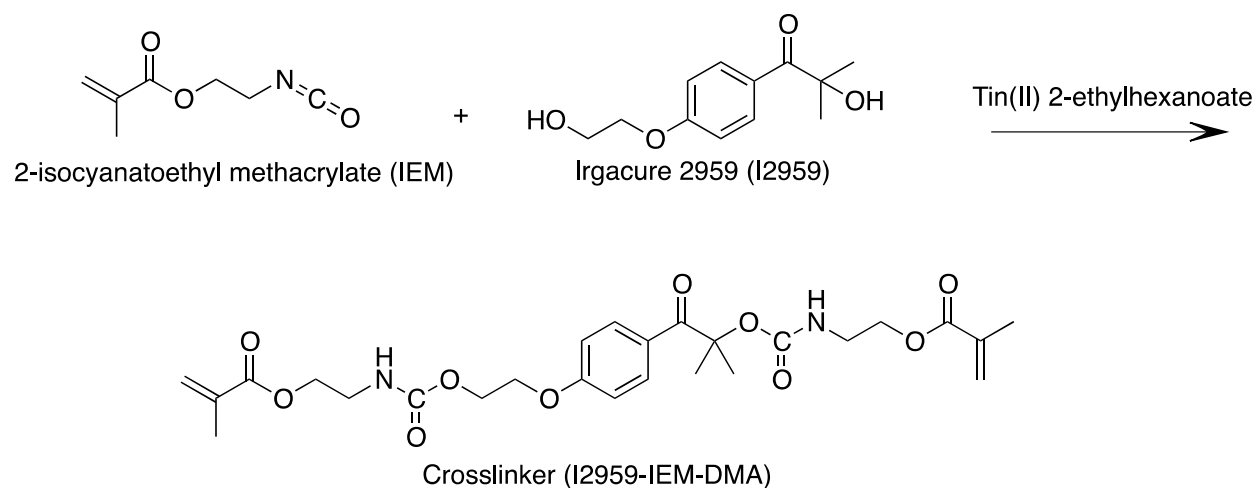
Scheme S1. Reaction scheme of IEM and I2959 to form photo-reactive crosslinker (I2959-IEM-DMA).

a

8.05, 8.03, 8.01; 6.88, 6.86; 6.11, 6.08; 5.59, 5.58, 5.57; 5.14, 5.07; 4.43, 4.23, 4.19, 4.14, 4.00, 3.90; 3.51, 3.32; 1.93, 1.67

f1 (ppm)

