Electronic Supplementary Material (ESI) for Polymer Chemistry.

Self-healing Magnetic Nanocomposites with Robust Mechanical Properties and High Magnetic Actuation Potential Prepared from Commodity Monomers *via* Graft-From Approach

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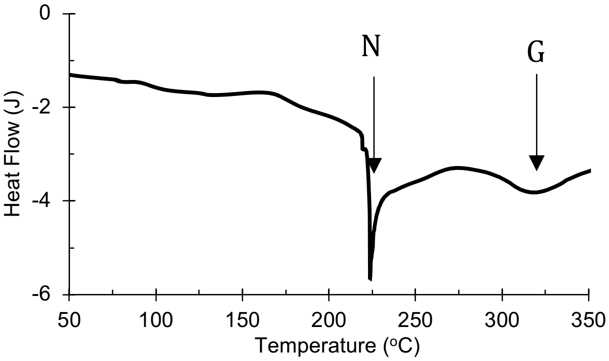
General Experimental Information

All commercial reagents were used as received and stirred with a magnetic stir bar unless otherwise noted. *n*-Butyl acrylate was passed through a basic alumina column to remove radical inhibitor prior to polymerization. Flash column chromatography was performed with silica gel using an automated column (CombiFlash® Teledyne Isco). Thin-layer chromatography (TLC) was performed on 0.2 mm silica gel-coated glass sheets with F254 indicator. TLC plates were also stained with basic potassium permanganate solution consisting of 1.5 g $KMnO_4$, 10 g K_2CO_3, and 1.3 mL 10 % NaOH in 200 mL water. All yields refer to isolated yields. Nuclear magnetic resonances (NMR) spectra were recorded at 500 MHz CRYO-500 spectrometers. ^{1}H NMR chemical shifts are reported as δ values in ppm relative to residual solvent: $CDCl_3$ (δ=7.26 ppm). ^{1}H NMR data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad), coupling constants in Hz, and relative integration in number of protons. Multiplets (m) are reported over the range of chemical shift at which they appear. Attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectra were collected on a Jasco 4700 FTIR equipped with ATR-PRO ONE single bounce ATR with monolithic diamond. Transmission electron microscopy (TEM) images were obtained by a FEI/Philips CM20 200kV LaB_6 with a side-mounted Gatan TEM CCD camera. For TEM imaging 200-mesh carbon grids were used. *J*-KEM Scientific (Model Apollo) was used for PID temperature control for the thermal decomposition of the iron-oleate precursor. Thermogravimetric Analysis (TGA) was conducted on TA Instruments Q500 TGA. Gel Permeation Chromatography (GPC) traces were obtained on an Agilent 1100 SEC system using a PLGel Mixed-C column from Polymer Labs (Amherst, MA). Dimethylformamide with 1 wt% LiBr was used as eluting solvent at a flow rate of 1.0 mL/min. Number averaged and weight averaged molecular weight distributions (Mn and Mw, respectively) of samples were measured with respect to polystyrene (PS) standards purchased from Aldrich (Milwaukee, WI).

Synthesis of Oleic Acid MNPs (OA MNPs)

