Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

for

Controlling Responsive Emulsion Properties via Polymer Design

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Materials

Poly(ethyleneglycol) methacrylate (M_n = 1,100 g.mol^{-1}, PEGMA), 2-(diethylamino)ethyl methacrylate (DEA), ethyleneglycol dimethacrylate (EGDMA), poly(ethyleneglycol) dimethacrylate (M_n = 875 g.mol^{-1}, PEGDMA), 1-dodedanethiol (DDT), 1-thioglycerol (TG), mercaptopropionic acid (MPA) and *n*-dodecane were all purchased from Aldrich and used as received. Azobis(isobutyronitrile) (AIBN) was purchased from BDH and recrystallized from methanol prior to use. Ethanol was standard laboratory grade.

Experimental Section

Branched copolymers were synthesised using a similar prodecure to that previously described.[1] PEGMA, DEA, branching monomer (either EGDMA or PEGDMA) and chain transfer agent where added to a glass vessel equipped with stirrer bar in pre-determined molar ratios (represented as subscripts in Table 1) and degassed by nitrogen purge for 30 mins. Ethanol was degassed separately and added to the monomer mixture to give a 10 % solution which was heated to 70 ^{o}C under an inert atmosphere. Polymerization was started by addition of AIBN and the reaction was left stirring for 48 h. After this time monomer conversions in excess of 97 % were typically achieved and ethanol was removed by evaporation at reduced pressure. Any unreacted components were removed by precipitation of the polymer into cold diethyl ether or *n*-hexane. The resulting materials were dried in a vacuum oven over night and then characterized (see below). ^{1}H NMR of the purified polymers ($CDCl_3$) revealed that the average molar DEA content was accurate within 8 mol. % when compared to the target polymer composition for samples **1**-**3**. Overlapping proton resonances of the long-chain PEGDMA branching monomer and PEGMA macromonomer prevented reliable compositional determination for samples **4**-**6** via ^{1}H NMR.

Emulsions were prepared by homogenization of aqueous polymer solutions (0.5 %) at pH 10 with an equal volume of *n*-dodecane oil using an IKA Ultra-Turrax T25 homogenizer at 24,000 rpm for 2 mins. Emulsions were left for at least 24 hrs to equilibrate before characterization.

Demulsification of the branched copolymer-stabilized emulsions was triggered by addition of HCl (1M, 100 μL) to the creamed emulsion after 24 hrs equilibration (1 mL). The extent of demulsification was determined visually by measuring the volume of oil which separated (as a clear top phase) from the emulsion as a function of time.

Characterization Techniques

Molecular weights, molecular weight distributions and Mark-Houwink α-values were measured using a Viscotek TDA-302 triple-detection gel permeation chromatography (GPC) equipped with two ViscoGel HHR-N columns and a guard column with a mobile phase of THF and triethylamine (2.5 %) at 35 ^{o}C and a flow rate of 1 mL.min^{-1}. ^{1}H NMR spectra were recorded on 1.0 % copolymer solutions in $CDCl_3$ using a Bruker DPX-400 spectrometer operating at 400 MHz. Dynamic light scattering (DLS) studies were performed using a Viscotek 802 instrument using single mode fibre optics and a 50 mW diode laser (λ = 832 nm) at 20 ^{o}C on 0.5 % aqueous copolymer solutions. Surface tension profiles of the branched copolymers solutions (1.0 %) were performed as a function of solution pH using a Kibron Delta-8 high-throughput surface tensiometer. The aqueous polymer solutions were equilibrated at each pH value for around 2 hrs prior to measurement.
Emulsions were analyzed by light microscopy and laser diffraction. For light microscopy, a drop of the emulsion was placed on a glass slide and viewed using a Meiji Techno MX9000 Series microscope equipped with a Luminera

Infinity 1digital camera. Emulsion droplet diameters and diameter distributions were measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000 SM dispersion unit. A drop of the emulsion was added to the dispersion unit containing approximately 100 mL water (adjusted to either pH 10 using NaOH or pH 2 using HCl) with a stirring rate of 1000 rpm. The cell was repeatedly rinsed using basic water and ethanol after each run. The volume-average droplet diameters ($D_{4/3}$) quoted are obtained from at least 20 repeat runs ($D_{4/3} = \sum D_i^4 N_i / \sum D_i^3 N_i$).

