

Multi-Responsive Polymer-Stabilized Magnetic Engineered Emulsions as Liquid-Based Switchable Magneto-responsive Actuators

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Materials.

Unfunctionalized superparamagnetic Fe₃O₄ mNPs were obtained as 20-30 nm nanopowders from Alfa Aesar. Dodecane, bromopropyl trimethoxysilane (Fluorochem) and 2-(diethylamino)ethyl methacrylate were purchased from Aldrich and used as received (DEAEMA monomer was passed through an alumina column). PEGMA/MAA branched copolymer was synthesized according to previous reports.¹

The magnet used was a rare earth NdFeB magnet (MagnetSales) with 10 mm diameter, 5mm thickness and 1.18T strength.

Characterization protocols.

¹H NMR. Spectra of branched copolymer **1** were recorded in CD₃OD using a Bruker DPX-400 spectrometer operating at 400 MHz.

FT-IR. FT-IR measurements were performed in reflection mode using a FTIR spectrometer (Tensor 27, HTS-XT, Bruker). FTIR spectra were generated using OPUS/MAP software.

Superconducting quantum interference device (SQUID). Magnetization measurements were performed using a Quantum Design MPMS SQUID magnetometer. Magnetization curves (MvH) as a function of magnetic field were measured at 300K for magnetic fields from -10 to 10 KOe. The samples were prepared by adding a small amount nanoparticles or emulsion (1.8 mg and 6.3 mg respectively) into a capsule filled with cotton.

Transmission electron microscopy. Transmission electron microscopy images were recorded using a Tecnai G2 Spirit BioTWIN model operating at an accelerating voltage of 100 kV. The samples were dispersed in a few milliliters of ethanol and a drop of this dispersion was placed on a copper grid and allowed to dry.

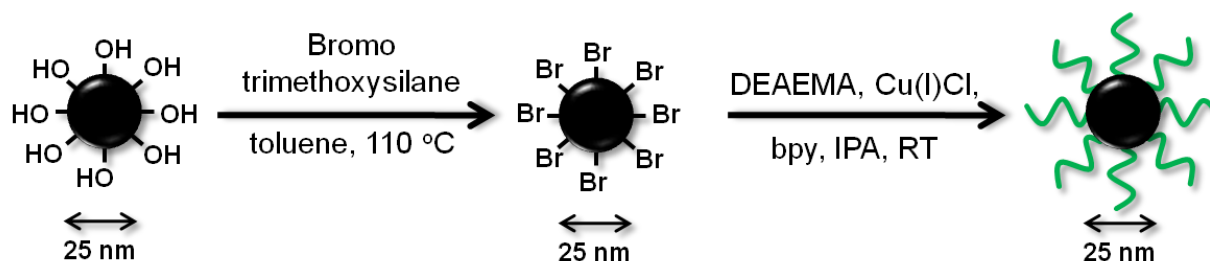
Laser Diffraction. Emulsion droplet diameters and diameter distributions (Spans) were measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000 SM dispersion unit. A 60 μL drop of the emulsion was added to the dispersion unit containing 100 mL water (pH adjusted to pH 10 using NaOH) with a stirring rate of 1000 rpm. The volume-average droplet diameters ($D_{4/3}$) quoted are obtained from at least 20 repeat runs ($D_{4/3} = \sum D_i^4 N_i / \sum D_i^3 N_i$). The span is a measure of the distribution of the droplet size distribution and is expressed as $(D(0.9) - D(0.1)) / D(0.5)$, where $D(0.9)$ is the diameter under which 90% of the particles fall, $D(0.5)$ is the diameter under which 50% of the particles fall and $D(0.1)$ is the diameter under which 10% of the particles fall. The cell was repeatedly rinsed using basic water and ethanol after each measurement run. Engineered emulsions which had been redispersed using 2–3 drops of 1 M NaOH were measured in the same way.

Light microscopy Light micrographs were recorded using a using an Olympus CX41RF microscope equipped with digital camera. Scale bars were created for each image using a graticule.

Rheometry. Rheological experiments were carried out on an Anton Parr Physica MCR301 rheometer. The measurement was performed at a temperature of 293K, with a parallel top plate geometry (50 mm diameter). A 1 mm gap distance was used in all experiments and, where appropriate, evaporation of water during the experiments was minimized by coating the sides of the plate with a low viscosity mineral oil. Amplitude sweeps were performed to measure the strain at which the engineered emulsions break down at a constant angular frequency of $\omega = 10\text{rad/s}$.

