SUPPORTING INFORMATION for

The role of responsive branched copolymer composition in controlling pH-triggered aggregation of "engineered" emulsion droplets

Robert T. Woodward & Jonathan V. M. Weaver*

* To whom correspondence should be addressed: *j.weaver@imperial.ac.uk*

Materials Poly(ethyleneglycol) methacrylate (Mn = 1,100 g.mol-1), methacrylic acid, ethyleneglycol dimethacrylate, 1-dodedanethiol, dodecane and 1-dodecanol were all purchased from Aldrich and used as received. TMS-diazomethane (2M in hexanes) was purchased from Aldrich. Ethanol, methanol and toluene were all standard laboratory grade.

Synthetic Protocols

Synthesis of Polymers: A mixture of PEGMA (6.732 g, 6 mm), MA (10.000 g, 116 mm), ethyleneglycol dimethacrylate (EGDMA, 2.302 g, 12 mm), and 1-dodecanethiol (0.474 g, 12 mm) was degassed. Ethanol (190 mL) was degassed separately and added to the monomer mixture. After heating to 70 ^{o}C, the polymerization was initiated by addition of AIBN (190 mg) and was left stirring for 48 h. Ethanol was then removed by distillation and the polymer was washed with cold diethyl ether and dried. In order to synthesise polymers with varying ratios of monomer composition, the initial ratios of PEGMA to MA were adjusted, while the EGDMA and DDT ratios remained unchanged. Triple-detection GPC (Viscotek TDA-302 system equipped with refractive index, viscometry and dual-angle light scattering detectors; in THF with a flow rate of 1 mL min^{-1}; two Viscotek GMPWXL columns and an additional guard column were used with an oven temperature of 35 °C) was used to determine the molar mass, molar mass distribution and Mark–Houwink α-values. Overlayed intrinsic viscosity vs. molar mass plots are shown in figure S1.

Esterification of methacrylic acid containing copolymers: Polymer (50mg) was placed in a glass vial, to which MeOH (0.2ml) was added. The resulting solution was then agitated by hand until a homogenous solution was formed. After which toluene (0.2ml) was added, and the vial was again agitated to obtain a homogeneous solution. TMS-diazomethane was then added dropwise, until a yellow colour was just apparent which did not become colourless upon agitation. Resulting solutions were purified via evaporation, and left to dry in the vacuum oven for 24hr. ^{1}H NMR was used to confirm the chemical composition by comparing the methyl ester peak of PMMA to peaks corresponding to PEGMA residues – figure S2 shows stacked ^{1}H NMR spectra for the esterified MA-co-PEGMA branched copolymers demonstrating the systematic variation in the MMA:EG ratio following esterfication. NOTE the relative and systematic variation in the intensity of the PEGMA (peaks *c* and *f*) relative to MMA (peak *h*) throughout the series.
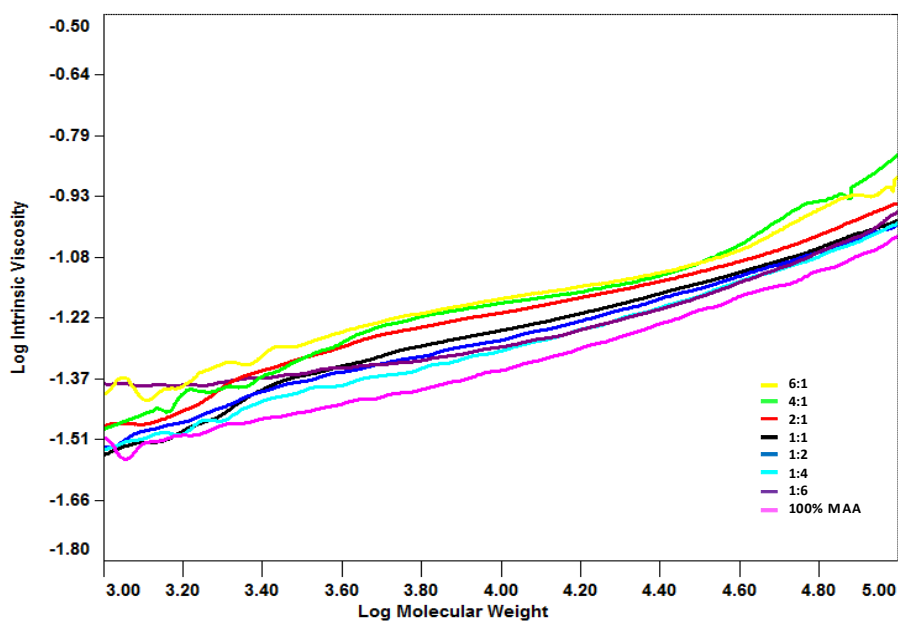
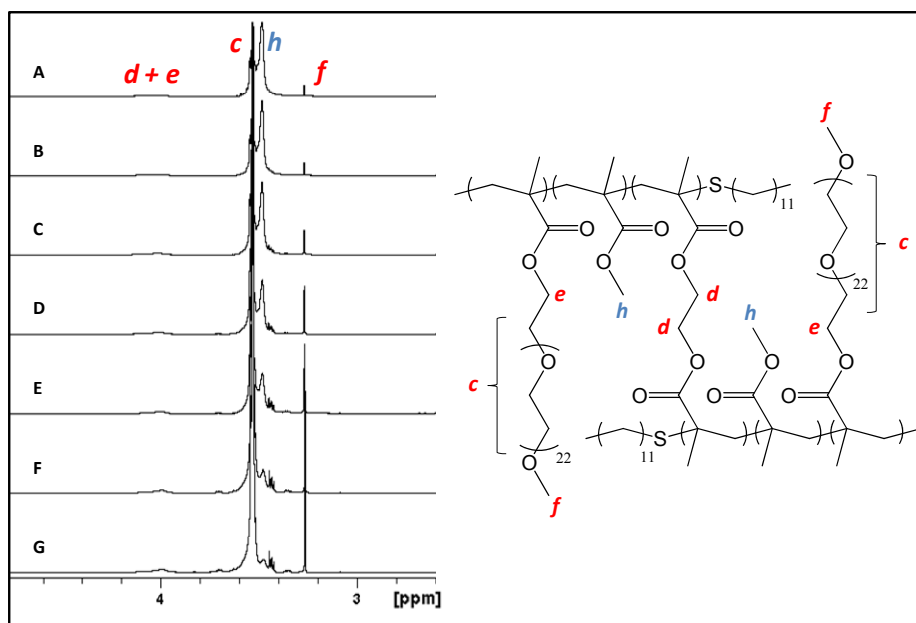**Figure S1.** Molar mass vs. Intrinsic viscosity plots for the MA and PEGMA-based branched copolymers.