Characterization Data

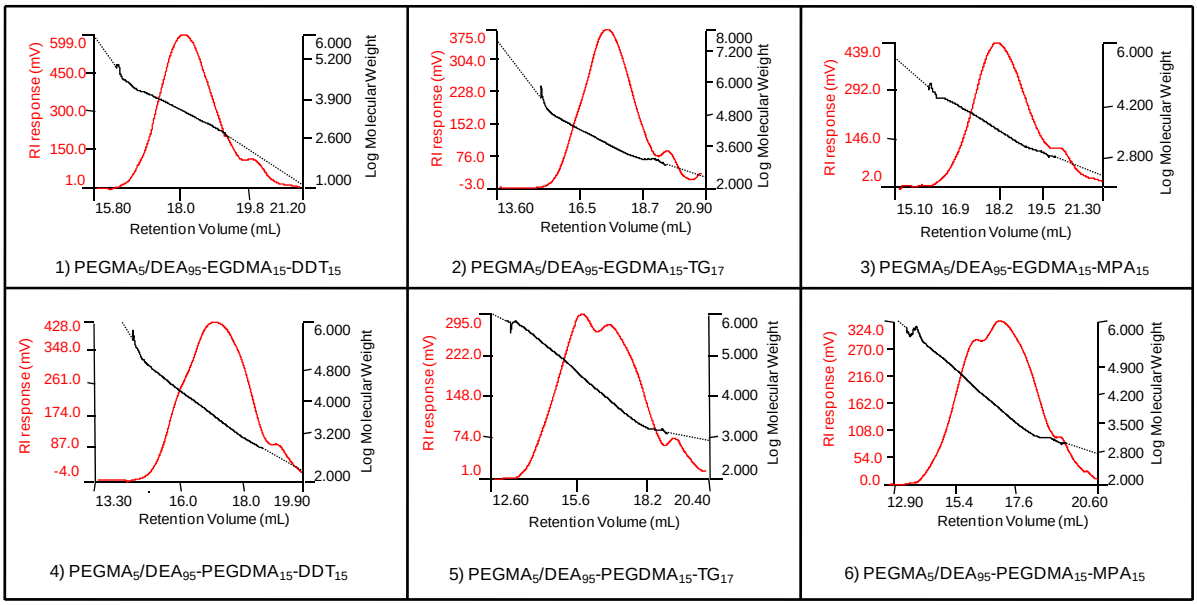

Figure S1. TD-GPC chromatograms (refractive index response and log Molecular weight versus retention volume) for each branched copolymer.