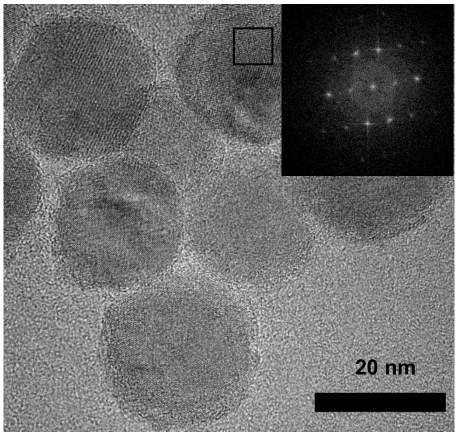
Step 1. A 100 mL round bottom flask equipped with a stir bar and reflux condenser was charged with $FeCl_3 \cdot H_2O$ (2.70 g, 10.0 mmol), sodium oleate (9.13 g, 30.0 mmol), ethanol (20 mL), water (15 mL), and hexanes (35 mL). The reaction flask refluxed for 4 hours. The reaction was cooled to room temperature, transferred to a separatory funnel, and washed with water (100 mL, x3). The organic layer was concentrated *in vacuo* to yield the red colored iron-oleate precursor. The iron-oleate precursor was dried at 100 °C under vacuum overnight. *Step 2.* A three neck, 100-mL round bottom flask equipped with a Schlenk adapter, reflux condenser, thermocouple, and stir bar were charged with the iron-oleate precursor (6.82 g, 7.58 mmol) and 1-octadecene (48.4 mL). The solution was then deoxygenated by reducing pressure and backfilling with nitrogen (x3) followed by a distillation to remove residual water. Oleic acid (0.80 mL, 2.53 mmol) was then added and heated to 320 °C and kept at this temperature for 1 hour. Particles were purified by precipitation with acetone (4 x 100 mL), dispersing in hexanes in between washes.

Figure S1: Differential Scanning Calorimetry of Iron-oleate Precursor



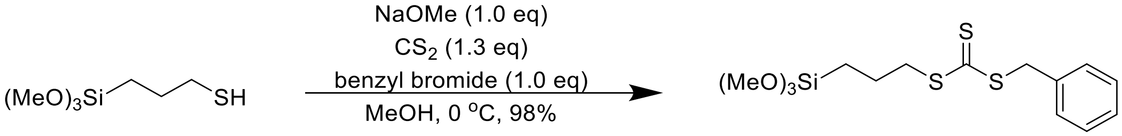
Differential Scanning Calorimetry (DSC) was done on a TA Instruments DSC Q2000 (endotherm down, exotherm up). 5 mg of iron-oleate precursor that had been dried at 100 °C under vacuum overnight was used. Tzero aluminum hermitically sealed pans were used. Reference pan was also an empty Tzero aluminum hermitically sealed. Nitrogen was used to purge the furnace at 50 mL/min. Sample pan and reference pan were equilibrated at 40 °C, followed by a temperature ramp at 10 °C/min until 400 °C. The nucleation (N) and growth (G) phases of nanoparticle synthesis endotherms are noted at 220 °C and 320 °C, respectively, which are in agreement with literature.[1]

Figure S2: High Resolution Transmission Electron Micrograph of OA MNPs



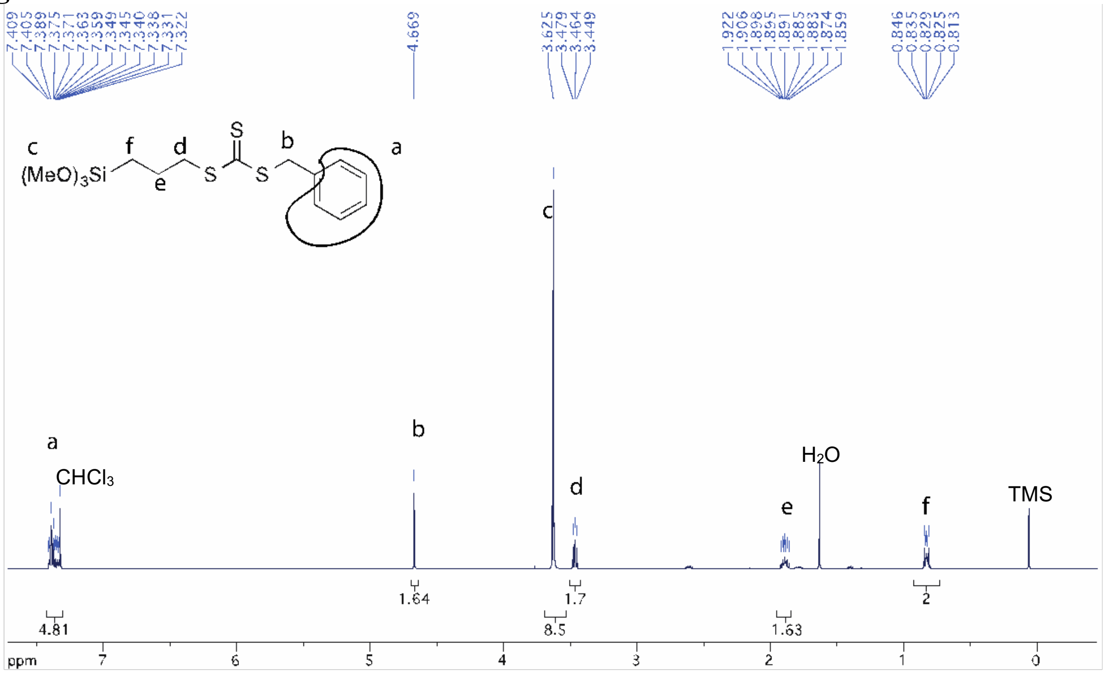
High resolution transmission electron micrograph, scale bar is 20 nm. Inset showing fast Fourier transform of the area outlined in the box showing lattice fringes indicative of crystallinity.