1) Synthesis and characterization of PDEAEMA-mNPs.

Hydrophilic superparamagnetic iron oxide nanoparticles (mNPs) with hydroxylated surfaces and average diameters of 25 nm (Alfa-Aesar) were functionalized using bromo trimethoxysilane to produce surface coverage of bromopropyl initiating groups. Atom transfer radical polymerisation was used to graft (2-diethylamino)ethyl methacrylate (DEAEMA) residues from the surfaces thus rendering the mNPs oleophilic (**Scheme S1**).



Scheme S1. Schematic of the synthetic route to PDEAEMA-mNPs.

Surface coverage of ATRP initiating groups: Iron oxide mNPs (1 g) were dispersed in toluene (50ml) using ultrasonic agitation (5 min). An excess of 3-bromopropyl trimethoxysilane (1.5 ml) was added dropwise and the mixture was sonicated for a further 5 min. The reaction mixture was then refluxed overnight using mechanical stirring. The bromine- functionalized nanoparticles (Br-mNPs) were collected using a

NdFeB permanent magnet, followed by repeated washing with acetone and drying under vacuum. Elemental analysis confirmed the degree of functionalization. Based on the carbon content of the nanoparticles (C: 0.94% and H: 0.39%) and their surface area of $46.5 \text{ m}^2 \cdot \text{g}^{-1}$ (calculated using the 25 nm particle size) a number of approximately 6600 functional groups/ mNP was estimated.

Surface Polymerization from mNPs: Br-mNPs (50 mg) were dispersed in isopropanol (10 mL) using ultrasonic agitation (2 mins). DEAEMA (5.0 g) monomer was added to the magnetic dispersion and the mixture was degassed. Copper (I) bromide (0.1 g) and bipyridyl (0.33 g) were added to the degassed mixture. The sealed reaction system was then agitated by rolling at room temperature for 24h. Polymer-grafted mNPs were collected using magnetic decantation, followed by repeated washing with water, ethanol, and hexane. TEM analysis confirmed the polymer-functionalized mNPs remained discrete (**Fig. S1**) and successful grafting was confirmed by FTIR and elemental analyses. FTIR spectra of the PDEAEMA-mNPs (**Fig. S2**) show the presence of typical bands for the functional groups of PDEAEMA such as methylene, methyl vibrations at region between $2980\text{-}2800 \text{ cm}^{-1}$ and carbonyl stretching at 1729 cm^{-1} .

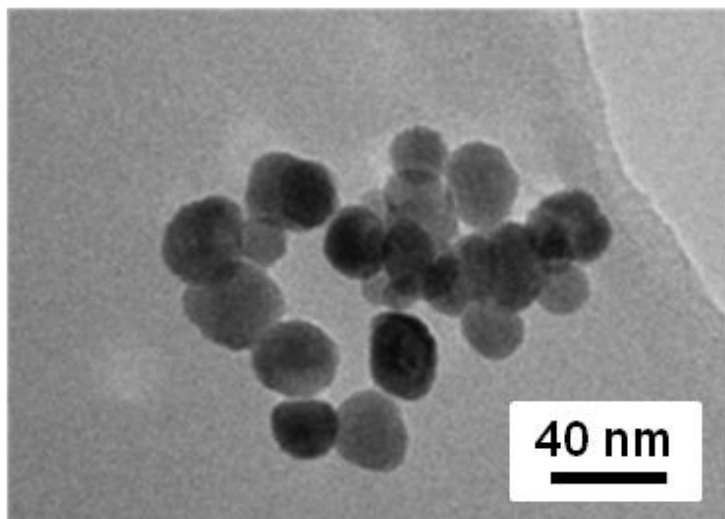


Figure S1. TEM image of the polymer-functionalized magnetic nanoparticles.