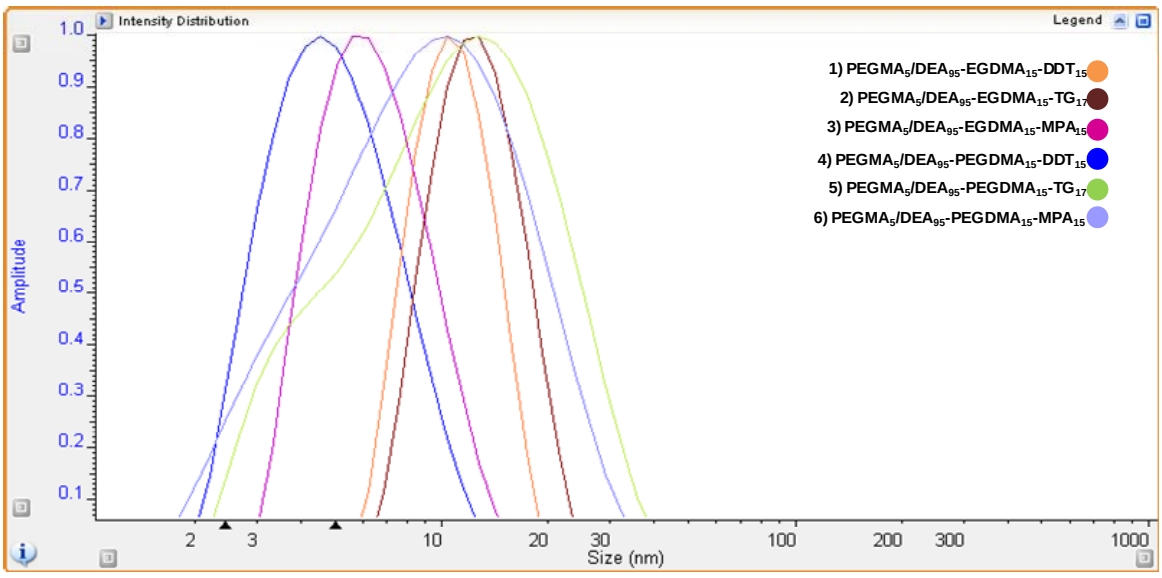

Figure S2. Dynamic light scattering chromatograms for aqueous solutions of each copolymer at pH 10 (0.5 %).

Light micrographs of each branched copolymer stabilized emulsion at pH 10 and pH 2 are shown in Figure S3. Light micrographs of the emulsion samples which remained completely stable at pH 2 (**1** and **4**) are representative of the entire emulsion sample; however the emulsions which remained partially stable at pH 2 (**2** and **3**) are representative of only the stable fraction of the emulsion. Light micrographs of the emulsions which show almost complete demulsification at pH 2 represent a sample taken at the interface between the phase separated liquids.

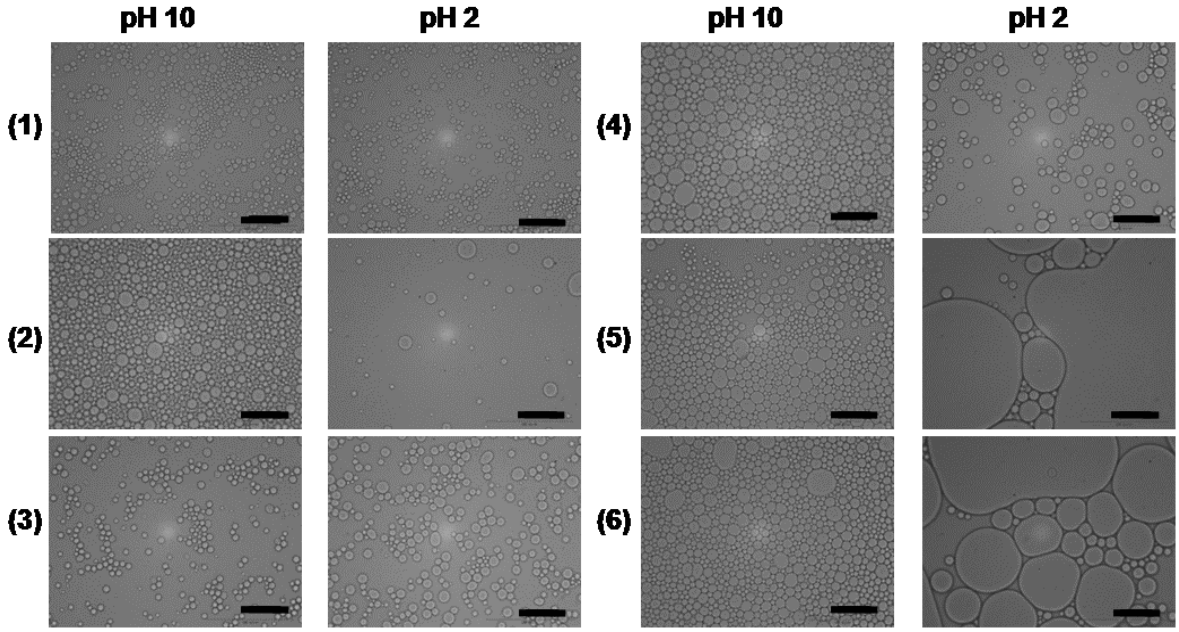

Figure S3. Light micrographs of each of the branched copolymer stabilized emulsions at pH 10 and pH 2. The bracketed numbers indicate the sample IDs in Table 1. Scale bars represent 50 microns.

