Supporting Information

Effect of Polymer Architecture and Composition on Gold Nanoparticle Fabrication

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Materials and Methods

Materials

Poly(ethylene glycol) methyl methacrylate (PEGMA, MM=300 g/mol^{-1}), 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%), calcium hydride (CaH$_2$, ≥90%), aluminum oxide activated basic (Al$_2$O$_3$·KOH), 2,2-diphenyl-1-picrylhydrazyl (DPPH), tetrahydrofuran (THF, HPLC grade, polymerisation solvent, ≥99.9%), 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS, polymerisation initiator), methacryloyl chloride (97%), propargyl alcohol (99%), triethylamine (99%), acetone (analytical grade), deuterated chloroform (CDCl$_3$, 99.8%), sodium, potassium and benzoic acid (99.5%) were purchased by Aldrich, UK. Hexane (precipitation solvent) and tetrabutylammonium hydroxide (40% in water) were purchased by Acros Organics, UK. Sodium hydroxide (NaOH, 97%) and hydrochloric acid solution (volumetric, 1M) were the basic and acidic solutions for titration. Gold(III) chloride trihydrate (MM=393.83 g/mol) was the gold source used to form gold nanoparticles.

The catalyst, tetrabutylammonium bibenzoate (TBABB), was previously synthesized by tetrabutylammonium hydroxide and benzoic acid, as reported by Dicker et al and kept dried and under argon until use.[1] Propargyl methacrylate (PMA) was synthesised by the reaction of propargyl alcohol with methacryloyl chloride in THF in the presence of triethylamine, similarly to our previous study.[2]

Purification of Materials

All methacrylate monomers were passed twice through basic Al_2O_3 columns, stirred over CaH_2 for several hours in the presence of DPPH. The monomers and the initiator were also kept under argon and stored in the fridge until they were freshly distilled before polymerization. THF was dried over sodium/potassium amalgam in an inert atmosphere.

Polymer Synthesis

All block copolymers were synthesized via sequential one-pot GTP, similarly to previous studies.[2-10] In a 250 mL round bottom flask that was under argon 10 mg of TBABB was added, followed by injection of 60 ml freshly distilled THF. Then 0.3 mL of MTS (1.5 mmol) was syringed into the flask followed by the addition of the first monomer PEGMA (12mL in 50v/v% in THF, 6.2g, 0.021 mol). The temperature increased from 25.2 to 29.0°C. After the completion of the exothermic reaction, two 0.1 mL samples were taken out of the flask for GPC and ^{1}H NMR analysis. Then the DEAEMA (7.7mL, 7.1g, 0.038 mol) was added and the temperature increased from 26.4 to 29.4°C. After sampling for NMR and GPC, PEGMA was added again (12mL in 50v/v% in THF, 6.2g, 0.021 mol) and the temperature increased from 26.8 to 29.6°C. GPC and NMR samples were taken. Finally, the last monomer, PMA (0.4 mL, 3 mmol) was added. The temperature increased from 28.2 to 28.5°C. Note that strictly speaking this polymer is a tetrablock but the last PMA 'block' is oligomeric and for the purpose of this study we are defining these polymers as a BAB triblock, considering only the DEAEMA (A) and PEGMA (B) blocks. The low DP for the PMA 'block' is not expected to significantly affect the properties of the polymers in solution and is present for post-polymerisation functionalisation via click chemistry. AB diblocks were prepared by adding the DEAEMA first, the PEGMA second and the PMA third. For the ABA triblock the DEAEMA was added first, then the PEGMA and PMA were added simultaneously and again the DEAEMA last. All polymers were

precipitated in cool hexane and then dried for at least 3 days in an oven at room temperature over vacuum.

Gold Particle Fabrication

Seven stock polymer solutions (2 wt%) were prepared; one for each polymer. One stock solution of AuNP was also prepared at 2 wt%. A DI water solution was also prepared. Each solution was adjusted to pH 7, as discussed in the main text. As the amino group of DEAEMA can interact with the AuNP, different ratio of amino groups to gold species were varied in order to investigate the effect of the different ratio on the synthesis of polymers with gold nanoparticles. Four different molar ratios of HAuCl4 to DEAEMA were chosen: 0.1, 0.3, 0.5 and 0.7. A control solution (without gold) was also prepared for each polymer. A total of 35 solutions were prepared in a matrix of 5x7. The final wt% of polymer in all the mixture solutions was set to 1 wt%. After mixing the solutions, the well-plate was left on a shaker at 200 tr/min. The samples were characterised at different time points.