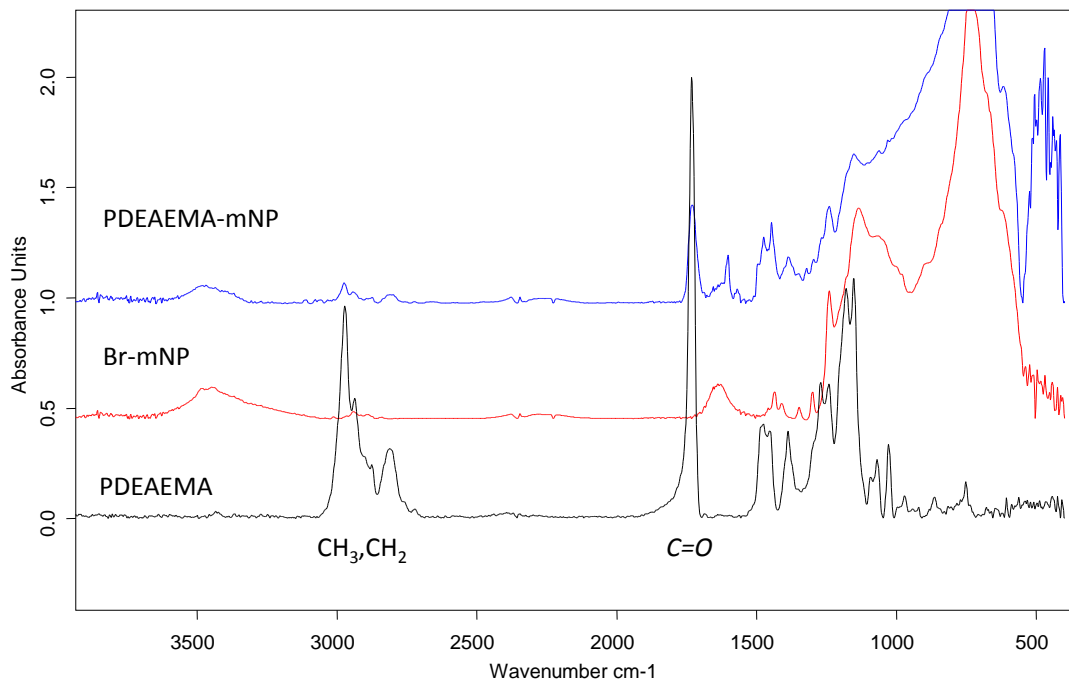


Figure S2. FTIR Spectra of: (i) Bromine-functionalized mNPs, (ii) PDEAEMA homopolymer, and (iii) PDEAEMA-mNP hybrid, oleophilic mNPs.

Elemental analysis was used to confirm the composition of the organic content of the PDEAEMA-mNPs. The Br-mNPs had C: 0.94%, H: 0.39% and no nitrogen. As expected, the PDEAEMA-mNPs showed higher organic content; C:3.61%, H:0.66%, and the presence of N: 0.54%. Subsequently, the grafted polymer component was calculated by abstraction of C and H contents in Br-mNPs from the PDEAEMA-mNPs. The calculated polymer grafted content was; C: 2.67%, H: 0.27 % and N: 0.54%, which in C: H: N mole ratio is 7.5:9:1 (theoretical C: H: N mole ratio of DEA is 10:19:1).

Thermal gravimetric analysis showed that the initiator functionalized magnetic nanoparticles comprised 4.2 wt. % organic component while the polymer-functionalized magnetic nanoparticles comprised 15.5 wt. % organic component (**Fig. S3**).

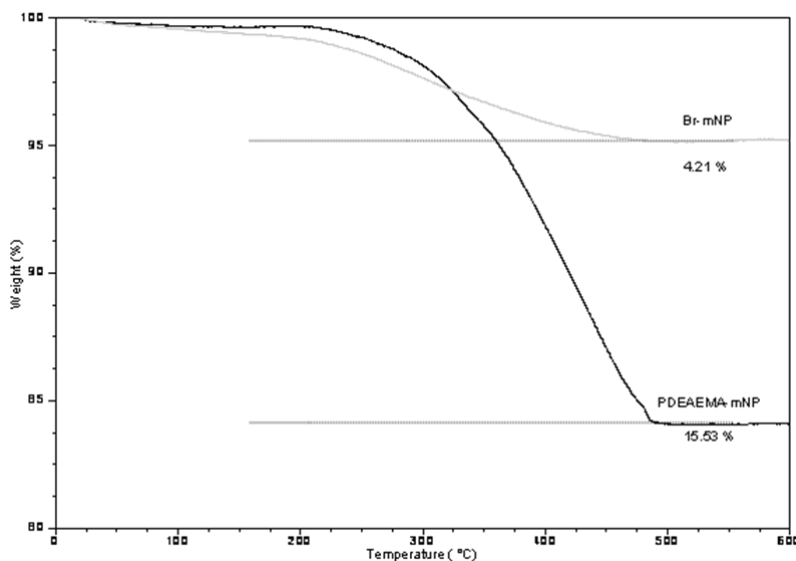


Figure S3. Thermogravimetric curves for the polymer functionalized (black curve, PDEAEMA-mNP) and initiator functionalized (gray curve, Br-mNP) magnetic nanoparticles.