b

197.68; 167.34, 161.73, 156.24, 154.87; 135.97, 131.09, 127.93, 126.17; 114.10; 84.11, 77.16; 69.45, 66.50, 63.70, 61.28; 40.31; 25.69, 18.37
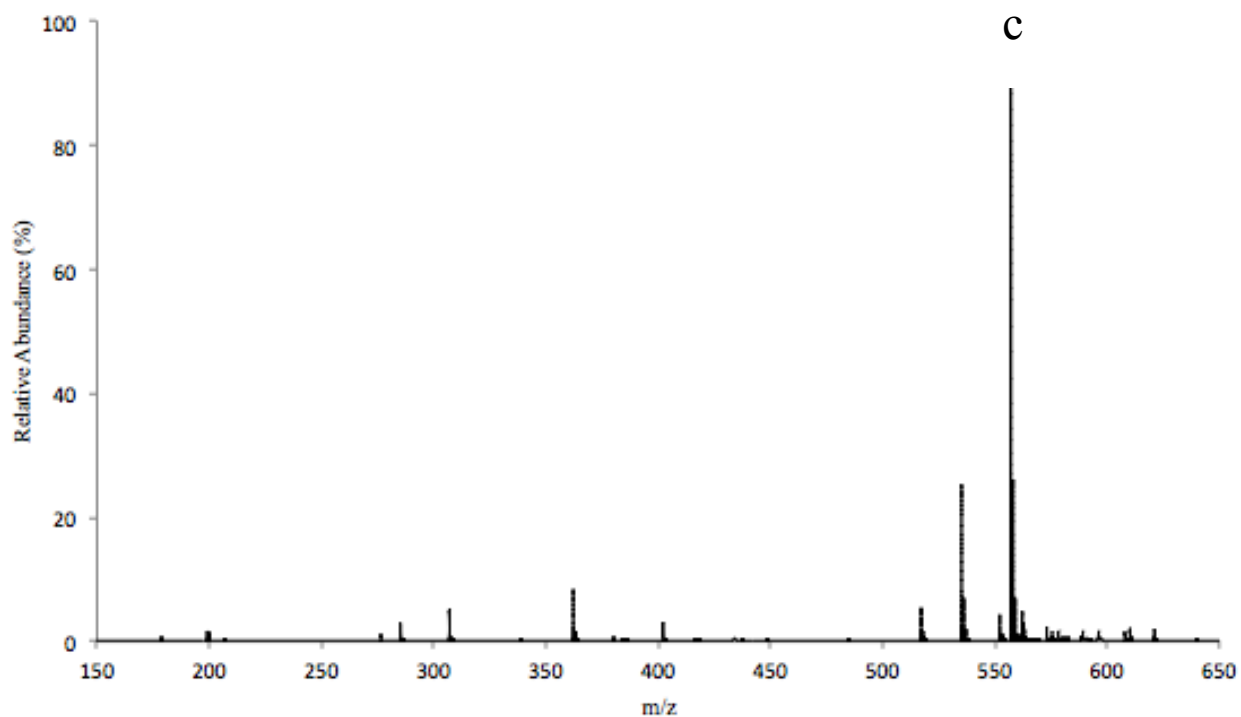
(ppm)