Characterisation

GPC analysis

The resulting, final copolymers and their precursors were analysed by GPC to obtain their molecular mass distribution and molecular mass. The GPC system used is an Agilent SECurity GPC system with a Polymer Standard Service (PSS) SDV analytical linear M column (Agilent technologies UK Ltd., Shropshire, UK). This system is equipped with a "1260 Iso" isocratic pump and an Agilent 1260 refractive index (RI) detector. THF with 5% vol triethylamine was used as the mobile phase at a flow rate of 1 mL·min^{-1}. The column is calibrated with six different linear poly(methyl methacrylate) (PMMA) standard samples of MM 2000, 4000, 8000, 20,000, 50,000, and 100,000 g·mol^{-1}, purchased from Fluka, Sigma Aldrich Co Ltd.

NMR analysis

The final copolymers and their precursors were analysed by NMR using a 400 MHz Avance Bruker NMR spectrometer (Bruker UK Ltd., Coventry, UK). Samples were dried in a vacuum oven at room temperature and diluted with $CDCl_3$. The weight percentage of DEAEMA and PEGMA were calculated by the integral ratio of the signals from the CH_2 ethyl group next to N and closer to ester at 2.6 ppm and the methoxy peak at 3.35 ppm, respectively.

Potentiometric titrations

1% w/w aqueous polymer solutions were titrated from pH 2 to 12 using a standard 0.25 M NaOH aqueous solution. The pH change was monitored by using a portable HI98103 pH checker from Hanna instruments. The pK_a was determined as the pH at 50% protonation of DMAEMA units.[4,11,12]

Dynamic light scattering

The hydrodynamic diameters of 1% w/w aqueous polymer solutions (in two different pHs, 7 and 8) and of the fabricated gold nanoparticles were determined by using a Zetasizer Nano ZSP (Malvern, UK) instrument. The measurements were taken at room temperature, using a backscatter angle of 173°. Three runs were performed for each sample and the results reported are the mean values. Before the DLS measurements, polymer the solutions were filtered through nylon 0.45 µm PTFE syringe filters and they were left to rest to remove the bubbles.

The theoretical hydrodynamic diameters of the micelles were also calculated and compared with the corresponding experimental ones. The calculations were based on two different models. (1) In the case of the BAB and the AB block copolymers the diameter was calculated by adding twice the DP of the PEGMA (B block) with the DP of the hydrophobic DEAEMA (A block) and multiplying by the projected length of one monomer unit (0.254 nm) (2) For the

ABA block copolymers the theoretical hydrodynamic diameter was calculated by adding the DP of the PEGMA block (B block) and the DEAEMA block (A) block and multiplying by the projected length of one monomer unit (0.254 nm). For the calculations, the experimental DPs were adjusted to GPC and ^{1}H NMR results. It should be noted that these calculations make the unrealistic assumption that chains are fully stretched, and also assume that the DEAEMA are hydrophobic thus non-ionised.

Cloud point.

An IKA RCT basic stirrer hotplate, equipped with an IKA ETS-D5 temperature controller, and a continuously stirred water bath were used for visually observing the cloud points of 1% w/w aqueous polymer solutions in glass vials. The solutions were heated from 20 to 80 °C and a visual observation was taken each degree.

Visual observations and UV-Vis Spectroscopy of the Gold Nanoparticle Solutions

Successful synthesis of polymer encapsulated AuNPs was visually confirmed by colour changes of the solutions from yellow to red. The results obtained were confirmed with by UV-vis Spectroscopy using a A SpectraMax M2 machine.

Transmission Electron Microscopy (TEM)

The TEM images were recorded by using an FEI Titan 80-300 instrument, equipped with an image corrector. The instrument operated at 80 kV and an objective aperture 70 mm in size was used in order to enhance contrast in bright field TEM mode. The TEM samples were prepared by pipetting 3.5 µL onto holey-carbon grids. Two minutes after the addition of the solution, any excess of solvent was removed by using a filter paper. The TEM grids were held at an angle of 45°. Any remaining excess solution was removed with a filter paper, and then the grids were left to dry.