Scheme S1: Synthesis of CTA



Benzyl(3-trimethoxysilylpropyl)trithiocarbonate (CTA): A 250 mL round bottom flask was charged 3-mercaptopropyltrimethoxysilane (19.6 g, 100 mmol) and anhydrous methanol (30.0 mL) under N_2. The solution was cooled with an ice bath before the dropwise addition of sodium methoxide (18.0 g, 100 mmole, 1.0 equiv.), in a 25% solution in MeOH over 30 min at 0 °C. The solution was stirred at room temperature for an additional 30 minutes before the dropwise addition of carbon disulfide (7.60 g, 100 mmol, 1.0 equiv.) which resulted in a color change from pink to yellow. The reaction was stirred for an additional 5 hours followed by the dropwise addition of benyl bromide (12.6 g, 100 mmol). Reaction was stirred overnight, then concentrated *in vacuo.* The remaining liquid was diluted with dichloromethane, filtered through a glass frit to remove salts, and concentrated *in vacuo.* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 4.67 (s, 2H), 3.63 (s, 8H), 3.46 (t, J = 7.4 Hz, 2H), 1.92-1.86 (m, 2H), 0.85-0.81 (m, 2H) which is in agreement with literature reports.[2]

Figure S3: ^{1}H NMR Characterization of CTA



Synthesis of CTA MNPs

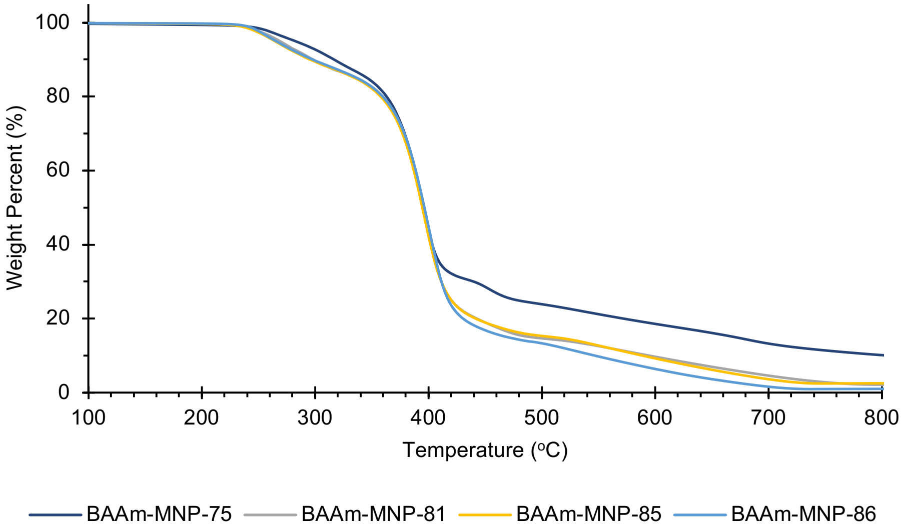
Oleic acid functionalized nanoparticles (25 mg) were suspended in toluene (5.0 mL) by ultrasonication for 15 minutes. To the nanoparticle solution, triethylamine (0.50 mL) and CTA (50 mg) were added. The reaction was stirred for 48 hours under N_2 atmosphere. The resulting nanoparticles were purified by concentrating *in vacuo,* followed by resuspending in dichloromethane, and precipitation with hexanes, and magnetic separation using a 2.54 cm^3