5

c

Figure S1. ^{1}H NMR (a), ^{13}C NMR (b) and mass spectroscopy spectra (c) of IEM-I2959-DMA.
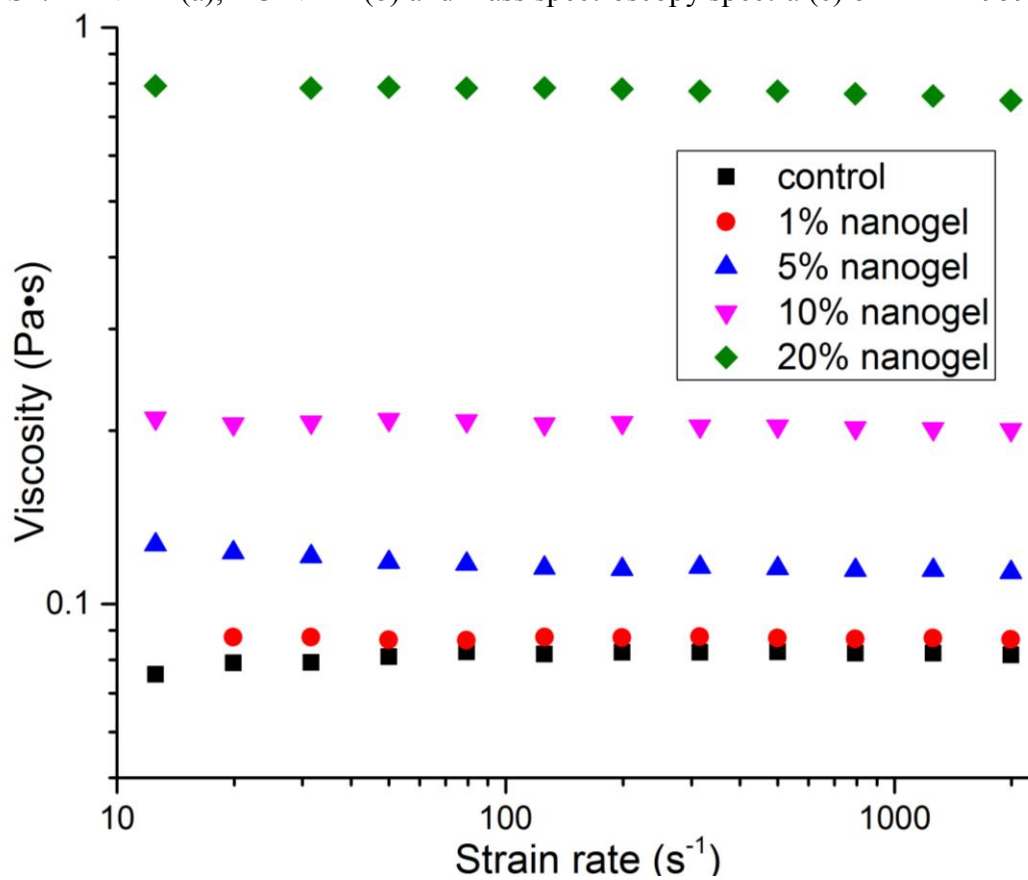
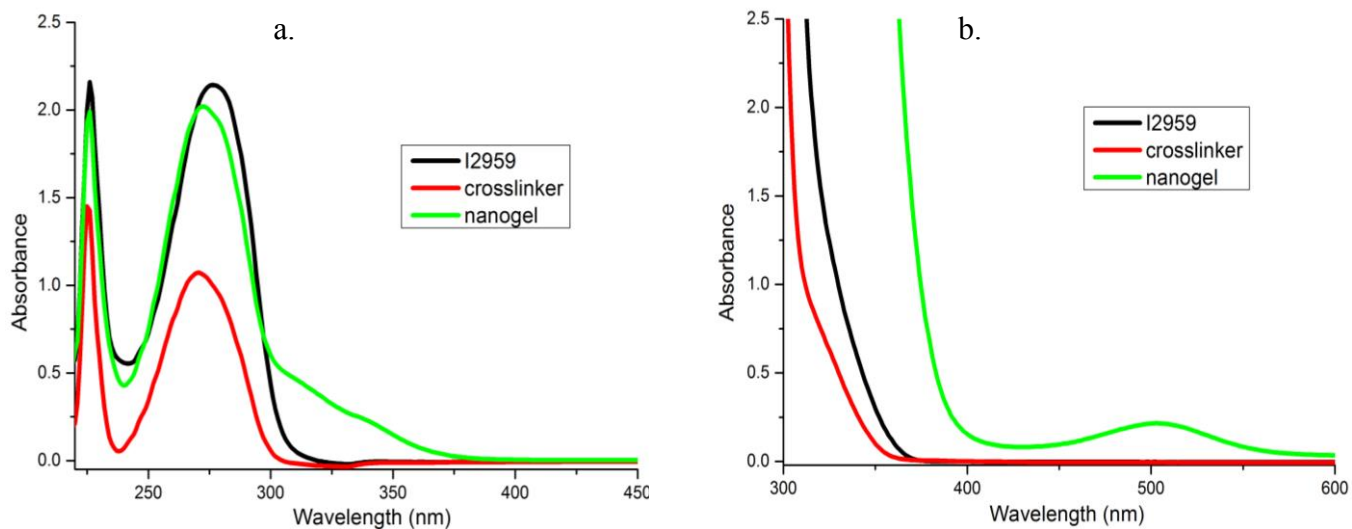Figure S2. Viscosity profile during strain rate sweep for nanogel solutions and control.

