Electronic Supplementary Information : Reversible assembly of pH responsive branched copolymer-stabilised emulsion *via* electrostatic forces

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1 Materials

2-(Dimethylamino) ethyl methacrylate (DMA), 2-hydroxyethyl methacrylate (HEMA), di(ethylene glycol) dimethacrylate (DEGDMA), 1-dodecanethiol (DDT), triethylamine (TEA), azobis (isobutyronitrile)(AIBN) and all the other reagents were obtained from Sigma-Aldrich unless mentioned and used as received. 3,3-Dilinoleyloxacarbocyanine perchlorate (DiO) and Nile Blue A oxazone (Nile Red) were obtained from Invitrogen and used without any pre-treatment. Acetone, ethanol, ethyl acetate, tetrahydrofuran and n-hexane were purchased in normal laboratory grade from Sigma-Aldrich UK and used as received. All organic solvents were standard laboratory grade. 2-Sulfobenzoic acid cyclic anhydride (SBA) was purchased from Acros Organics.

2 Experimental section

2.1 Synthesis of pDMA (DMA_{100}-$DEGDMA_{13}$-DDT_{15})

DMA (15 g, 95 mmol), DEGDMA (2.830 g, 12 mmol) and DDT (2.83 g, 17 mmol) were added to a 500ml round bottom flask with a magnetic stirrer. Ethanol (206 ml, 10.0 w/v% with respect to reagents) was subsequently added to the mixture. The solution was degassed using N_2 for 30 mins. AIBN (0.219 g, 1.3 mmol) was dissolved in ethanol

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and degassed with N_2 separately for 15 mins. Then, the initiator was then transferred into the round bottom flask and the temperature was raised to 60^{o}C. The reaction mixture was left stirring under an inert atmosphere for 48h. The reaction solution was concentrated under vacuum and purified in cold n-hexane. The polymer was left to dry in a vacuum oven over night at 40^{o}C.

2.2 Synthesis of pHEMA ($HEMA_{100}$-$DEGDMA_{13}$-DTT_{15})

HEMA (15 g, 115 mmol), DEGDMA (3.427 g, 14 mmol) and DDT (3.496 g, 17 mmol) were placed in a 500 mL round bottom flask with a magnetic stirrer. Ethanol (219 ml, 10.0 w/v% with respect to reagents) was then added to the mixture. The solution was degassed by using N_2 for 30 minutes. AIBN (0.205 g) was dissolved in ethanol and degassed with N_2 separately for 15 mins and transferred to the reaction vessel which was subsequently heated to 60^{o}C for 48h. The reaction solution was concentrated under vacuum and purified in cold ethyl acetate. The polymer was left to dry in a vacuum oven over night at 40^{o}C.

2.3 Esterification of hydroxylated branched polymer (pHEMA) using SBA in THF

The esterification of pHEMA was carried out following the protocol given by Vo *et. al*[1]. 100% Esterification was targeted. pHEMA was dissolved (swollen) in THF at 2.5 wt/V% and SBA was added at a molar ratio of 2:1 to the hydroxyl residue. After 30 minutes, an equimolar amount of TEA to SBA was added. The system was left to stir for 48h at room temperature. The solution was then filtered and concentrated by using a rotary evaporator. The final product (pSHEMA) was precipitated in diethyl ether and dried under vacuum overnight leading to a yield of 85%.

2.4 Oil in water emulsion preparation using pHEMA and pDMA

Emulsions were prepared by dissolving 2 wt/vol% branched copolymers in pH 2 adjusted (1M HCl) deionised water. The same quantity of dodecane oil was then added and both

[1]C.-D. Vo, P. D. Iddon and S. P. Armes, Polymer, 2007, 48, 1193–1202.

phases were homogenised by using Cole Permer LABGEN 7 homogenizer at 35000 rpm for 120 seconds. Emulsions were left to equilibrate overnight. When the emulsions were prepared for confocal imaging, 0.03 w/v% hydrophobic florescent dye was dissolved in Dodecane oil prior to emulsion. pDMA was loaded with DiO and pSHEMA with Nile Red.