Synchotron Small Angle X-ray Scattering (SAXS)

Synchotron SAXS was used to determine the diameter of gold nanoparticles for selected polymers of different architectures. Data were measured on beamline I22 at the Diamond Light Source, U.K,[13] and analysed using SANSview software,[14] using the SphereModel built in model,

$$P(q) = \frac{scale}{V} \left[\frac{3V(\Delta\rho)[\sin{(qR)} - qR\cos{(qR)}]}{(qR)^3} \right] + background$$

where *P(q)* is the form factor, *scale* is a prefactor proportional to the volume fraction, *V* is the particle volume, *q* is the momentum transfer, *R* is the sphere radius, and $\Delta\rho$ is the difference in scattering length density between the particle and the solvent. Polydispersity was modelled with a Gaussian distibution. Scattering length densities were taken as: gold 126×10^{-6} Å^{-1}, water 9.44×10^{-6} Å^{-1} using the NIST calculator[15] and tabulated densities.[16]

Table S1: Molar mass (MM) values (theoretical and experimentally determined by GPC) and dispersity indices of the polymers and their precursors.

No.	Theoretical Polymer Structure [a]	MM$^{theor.}$ [b] (g mol^{-1})	M_n [c] (g mol^{-1})	M_p [c] (g mol^{-1})	Đ [c]
P1	PEGMA$_{14}$	4300	6400	6800	1.10
	PEGMA$_{14}$-*b*-DEAEMA$_{19}$	7900	11400	13000	1.12
	PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$	12100	17100	21100	1.19
	PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$-*b*-PMA$_2$	12348	17400	21900	1.19
P2	PEGMA$_{12}$	3700	5100	5600	1.11
	PEGMA$_{12}$-*b*-DEAEMA$_{26}$	8500	11000	12400	1.15
	PEGMA$_{12}$-*b*-DEAEMA$_{26}$-*b*-PEGMA$_{12}$	12100	15800	19200	1.20
	PEGMA$_{12}$-*b*-DEAEMA$_{26}$-*b*-PEGMA$_{12}$-*b*-PMA$_2$	12348	15400	19500	1.22
P3	PEGMA$_{10}$	3100	4900	5500	1.10
	PEGMA$_{10}$-*b*-DEAEMA$_{32}$	9100	12200	14600	1.14
	PEGMA$_{10}$-*b*-DEAEMA$_{32}$-*b*-PEGMA$_{10}$	12100	16100	20100	1.21
	PEGMA$_{10}$-*b*-DEAEMA$_{32}$-*b*-PEGMA$_{10}$-*b*-PMA$_2$	12348	17100	20900	1.19
P4	DEAEMA$_{19}$	3700	5000	5500	1.08
	DEAEMA$_{19}$-*b*-PEGMA$_{28}$	12100	15000	17900	1.19
	DEAEMA$_{19}$-*b*-PEGM$_{28}$-*b*-PMA$_2$	12348	14700	17900	1.20
P5	DEAEMA$_{26}$	4900	7400	8100	1.08
	DEAEMA$_{26}$-*b*-PEGMA$_{24}$	12100	16800	20300	1.15
	DEAEMA$_{26}$-*b*-PEGMA$_{24}$-*b*-PMA$_2$	12348	16500	19400	1.17
P6	DEAEMA$_{32}$	6100	8700	9500	1.08
	DEAEMA$_{32}$-*b*-PEGMA$_{20}$	12100	16000	18100	1.12
	DEAEMA$_{32}$-*b*-PEGMA$_{20}$-*b*-PMA$_2$	12348	16400	19200	1.12
P7	DEAEMA$_{10}$	1900	2700	3000	1.11
	DEAEMA$_{10}$-*b*-(PEGMA$_{28}$-*co*-PMA$_2$)	10448	12200	15500	1.24
	DEAEMA$_{10}$-*b*-(PEGMA$_{28}$-*co*-PMA$_2$)-*b*-DEAEMA$_{10}$	12348	13900	18600	1.29

[a] PEGMA, DEAEMA and PMA stand form penta(ethylene glycol)methyl ether methacrylate, 2-(diethylamino)ethyl methacrylate, and propargyl methacrylate, respectively.

[b] The theoretical molar mass values have been calculated by adding the product of the molar mass of each repeated unit by the degree of polymerisation. 100 g mol^{-1} corresponds to the part of the initiator that stays on the polymer chain after the completion of the polymerisation, thus it is added to the result.