Figure S3. UV-vis absorbance spectra for I2959,crosslinker (I2959-IEM-DMA) and CPBD nanogel in DCM. (a) [I2959] = 22.5 μM; and (b)[I2959] = 4.5 mM.
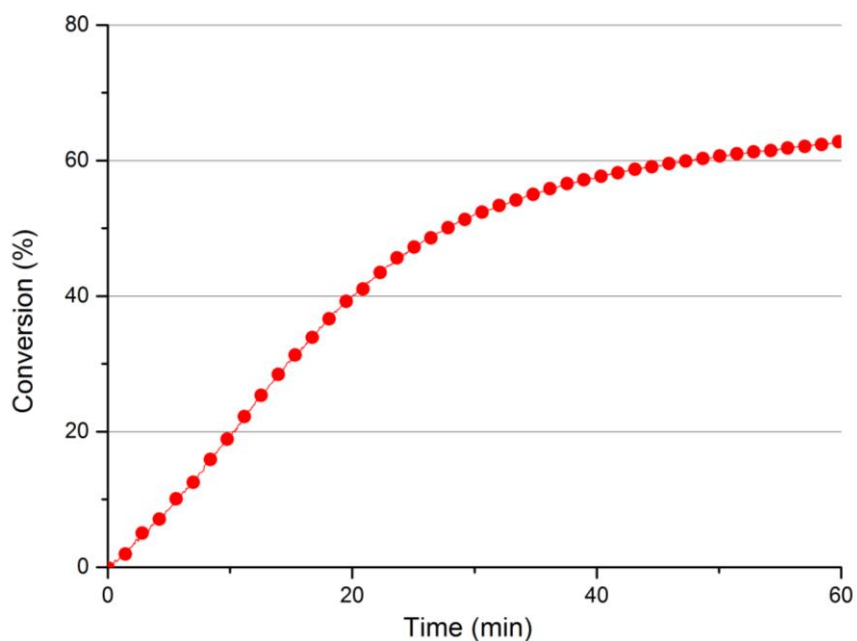

Figure S4. Real-time conversion profiles for BisEMA-TEGDMA resin with 0.7 % CPBD (CPBD amount is equivalent to 20 % CPBD nanogel dispersion) under 365 nm light at 35 mW/cm^2.
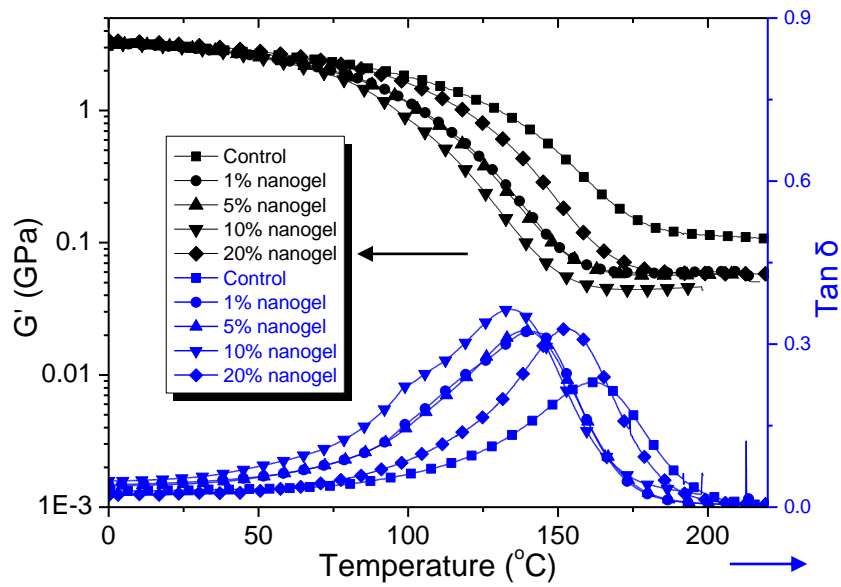
Figure S5. DMA traces for the control and 1, 5 and 20 % CPBD nanogel systems.

Storage modulus (G') curves are shown in black and tan δ in blue.

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(2)   Lu, H.; Stansbury, J. W.; Dickens, S. H.; Eichmiller, F. C.; Bowman, C. N. *J Mater Sci-Mater M* **2004**, *15*, 1097.
(3)   Pfeifer, C. S.; Wilson, N. D.; Shelton, Z. R.; Stansbury, J. W. *Polymer* **2011**, *52*, 3295.