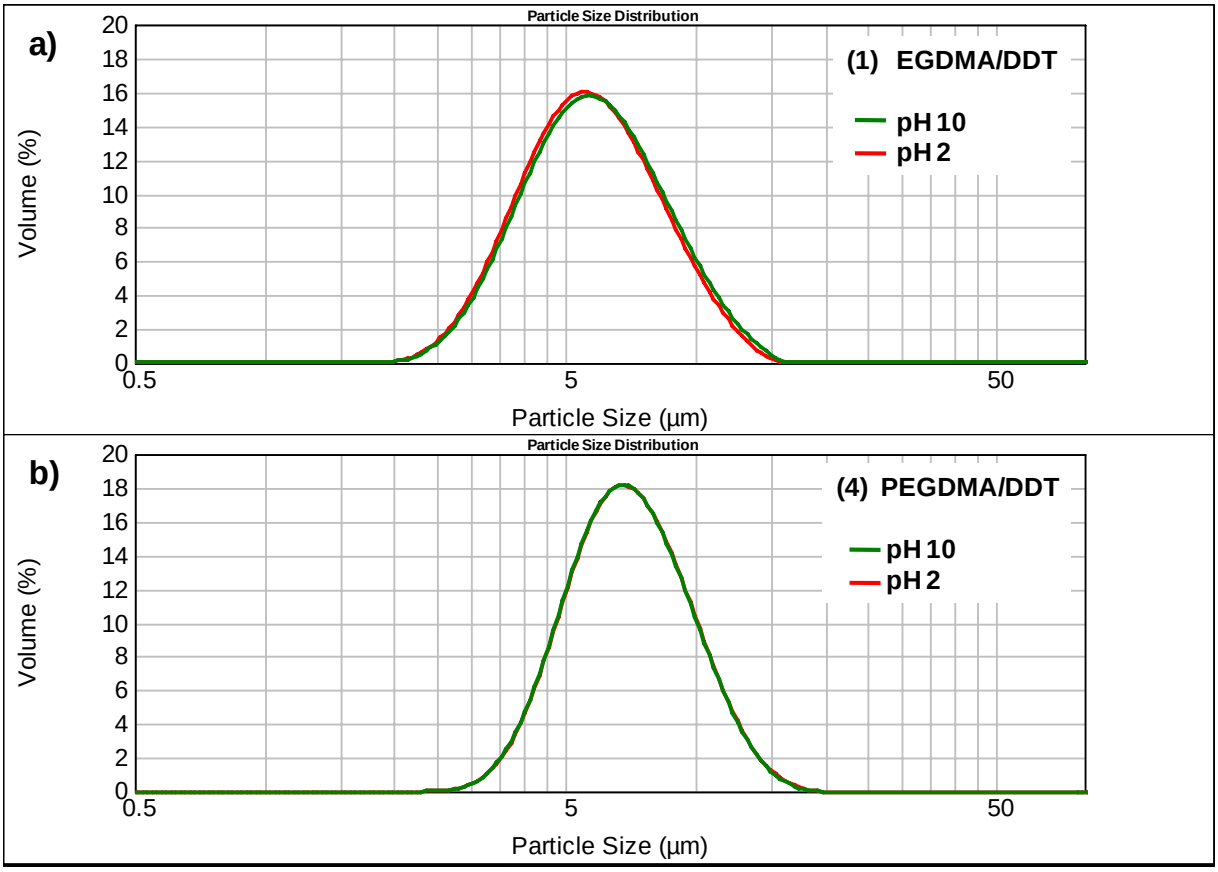

Figure S4. Laser diffraction chromatograms showing droplet size distributions at pH 10 (green) and pH 2 (red) for the 2 emulsions stabilized with branched copolymers with hydrophobic DDT chain-ends (**1** and **4**). a) Sample **1** (short-chain brancher, EGDMA) and b) Sample **4** (long-chain brancher, PEGDMA). [**Note:** The distribution curve for sample **4** at pH 2 in Fig. S4(b), overlays almost identically with the distribution curve recorded at pH 10.]

References

1 J. V. M. Weaver, R. T. Williams, B. J. L. Royles, P. H. Findlay, A. I. Cooper and S. P. Rannard, *Soft Matter*, 2008, **4**, 985.