[c] The values of the number-average molar mass (M_n), the molar mass that corresponds to the maximum of the peak (M_p), and the dispersity indices (Đ) are based on a linear calibration using well-defined poly(methyl methacrylate) standard samples of molar mass equal to 2000, 4000, 8000, 20000, 50000, 10000 100 g mol^{-1}.
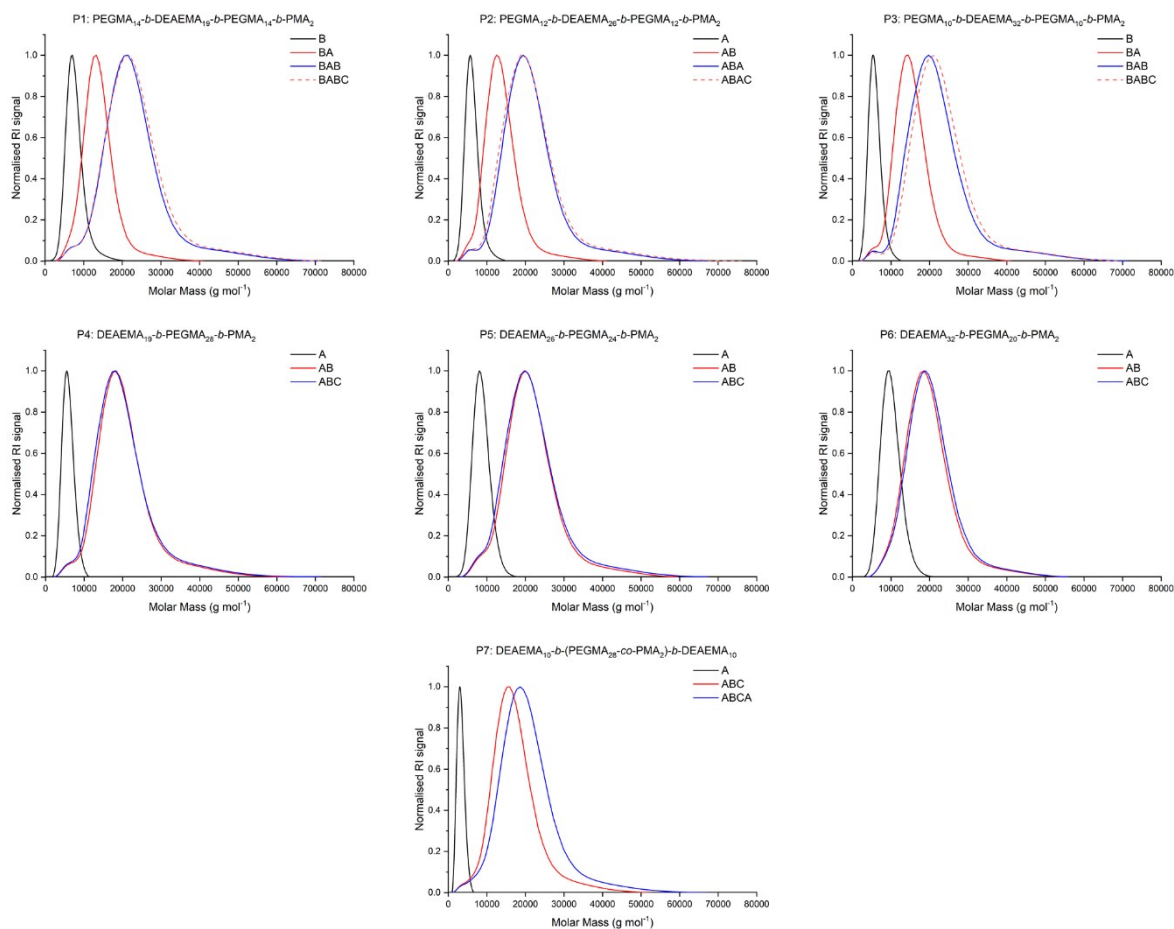