2.5 Preparation of engineered emulsion monolith assembly

To show selective assembly and strength of emulsion droplets during aggregation engineered monoliths were prepared and digital images were recorded. For this purpose 75μL of pDMA and pSHEMA emulsion dispersed at pH 10 were added to a mould. The pH was then lowered by adding 250μL 1M HCl and left to equilibrate overnight.

3 Characterisation Techniques

3.1 ^{1}H NMR

^{1}H NMR spectra were recorded using Bruker AV400 spectrometer operating at 400 MHz. Spectra were analysed using MestRenova 7.0 software. Samples were prepared by dissolving in deuterated at a 0.2 w/v% ratio. $CDCl_3$ was used for pDMA and D_4-Methanol was used for pHEMA and pSHEMA.

3.2 Gel permeation Chromatography

Average molecular weights, polydispersities and molecular weight distributions were assessed by size exclusion chromatography. For pDMA and pHEMA, a triple detection Viscotek TDA 305 instrument equipped with a Viscotek D6000M and D2500M in line columns was used, calibrated with near monodisperse poly(methyl methacrylate) standards. Dimethylformamide with 0.075% lithium bromide was used as mobile phase flowing at 0.7 mL.min^{-1} at 35^{o}C. pSHEMA was run on a agilent 1260 triple detection GPC equipped with aquagel OH columns, calibrated with poly(ethylene oxide) standards. 0.5 M Sodium acetate pH 4.5 + 30% methanol was used as eluent at 0.8 mL.min^{-1}, 35^{o}C. Samples were prepared by dissolving 10mg in the eluent.

3.3 Interfacial Surface Tension

Pendant drop tensiometer Kruss DSA100 was used to determine the dodecane/water surface tension. Interfacial tension was calculated using computed assisted edge detection and fitting of the Laplace-Young equation. Prior to measurement, 2 wt/vol% of branched copolymer was dissolved in water at pH 2 for pDMA and pH 7 for pSHEMA. A control consisting of polymer-free dodecane/water system was performed.

3.4 Titration

30 mg of polymer (1 mL of emulsion) were dispersed in 25 mL of distilled water adjusted at pH 2, stirred at 100 r.p.m. A 50 μL aliquot of 0.1 M NaOH was then added every 2 minutes and the pH recorded before the addition. pH was measured with a potentiometer OAKTON pH6 Acorn series. pK_as are given on the basis of 5 repeat.

3.5 Dynamic Light Scattering and Zeta Potential

A Malvern Zetasizer (instrument 2000) was used to measure polymers zeta potential and hydrodynamic radius in a solution of NaCl 0.01 M at pH 10, 7 and 2 (adjusted with NaOH 1 M and HCl 1 M). 0.75 mL of solution was used for each measurement. Hydrodynamic radius was recorded at pH 2.

3.6 Particle size by laser diffraction

The Average diameter of emulsion droplets D(4,3) was obtained using a Malvern Mastersizer 2000E equipped with Hydro 2000SM. First the sample dispersion unit was filled with 100 ml of pH10 water and the system was equilibrated for 10 mins at 900 rpm. 20 measurements were recorded at 60 seconds interval from pH10 to pH2 and vice versa.

3.7 Confocal imaging

A Leica SP5 system was used equipped with continuous wave lasers (an Ar-ion laser emitting 458, 475, 488, 496 and 514 nm are directed into the scanning unit to excite the fluorescence of the sample. For this purpose, 50μL of emulsion was diluted using 5ml of

pH10 water and was applied to glass slides. Images were recorded at relevant wavelength of fluorescent dyes.

3.8 Light microscope

A drop of emulsion was placed on a glass slide and viewed using a calibration Olympus BX51.