neodymium magnetic with a 54 kg pull force.

Synthesis of BAAm MNPs

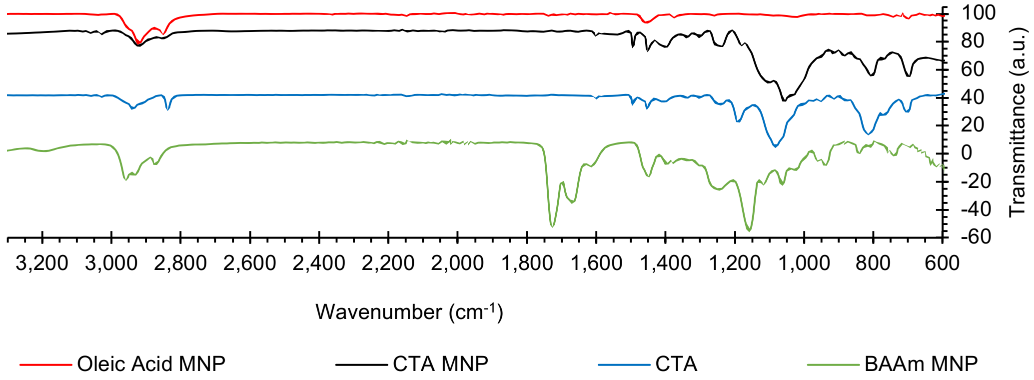
CTA-MNPs (0.0626 g, 4.6 mmole CTA/g as determined by thermogravimetric analysis) were dispersed in DMF (120 mL) using ultrasonication. A Schlenk flask was charged with n-butyl acrylate (15.7642 g), acrylamide (3.7468 g), mesitylene (2.300 g, as internal standard), AIBN (9.6 mg), and the CTA-MNPs dispersed in DMF (monomer:CTA = 600:1). The flask was sealed with copper wire and a septum. The side arm was used for deoxygenation via bubbling nitrogen for 1.5 h. Prior to immersing in oil bath set at 57 °C a 100 µL aliquot was taken out and the MNP are removed magnetically to allow for NMR analysis. The conversion and subsequent degree of polymerization was calculated with ^{1}H NMR by comparing the integration of vinyl protons with respect to mesitylene protons. Once desired percent conversion was obtained (all kept <50%), 4-methoxyphenol was added as radical inhibitor. The polymer solution was precipitated by slow addition to 1 L of methanol-water mixture, (1:1 v/v), followed centrifugation in 250 mL Nalgene tubes at 7,000 rcf. The supernatant was discarded, and the polymer was solubilized in methanol-chloroform (1:1 v/v). The precipitation process was repeated 3 times. Polymer was then precipitated in 1 L hexanes (x2) followed by another two precipitations in methanol-water (1:1 v/v). Polymers were then dried overnight at 100 °C under vacuum and stored in a desiccator. Due to the magnetic nature of the nanoparticles NMR analysis of the resulting polymers could not be conducted.