2) Preparation and characterization of magnetic emulsion materials.

Surface-functionalized Magnetic Emulsion Preparation: All studies were performed on emulsions stabilized with copolymer **1** at a concentration of 1 wt% based on the total volume of liquid. All emulsions were produced under identical conditions. An aqueous solution of **1** was prepared (2.0 w/v %) and the pH adjusted to pH 10. An equal volume of dodecane was added containing PDEAEMA-mNPs (0.166 w/v %) and this biphasic mixture was homogenized at 24 000 rpm for 2 min. Following homogenization the emulsions were left to equilibrate for 24 h before characterization. Non-magnetic emulsions were prepared under identical conditions except pure dodecane alone was used.

Magnetic Engineered Emulsion Preparation: All engineered emulsions were created using the creamed layer of the emulsion ($\phi_{oil} = 0.71$) formed after equilibration. The creamed emulsion was pipetted into a tapered vial and HCl was added to trigger hydrogen bonding between the protonated MA and EG residues on the droplet surfaces. Removal of the vial left a self-supporting, monolithic emulsion assembly, which conformed to the dimensions of the vial template in the case of the monolith with an aspect ratio of 1:2. For the monolith with an aspect ratio of 2:1, the same original monolith was sculpted to half its original size using a scalpel ensuring it remained hydrated throughout the process using 1M HCl. Magnetic engineered emulsion spheroids were made by simply dripping aliquots of emulsion (10 μ l) into aqueous acid using a micropipette. Engineered emulsions containing site isolated magnetic engineered emulsion were made by firstly creating a monolithic emulsion assembly using the PDEAEMA-mNP containing emulsion. Upon vial removal a larger vial was placed around the monolith and non-magnetic pH responsive emulsion was aggregated. After 24h aggregation, the larger vial was

removed, and the resulting monolith was sliced horizontally to give 1-2 mm thick 'discs' of this 2-component engineered emulsion with localised magnetic domains.

Demonstration of acid-triggered magnetic emulsion droplet assembly in dilute solution: Aqueous dispersions of the magnetic engineered emulsions (pH 10) were analyzed by laser diffraction. Volume average droplet diameters ($D_{(4,3)}$) were 6.9 μm . On addition of acid ($t = 2$ mins, **Fig. S4**) these averaged sizes increased due to droplet aggregation events. Thus acid-triggered magnetic emulsion aggregation occurs in dilute solution.

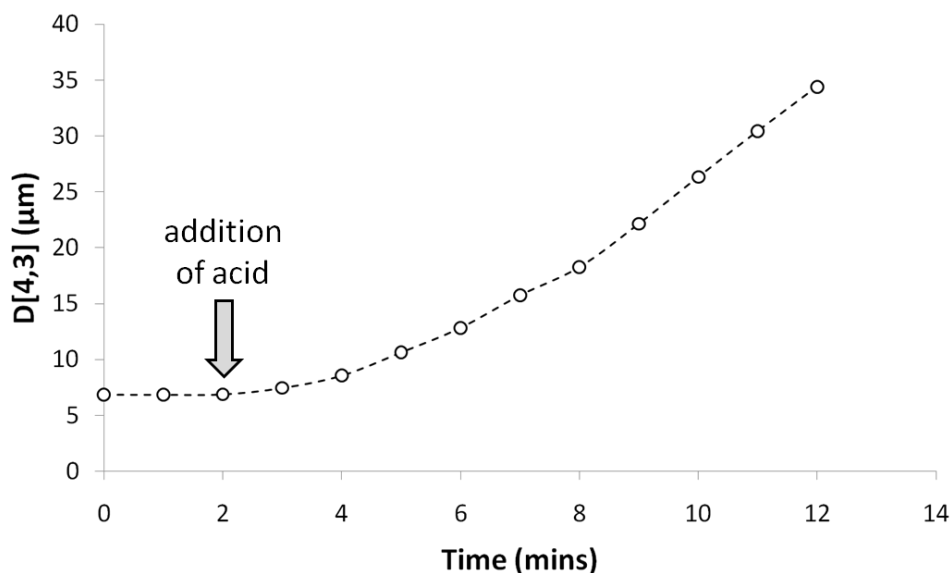


Figure S4. Plot to show the increase in volume average droplet diameter as a function of time following addition of acid.

3) Quantification of Magnetoactuation.