Figure S1: The GPC traces for all synthesised polymers and their precursors. The GPC traces of the homopolymers and the diblock copolymers are shown in black and red, respectively. The GPC traces resulted after the third and fourth addition (if any) are coloured in blue solid and red dotted lines, respectively.
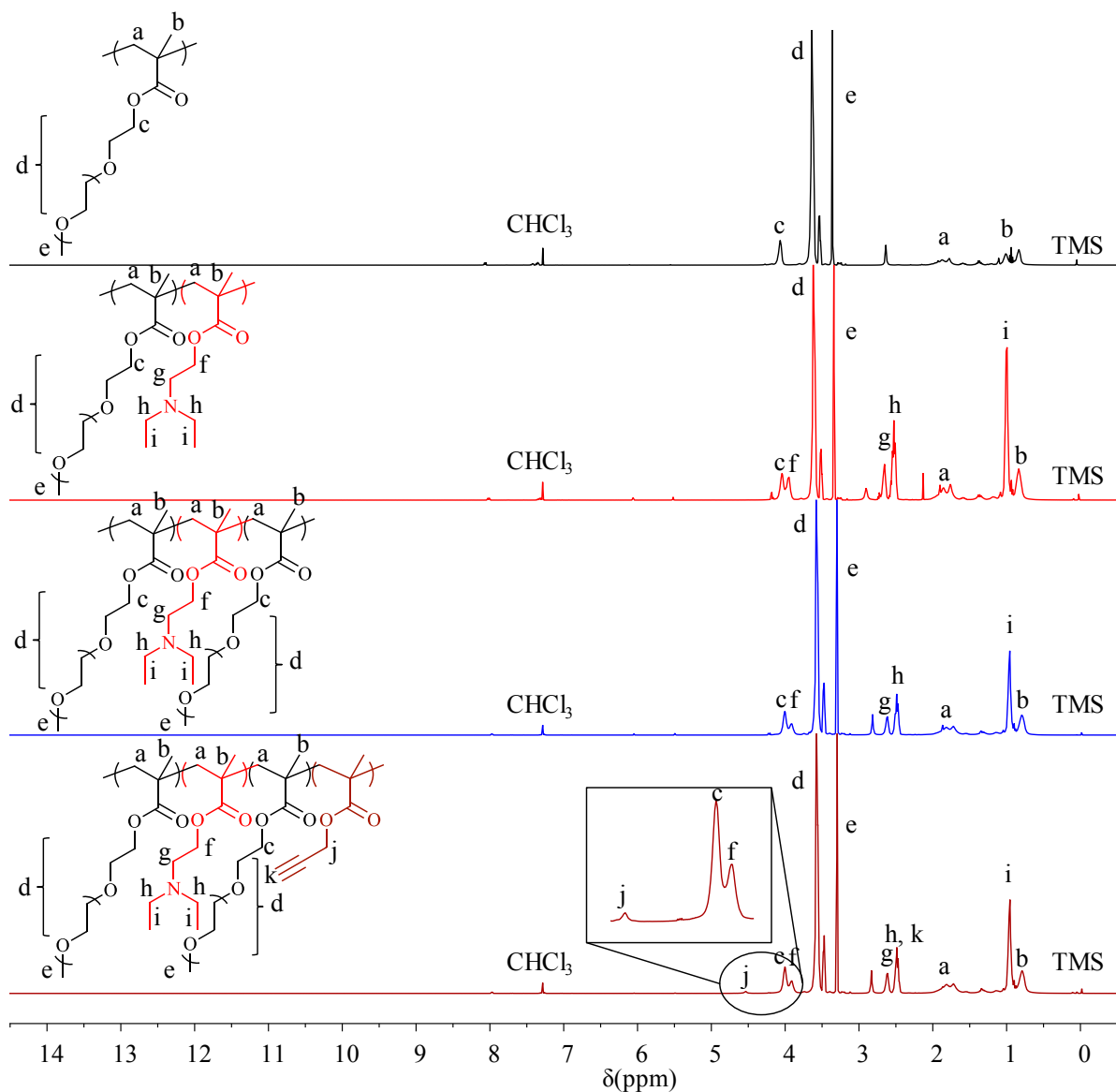
Figure S2: The ^{1}H NMR spectra of Polymer 1 with theoretical chemical structure PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$-*b*-PMA$_2$ (shown in dark red-bottom) and its linear precursors: PEGMA$_{14}$ shown in black, PEGMA$_{14}$-*b*-DEAEMA$_{19}$ shown in red and PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$ shown in blue, respectively.
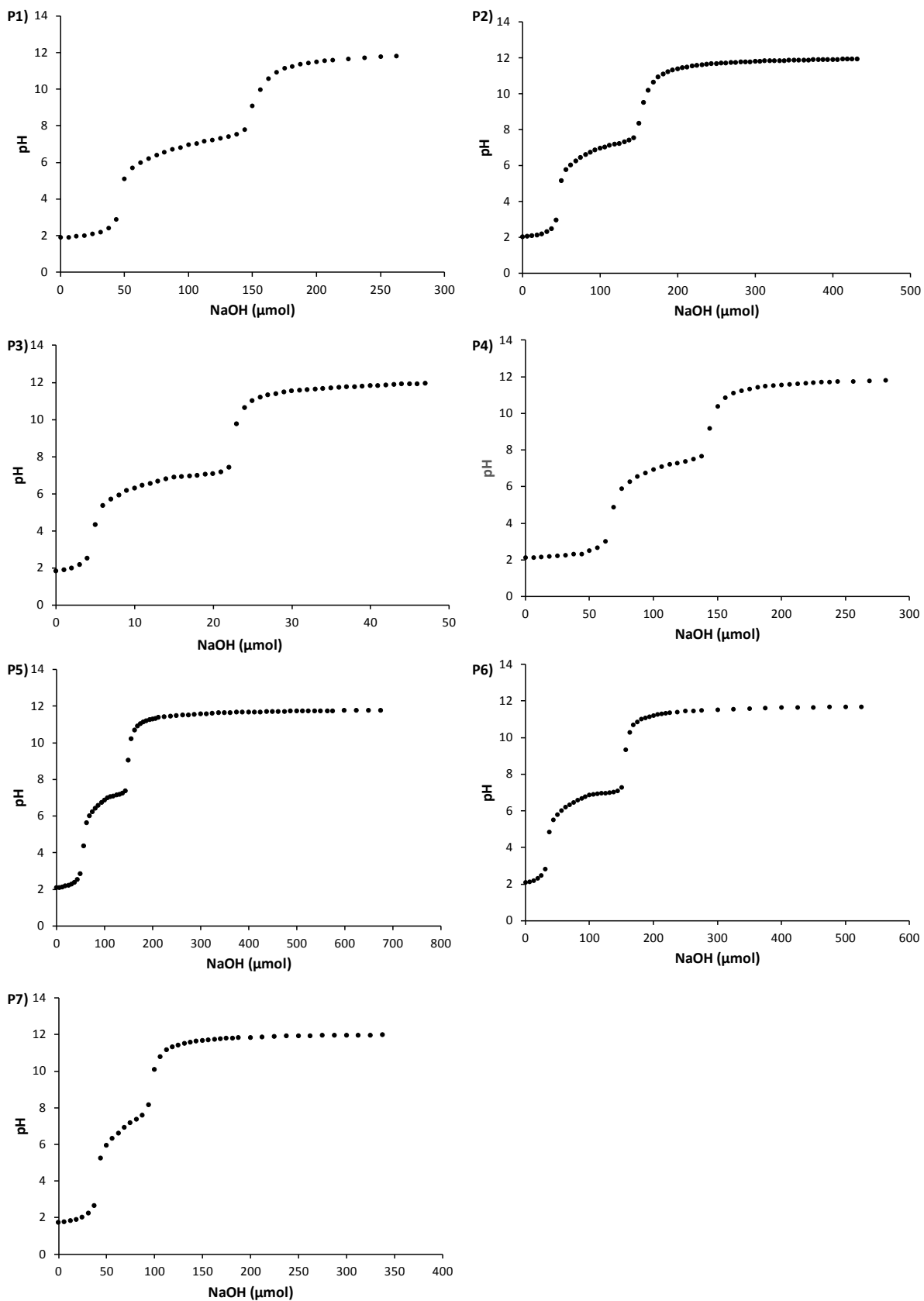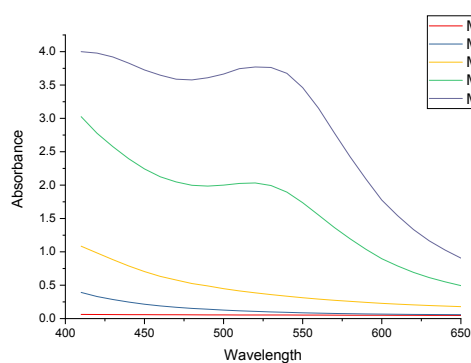
Figure S3: Titration curves of the polymers studied in the current study.