Figure S4: Thermogravimetric Analysis of BAAM-MNP Composites



Thermogravimetric Analysis (TGA) was conducted on TA Instruments Q500 TGA. Samples were equilibrated at 100 °C for 30 minutes under nitrogen, followed by a temperature ramp of 10 °C/min to 800 °C.

Figure S5: ATR FTIR Spectroscopy



Mechanical Testing Procedure

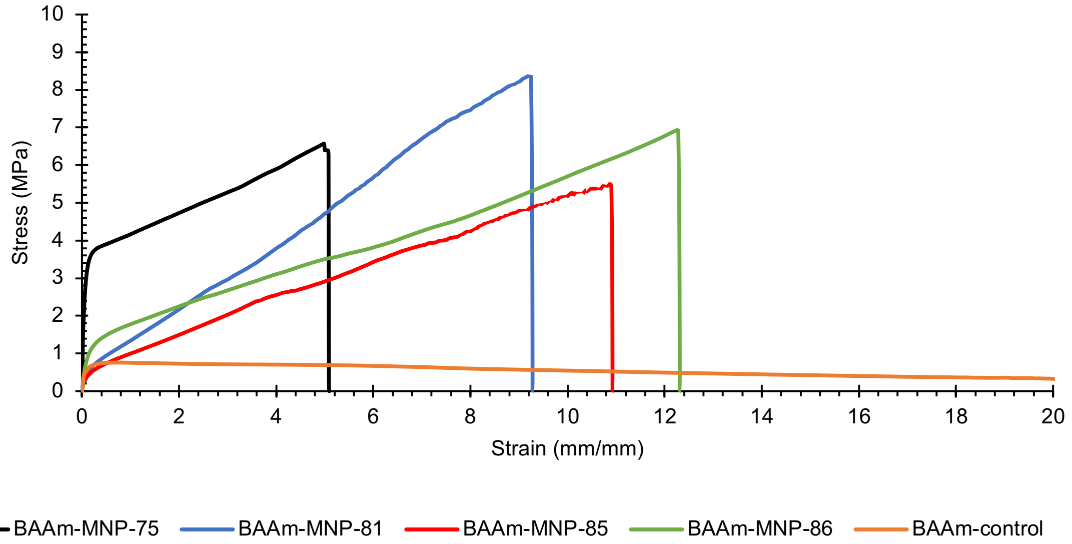
Samples were prepared by hot-pressing the composite into heated dog-bone Teflon molds at 100 °C followed by cooling to room temperature while maintaining the pressure (cooling time approximately 20 min). Average sample size was 13 mm × 3 mm × 1 mm (length, width, thickness). The mechanical properties of the composites were measured using an Instron 3365 machine in standard stress/strain experiments. The specimen was extended at 100 mm/min at room temperature. Each measurement was repeated at least three times.

Table S1: Mechanical and Thermal Properties of BAAm-MNP

Sample	wt % [a]	E (MPa) [b]	ε (mm/mm) [c]	σ (MPa) [d]	U (MJ/m^3) [e]
OA-MNP	7	N/A	N/A	N/A	N/A
CTA-MNP	25	N/A	N/A	N/A	N/A
BAAm-MNP-75	75	70 ± 10	5.4 ± 0.7	6.9 ± 0.8	28 ± 6
BAAm-MNP-81	81	10 ± 4	10 ± 1	8 ± 1	38 ± 6
BAAm-MNP-85	85	11 ± 4	11.3 ± 0.8	6 ± 1	40 ± 8
BAAm-MNP-86	86	16 ± 4	11.8 ± .8	8.0 ± 0.8	52 ± 6
BAAm-control[g]	100	12 ± 4	[f]	0.8 ± 0.1	[f]

[a] Weight percent (wt %) of volatile organic material as determined by thermogravimetric analysis (TGA). [b] Youngs modulus (E) is determined by calculating the initial slope from the uniaxial mechanical testing. [c] Extensibility at break (ε) is reported at a mm/mm. [d] The maximum stress at break (σ) is reported in MPa. [e] The toughness (U) is calculated by taking the area under the curve for the stress-strain curve. [f] BAAm-control is a linear copolymer BAAm with no MNP as control synthesized with small molecule CTA analogue and has a Mw of 38 kDa as determined by gel permeation chromatography. [f] No ε or U reported because samples did not break.