4 Characterisation data

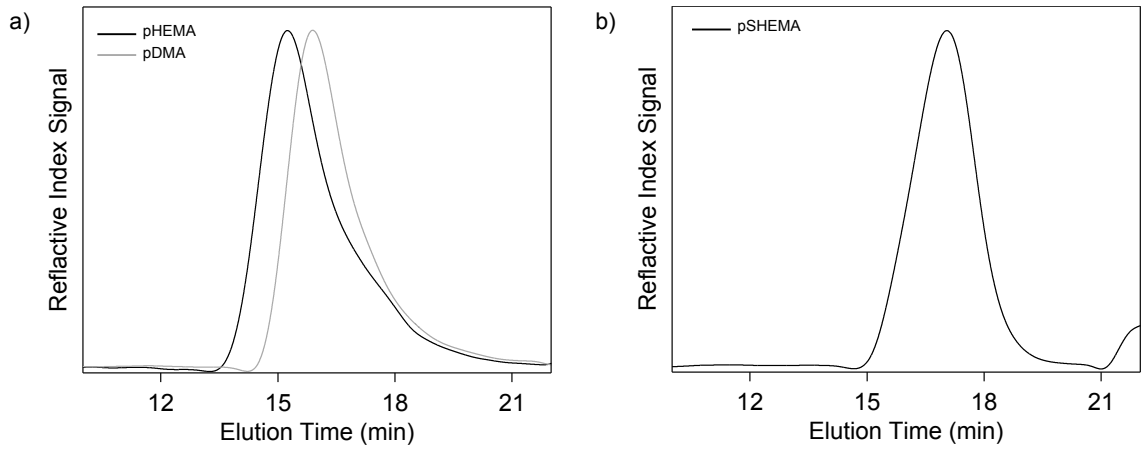

Figure 1: Gel permeation chromatography of a) pDMA and pHEMA in DMF at 0.7 mL.min^{-1} and b) pSHEMA in 0.5M Sodium acetate pH 4.5 + 30% methanol at 0.8 mL.min^{-1}

Table 1: Interfacial surface tension values of dodecane in water at pH 2 and 10.

Entry	IFT (mN.m^{-1})	
	pH 2	pH 10
Polymer-free	40.24	40.05
pDMA	8.18	3.25
pSHEMA	8.17	14.45
pDMA + pSHEMA	8.17	2.99