Table S2: Theoretical polymer structures and experimental diameter values and polydispersity (PDI) values, as resulted by dynamic light scattering (DLS) for i) non-loaded micelles at pH ≈ 8, ii) non-loaded micelles at pH ≈ 7, and iii) Au-loaded micelles at pH ≈ 7 and molar ratio of HAuCl4 to DEAEMA 0.5 (Average of 2 runs)

No.	Theoretical Polymer Structure	Diameter / nm					PDI
		Average ± Std Dev (by Intensity)	Z-Average	Maximum by Intensity	Maximum by Number	Maximum by Volume	
i)	**Non-loaded micelles at pH ≈ 8**						
P1	PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$-*b*-PMA$_2$	15 ± 7 (98.6%)	12.5	13.5	6.5	7.5	0.182
		4000 ± 1000 (1.4%)		4800.0			
P2	PEGMA$_{12}$-*b*-DEAEMA$_{26}$-*b*-PEGMA$_{12}$-*b*-PMA$_2$	12 ± 4 (100%)	11.2	11.7	7.5	8.7	0.084
P3	PEGMA$_{10}$-*b*-DEAEMA$_{32}$-*b*-PEGMA$_{10}$-*b*-PMA$_2$	13 ± 4 (100%)	12.1	11.7	7.5	8.7	0.064
P4	DEAEMA$_{19}$-*b*-PEGMA$_{28}$-*b*-PMA$_2$	27 ± 14 (72.0%)	28.7	21.0	11.7	13.5	0.366
		150 ± 70 (28.0%)		164.0			
P5	DEAEMA$_{26}$-*b*-PEGMA$_{24}$-*b*-PMA$_2$	21 ± 6 (100%)	19.5	21.0	11.7	13.5	0.062
P6	DEAEMA$_{32}$-*b*-PEGMA$_{20}$-*b*-PMA$_2$	28 ± 9 (100%)	24.7	24.4	15.7	18.2	0.110
P7	DEAEMA$_{10}$-*b*-(PEGMA$_{28}$-*co*-PMA$_2$)-*b*-DEAEMA$_{10}$	19 ± 7 (48.7%)	16.8	18.2	10.1	11.7	0.113
ii)	**Non-loaded micelles at pH ≈ 7**						
No.	Theoretical Polymer Structure	Average ± Std Dev (by Intensity)	Z-Average	Maximum by Intensity	Maximum by Number	Maximum By Volume	PDI
P1	PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$-*b*-PMA$_2$	130 ± 70 (77.8%)	29.7	106.0	1.5	1.7	1.000
		2 ± 1 (17.4%)		2.0			
		14 ± 4 (4.8%)		13.5			
P2	PEGMA$_{12}$-*b*-DEAEMA$_{26}$-*b*-PEGMA$_{12}$-*b*-PMA$_2$	19 ± 8 (92.6%)	14.6	18.2	1.7	10.1	0.262
		1.9 ± 0.4 (5.8%)		2.0			
		4400 ± 900 (1.6%)		5560			
P3	PEGMA$_{10}$-*b*-DEAEMA$_{32}$-*b*-PEGMA$_{10}$-*b*-PMA$_2$	15 ± 6 (100%)	12.9	13.5	7.5	8.7	0.139
P4	DEAEMA$_{19}$-*b*-PEGMA$_{28}$-*b*-PMA$_2$	29 ± 13 (72.6%)	30.2	24.4	13.5	15.7	0.413
		200 ± 100 (27.4%)		190.0			
P5	DEAEMA$_{26}$-*b*-PEGMA$_{24}$-*b*-PMA$_2$	23 ± 7 (100%)	21.2	21.0	13.5	15.7	0.066
P6	DEAEMA$_{32}$-*b*-PEGMA$_{20}$-*b*-PMA$_2$	29 ± 9 (100%)	26.8	28.2	15.7	18.2	0.109
P7	DEAEMA$_{10}$-*b*-(PEGMA$_{28}$-*co*-PMA$_2$)-*b*-DEAEMA$_{10}$	19 ± 9 (48.7%)	17.8	18.2	1.5	1.7	0.722
		110 ± 50 (35.7%)		5560			
		2.1 ± 0.4 (13.8%)		2.3			
iii)	**Au-loaded micelles at pH ≈ 7 and molar ratio of HAuCl$_4$ to DEAEMA 0.5 (Average of 2 runs)**						
No.	Theoretical Polymer Structure	Average ± Std Dev (by Intensity)	Z-Average	Maximum by Intensity	Maximum by Number	Maximum By Volume	PDI
P1	PEGMA$_{14}$-*b*-DEAEMA$_{19}$-*b*-PEGMA$_{14}$-*b*-PMA$_2$	200 ± 70 (57.9%)	68	31	17.0	20.0	0.514
		35 ± 9 (39.4%)					
		5100 ± 550 (3.1%)					
P2	PEGMA$_{12}$-*b*-DEAEMA$_{26}$-*b*-PEGMA$_{12}$-*b*-PMA$_2$	250 ± 100 (80%)	136	31	18.0	20.0	0.556
		14 ± 5 (15.7%)					
		4500 ± 900 (4.3%)					
P3	PEGMA$_{10}$-*b*-DEAEMA$_{32}$-*b*-PEGMA$_{10}$-*b*-PMA$_2$	180 ± 100 (61.9%)	79	31	19.6	21.0	0.451
		30 ± 20 (37.2%)					
		2500 ± 400 (0.9%)					
P4	DEAEMA$_{19}$-*b*-PEGMA$_{28}$-*b*-PMA$_2$	160 ± 90 (79.6%)	82	33	20.0	24.4	0.489
		20 ± 5 (18%)					
		4900 ± 700 (2.5%)					
		300 ± 100 (85.9%)					