Figure S6: Mechanical Properties in Comparison to BAAm-control

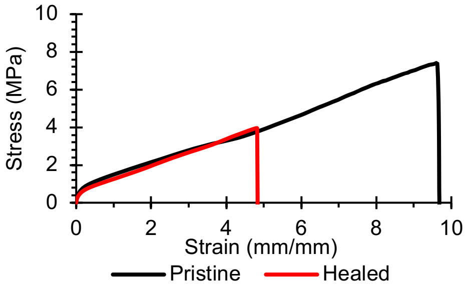


Samples strained at 100 mm/min

Sample Damaging and Healing Tests

For self-healing tests, samples were prepared by hot-pressing the composite into heated dog-bone Teflon molds at 100 °C and cooling to room temperature while maintaining pressure (cooling time approximately 20 min). Average sample size was 13 mm × 3 mm × 1 mm (length, width, thickness). Samples were cleanly cut to 50% the width of the sample using a razor blade. The cut interfaces were gently pressed together for 1 minutes. Then samples were subject to different self-healing conditions. A pristine or uncut sample was subject to the same subsequent conditions and used for controls to determine self-healing efficiency. The samples were then allowed to cool down to room temperature (15 min) and were subjected to stress-strain tests at room temperature using an Instron 3365 machine in standard stress/strain experiments. Each experiment was repeated at least three times.

Figure S7: Strain-strain Curves BAAm-MNP-85 at 30 °C for 2 h



Samples strained at 100 mm/min.

Table S2: Mechanical Properties of Healed and Pristine BAAm-MNP-75 & 85 (ambient conditions)

Sample	Healing (h)	Healing (ºC)	E (MPa)	ε (mm/mm)	σ (MPa)	U (MJ/m^3)
BAAm-MNP-75	5	30	6 ± 1	7 ± 2	1.4 ± 0.2	7 ± 2
BAAm-MNP-75- Pristine	5	30	6 ± 1	16 ± 2	3.6 ± 0.6	29 ± 7
BAAm-MNP-85	2	30	17 ± 5	4.4 ± 0.4	4.1 ± 0.6	11 ± 2
BAAm-MNP-85-Pristine	2	30	13 ± 1	11 ± 3	7 ± 1	37 ± 14

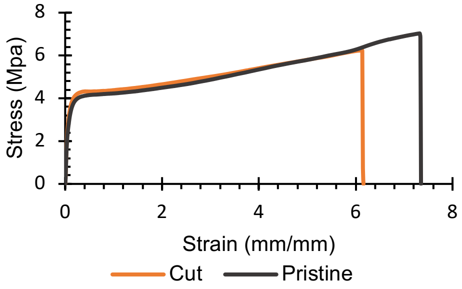
Mechanical properties calculated from stress-strain curves at 100 mm/min and average and standard deviation reported from minimum of three samples. Youngs modulus (E) is determined by taking the slope of the second to seventh data point from the uniaxial mechanical testing. Extensibility at break (ε) is reported at a mm/mm. The maximum stress at break (σ) is reported in MPa. The toughness (U) is calculated by taking the area under the curve for the stress-strain curve.