Figure S2. ^{1}H NMR spectra recorded in CDCl$_3$ for the esterified MA-co-PEGMA branched copolymers: (A) EG:MA 1:6, (B) EG:MA 1:4, (C) EG:MA 1:2, (D) EG:MA 1:1, (E) EG:MA 2:1, (F) EG:MA 4:1, and (G) EG:MA 6:1

Surface tensiometry: Surface tension profiles of the branched copolymers solutions were performed as a function polymer concentration. A stock solution of each branched (co)polymer was prepared (8.0 w/v %) and this stock solution was diluted by 50 % 1 times and the surface tension of each dilution measured using a Kibron Delta-8 high-throughput tensiometer.

Emulsion fabrication and characterization: An aqueous solution of branched polymer (2.0 w/v %) at pH 10 was prepared and an equal volume of oil was added. This biphasic mixture was homogenized at 24 000 rpm for 2 min using anT25 digital Ultra-Turrax. Following homogenization the emulsions were left to equilibrate for 24 h before characterisation. All emulsion sizes and spans were recorded using laser diffraction (Malvern Mastersizer 2000 equipped with a Hydro 2000 SM dispersion unit). A 40 µL drop of the emulsion was added to the dispersion unit containing 80 mL water (pH adjusted to pH 10 using 1 M NaOH) with a stirring rate of 1200 rpm. The volume-average droplet diameters ($D_{4/3}$) quoted are obtained from at least 5 repeat runs ($D_{4/3} = \Sigma D_{i4}N_i / \Sigma D_{i3}N_i$). The span is a measure of the distribution of the droplet size distribution and is expressed mathematically 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. Images of emulsion droplets and engineered emulsions were obtained using light microscopy (calibrated Meiji MX9300 microscope equipped with digital camera).
1-dodecanol emulsions were prepared using an identical procedure to the other emulsifications however the temperature of all materials, glassware and equipment was maintained between 30 °C and 40 °C. When homogenization was complete, the resulting emulsion was immediately diluted in water (40 °C, 120ml, pH 10) and left to stir overnight, to prevent 'jamming' of the resulting emulsion droplets, due to their non-spherical morphologies.

Engineered Emulsion characterization using laser diffraction: Aggregation of dilute dispersions of the emulsions on addition of acid was measured as a function of time using laser diffraction. All measurements were performed under the aforementioned conditions, but with 20 repeat runs, to provide sufficient time to ascertain the relative rates of droplet interaction. After three repeat measurements of the droplets dispersed at pH 10, HCl (0.8ml, 1M) was added to the dispersion unit, to produce a pH 2 solution. The change in volume-average droplet diameter ($D_{4/3}$) was measured as a function of time.

Engineered Emulsion characterization using rheometry: All rheological experiments were carried out on an Anton Parr Physica MCR101 rheometer, using a parallel top plate with a diameter of 50 mm. 1 mm gap distance was used in all experiment. Amplitude sweeps were performed on all samples measured. An amplitude sweep measures the strain an engineered emulsion can withstand without breaking down at a constant angular frequency ($\omega = 10$ rad s^{-1}).

All engineered emulsions were created using the creamed layer of the resulting emulsion (2.5ml), to which HCl was added (1M, 300ul) homogeneously, while on the rheometer. The resulting mixture was then left to aggregate for 1.5 h in all cases. After this time any excess HCl still present on the surface of the engineered emulsion was removed before measurements were performed. For emulsions which do not aggregate upon the lowering of pH, HCl (1M, 300ul) was added to the emulsion in a vial, allowed to separate for 1.5 h, and then the resulting cream layer was removed (2.5ml) and measured on the rheometer.

Selective aggregation of binary mixtures of contra-functional droplets: For aggregation measurements in the mastersizer, the aforementioned conditions were applied, dividing the initial 40µl into 20µl 100%MA and 20µl 100%EG. Therefore 2.5ml of creamed emulsion sample consisted of 1.25ml of 100%MA and 1.25ml of 100%PEGMA before the addition of acid to trigger aggregation. Light microscope images of the binary mixtures of 100%MA/1-dodecanol and 100%EG/dodecane emulsions were achieved by first imaging the isolated droplets at high and low pH. In order to image the selective binary aggregated droplets two emulsions were then mixed in a vial at pH 10 and then HCl (50µl, 1M) was added to make the solution pH2. The resulting solution was stirred gently and then imaged. NOTE within the images recorded there was evidence of MA-MA droplet interactions

and some multi-droplet aggregation events where MA droplets appear to bridge two EG droplets, however the resolution of this approach was insufficient to draw further conclusions surrounding multiple aggregation events. No EG-EG droplet interactions were observed.