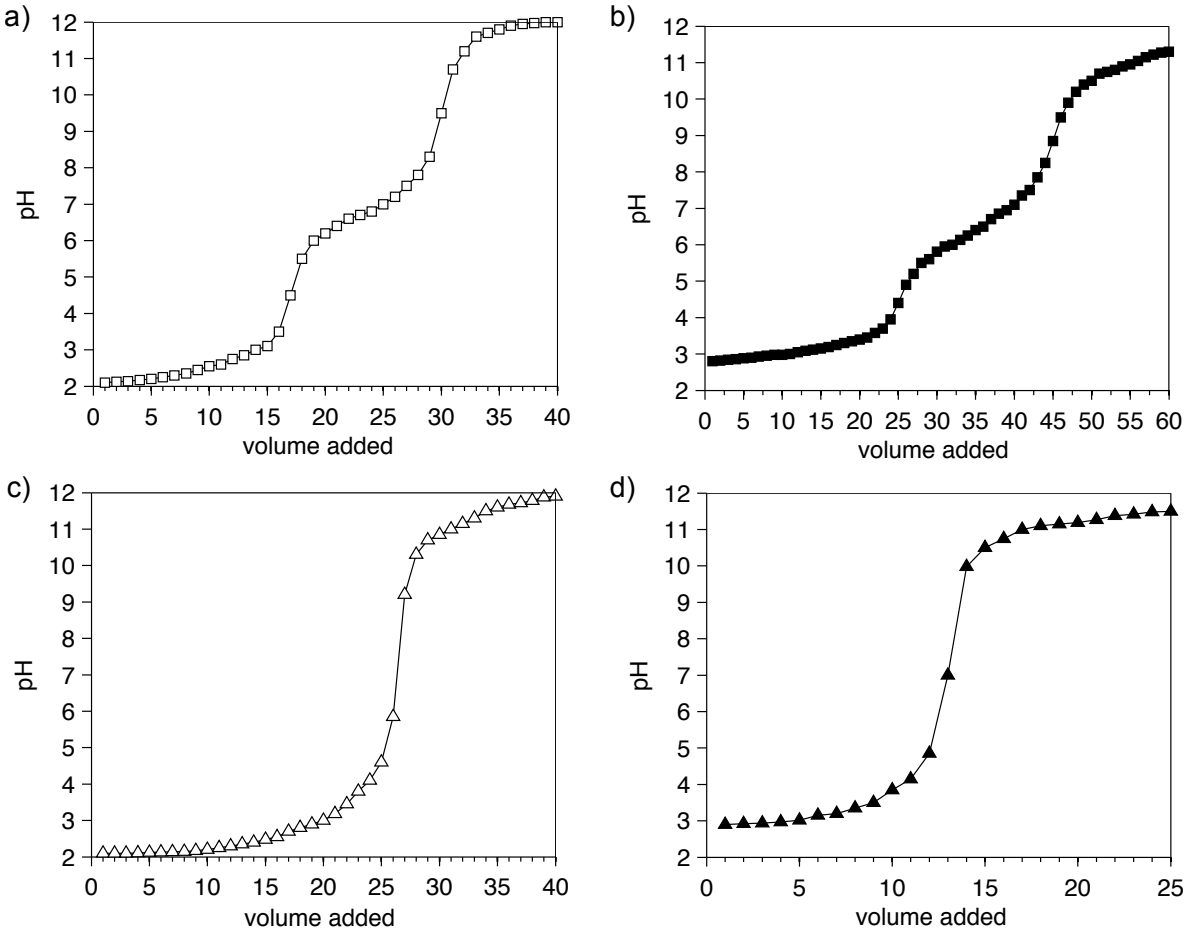

Figure 2: pH response of a) free pDMA b) pDMA stabilised emulsion c) free pSHEMA and d) pSHEMA stabilised emulsion. Unit of volume corresponds to 50 μL 0.1 M NaOH.

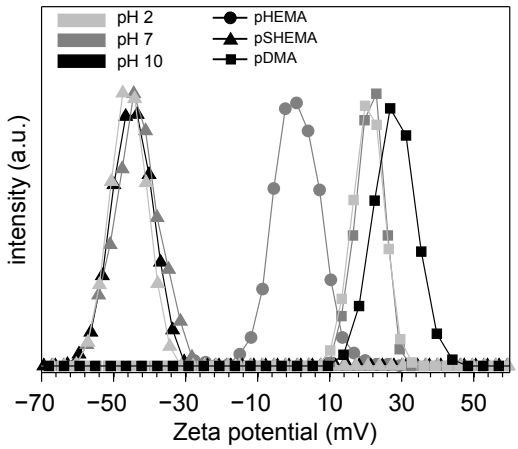

Figure 3: Zeta potentials of pHEMA, pSHEMA and pDMA at different pH.

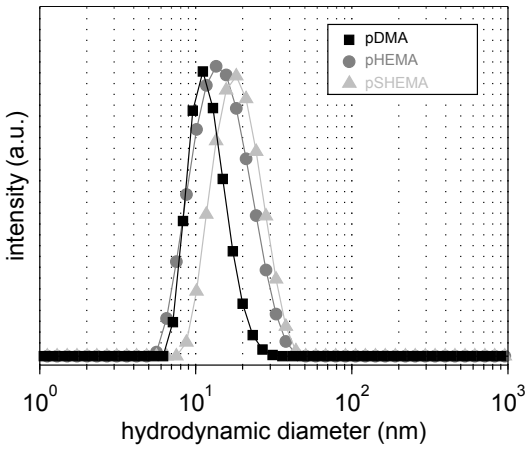

Figure 4: Hydrodynamic radius of the pDMA, pHEMA and pSHEMA at pH 2 obtained by dynamic light scattering.

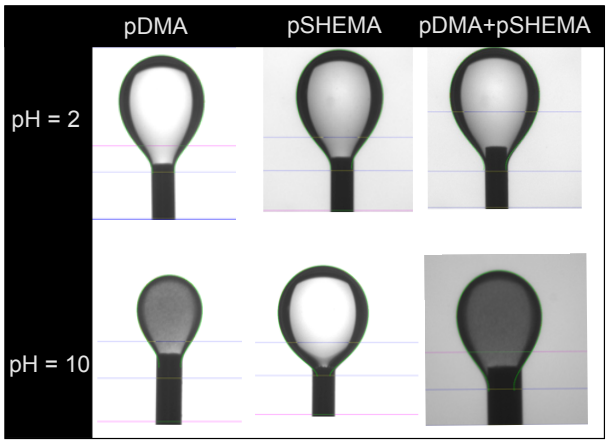

Figure 5: Pendant drops of dodecane in water at pH 2 and 10. Prior to measurement, pDMA, pSHEMA or a equimolar mix was dissolved at 2 wt/vol% in dodecane.