Table S3: Self-healing Efficiency BAAm-MNP-75 & 85 (ambient conditions)

Samples	Healing (h)	Healing (ºC)	Recovery % of E (MPa)	Recovery % of ε (mm/mm)	Recovery % of σ (MPa)	Recovery % of U (MJ/m^3)
BAAm-MNP-75	5	30	90 ± 21	46 ± 13	39 ± 6	23 ± 6
BAAm-MNP-85	2	30	123 ± 38	41 ± 4	55 ± 9	25 ± 5

Youngs modulus (E) is determined by taking the slope of the second to seventh data point from the uniaxial mechanical testing run at 100 mm/min. Extensibility at break (ε) is reported at a mm/mm. The maximum stress at break (σ) is reported in MPa. The toughness (U) is calculated by taking the area under the curve for the stress-strain curve. The percentage is the percent of the property that was recovered of a damaged sample relative to an undamaged sample subject to the same environmental conditions.

Figure S8: Strain-strain Curves BAAm-MNP-75 at 80 ºC for 5 h (under reduced pressure)



Samples strained at 200 mm/min.

Table S4: Mechanical Properties of Healed and Pristine BAAm-MNP-33 (80 ºC, 5h)

Sample	Healing (h)	Healing (ºC)	E (MPa)	ε (mm/mm)	σ (MPa)	U (MJ/m^3)
BAAm-MNP-75	5	80	54 ± 10	6.0 ± 0.9	6.2 ± 0.1	2216 ± 333
BAAm-MNP-75-Pristine	5	80	47 ± 19	8.6 ± 1.3	6.9 ± 0.3	3206 ± 1369

Mechanical properties calculated from stress-strain curves at 200 mm/min and average and standard deviation reported from minimum of three samples. Youngs modulus (E) is determined by taking the slope of the second to seventh data point from the uniaxial mechanical testing. Extensibility at break (ε) is reported at a mm/mm. The maximum stress at break (σ) is reported in MPa. The toughness (U) is calculated by taking the area under the curve for the stress-strain curve.

Table S5: Self-healing Efficiency BAAm-MNP-75 (80 ⁰C, 5h, reduced pressure)

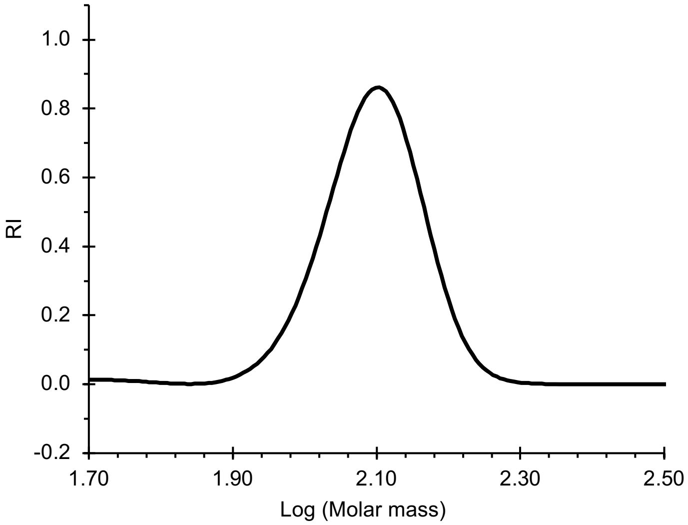
Samples	Healing (h)	Healing (⁰C)	Recovery % of E (MPa)	Recovery % of ε (mm/mm)	Recovery % of σ (MPa)	Recovery % of U (MJ/m^3)
BAAm-MNP-75	5	80	110 ± 22	74 ± 6	90 ± 1	75 ± 5

Youngs modulus (E) is determined by taking the slope of the second to seventh data point from the uniaxial mechanical testing at 200 mm/min. Extensibility at break (ε) is reported at a mm/mm. The maximum stress at break (σ) is reported in MPa. The toughness (U) is calculated by taking the area under the curve for the stress-strain curve.