Figure 3i (main text) was assembled from the following measurements, where (with reference to **Fig. S5**):

A = Extent of monolith Magnetoactuation / mm.

B = Magnet distance from monolith / mm.

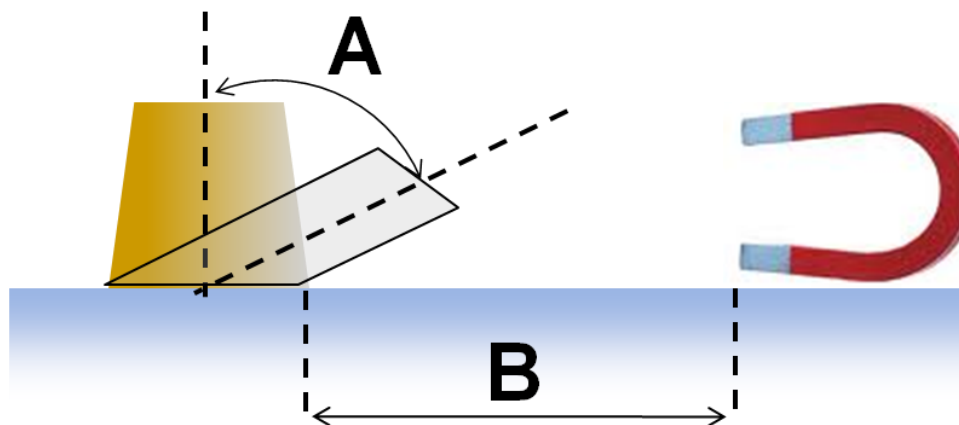


Figure S5. Schematic of the recorded dimensions of Magnetoactuation.

4) Rheometry of magnetic (and non-magnetic) engineered emulsions.

Aggregated engineered emulsions for both mNP-loaded and unloaded (conventional) droplets were assembled *in-situ* on a rheometer plate. Amplitude sweeps were performed on each sample (Fig. S6). The magnitude of G' and the cross-over points (where $G' = G''$) for each sample were in good agreement which confirms the stiffness and strain at which the materials breaks down of these materials are comparable and are not affected by the presence of mNPs.

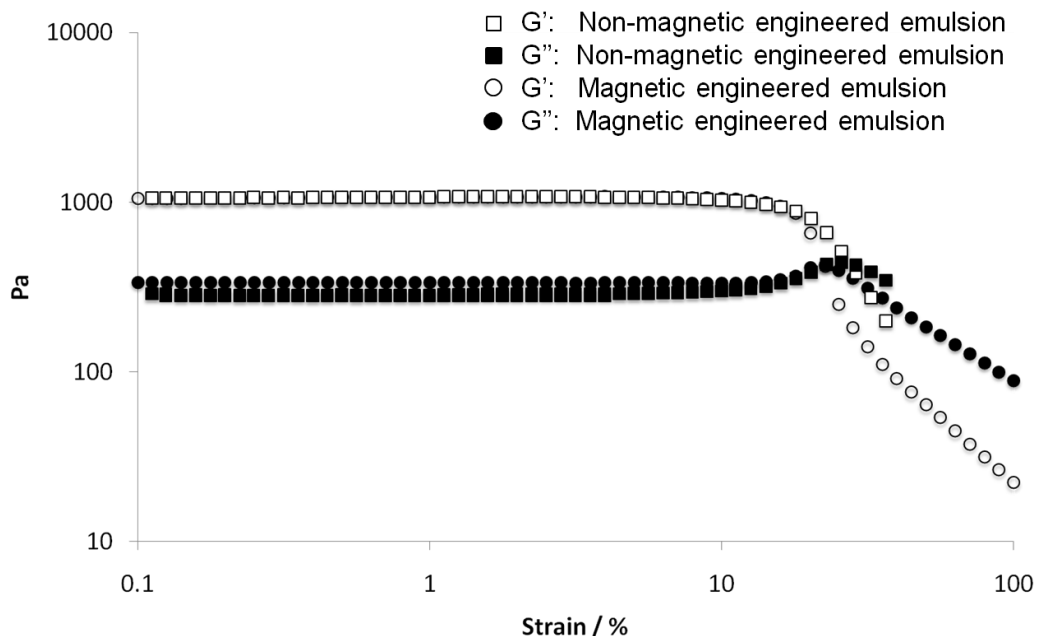


Figure S6. Amplitude sweeps for the native engineered emulsion and magnetic engineered emulsion.