Figure 6: Photograph of emulsions prepared with (right) pDMA and (left) pSHEMA, scale represents 1 cm.

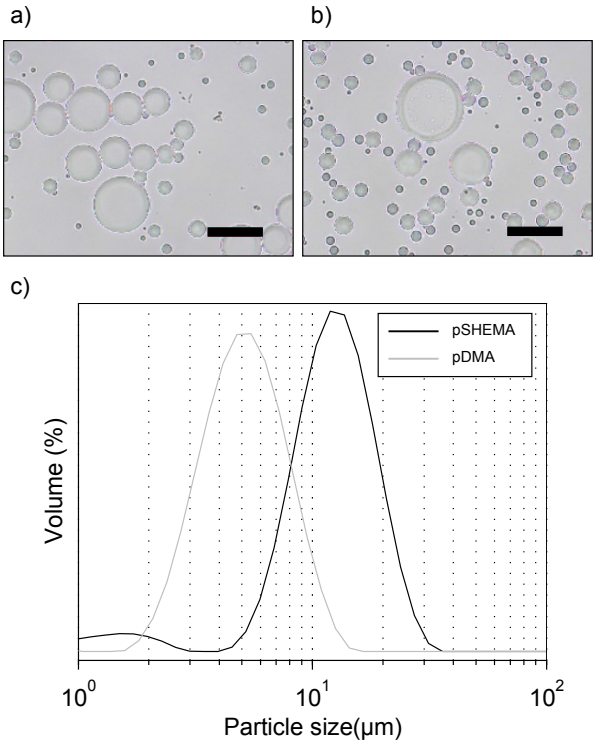

Figure 7: Light microscope photographs of emulsions prepared with a) pSHEMA and b) pDMA with c) their corresponding particle size obtained by laser diffraction, scale for a and b 10 μm.

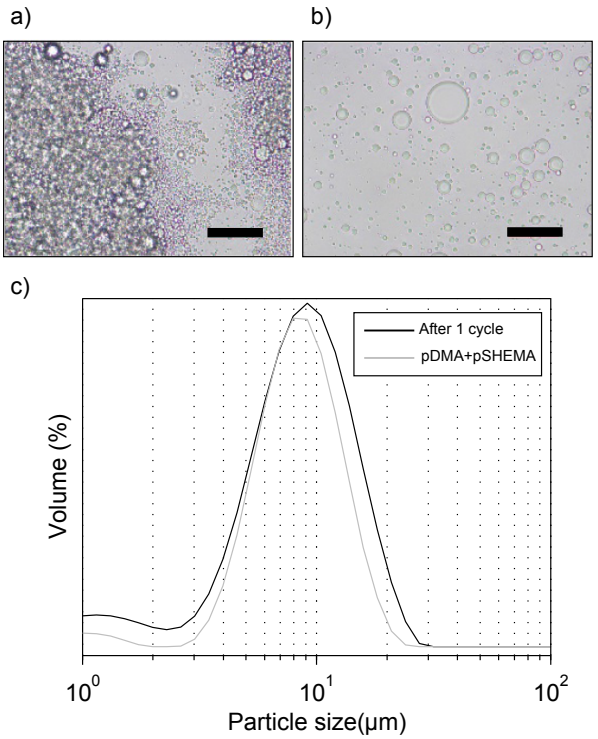

Figure 8: Light micrographs of a) the engineered emulsions prepared from a mix of pSHEMA and pDMA emulsion droplets and b) after redispersion at pH 10, scale bars represent 10 μm. c) Particle size of the pSHEMA, pDMA emulsion droplet mix before and after 1 aggregation cycle.