Cleaving of BAAm Polymer from MNPs

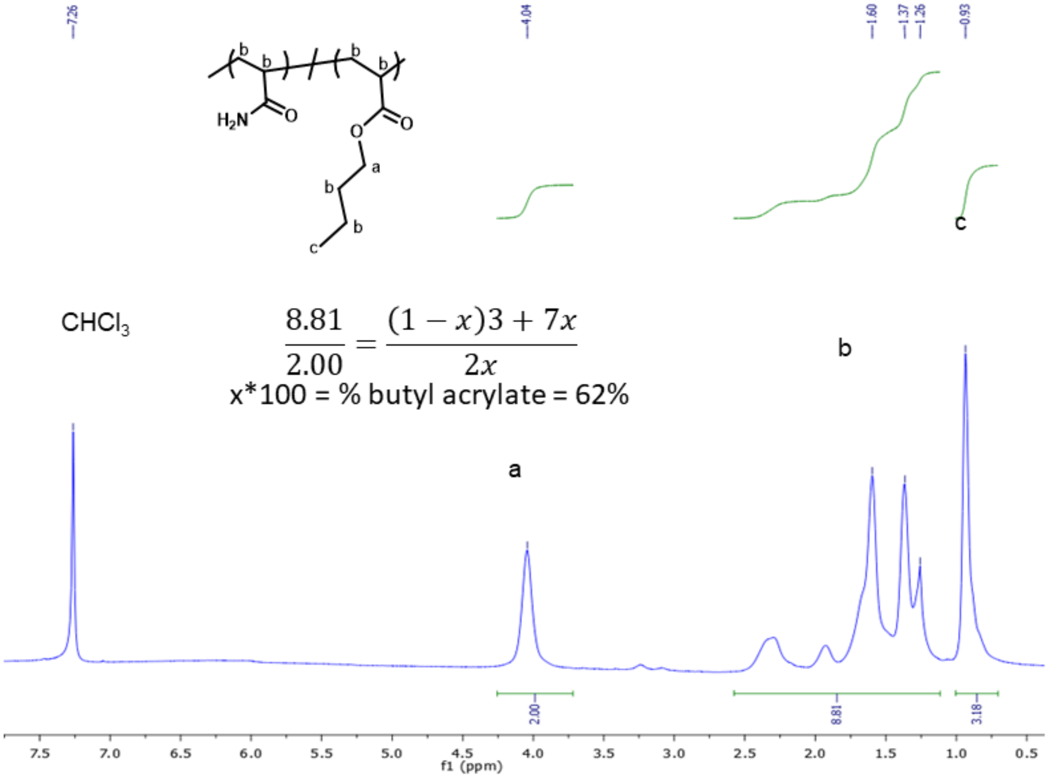
100 mg of the BAAm-MNP-86 composite was dissolved in 3.5 mL of toluene in a high density polyethylene bottle. Hydrofluoric acid (3.5 mL, 5%) was added and the solution was stirred at room temperature overnight. 4.0 mL of a saturated sodium bicarbonate solution was added and the resulting emulsion was precipitated in 200 mL of MeOH:H_2O (1:1) solution. The resulting solid was characterized by gel permeation chromatography and H NMR spectroscopy to determine molecular weight and percent incorporation of acrylamide.

Figure S9: GPC of Cleaved BAAm Polymer from MNPs



Gel permeation chromatogram (GPC) of cleaved BAAm polymer from MNPs. M_n=71.2 kDa M_w=115 kDa and polydispersity index of 1.62. The polymer corresponds to BAAm-MNP-86.

Figure S10: NMR of Cleaved BAAm Polymer from MNPs



NMR analysis of BAAm-MNP-86 after cleaving from MNP using hydrofluoric acid. The calculation for percent incorporation of butyl acrylate is shown above. The percent incorporation of butyl acylate is 62% and for acrylamide it's 38% given a feed ratio of 60% and 30% of butyl acrylate and acrylamide, respectively.

References

1 L. M. Bronstein, X. Huang, J. Retrum, A. Schmucker, M. Pink, B. D. Stein and B. Dragnea, *Chem. Mater.*, 2007, **19**, 3624–3632.
2 Y. Zhao and S. Perrier, *Macromolecules*, 2007, **40**, 9116–9124.