		32 ± 8 (11.7%)					
		5000 ± 500 (2.4%)					
		190 ± 90 (69.4%)					
P6	DEAEMA$_{32}$-b-PEGMA$_{20}$-b-PMA$_2$	40 ± 10 (28.7%)	84	39	21.0	25.0	0.565
		5100 ± 600 (2%)					
		220 ± 90 (45.1%)					
P7	DEAEMA$_{10}$-b-(PEGMA$_{28}$-co-PMA$_2$)-b-DEAEMA$_{10}$	40 ± 20 (51.9%)	64	31	18	21.0	0.436
		4900 ± 700					

(a) After 24h

(b) After 48h
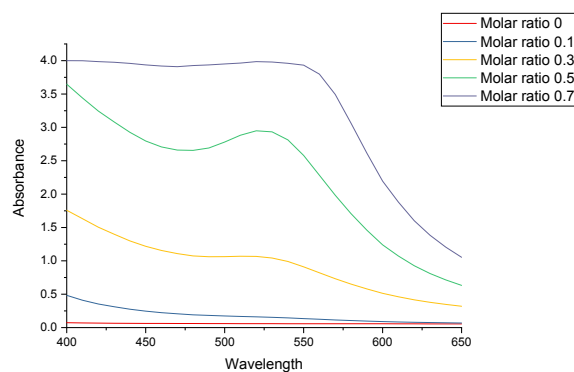
Figure S4: Original UV-Vis spectra of Polymer 6, DEAEMA$_{32}$-b-PEGMA$_{20}$-b-PMA$_2$, at different ratios of HAuCl$_4$ to DEAEMA groups (a) after 24h, and (b) after 48h.
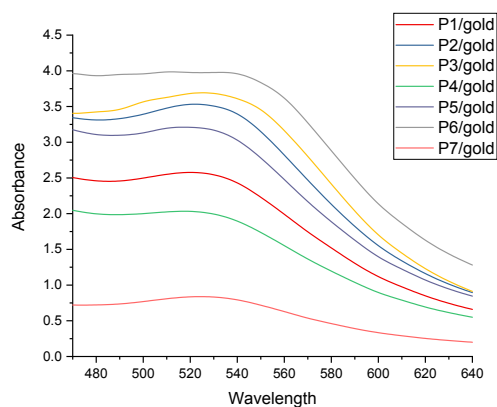

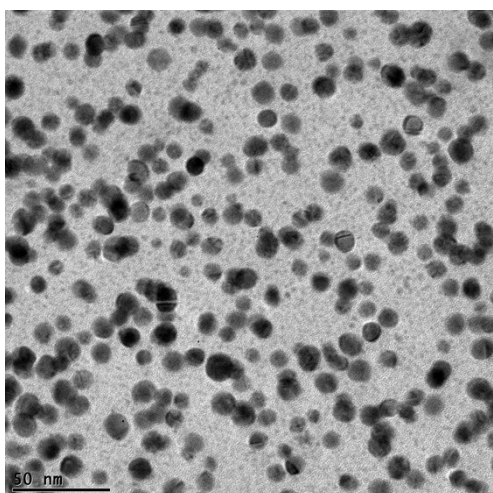**Figure S5:** Original UV-Vis spectra of all the polymers at HAuCl$_4$ to DEAEMA ratio of 0.5 after 24h.

Figure S6: TEM image of the AuNPs formed by Polymer 6 with theoretical polymer structure DEAEMA$_{32}$-*b*-PEGMA$_{20}$-*b*-PMA$_2$ at a HAuCl$_4$:DEAEMA molar ratio of 0.5.
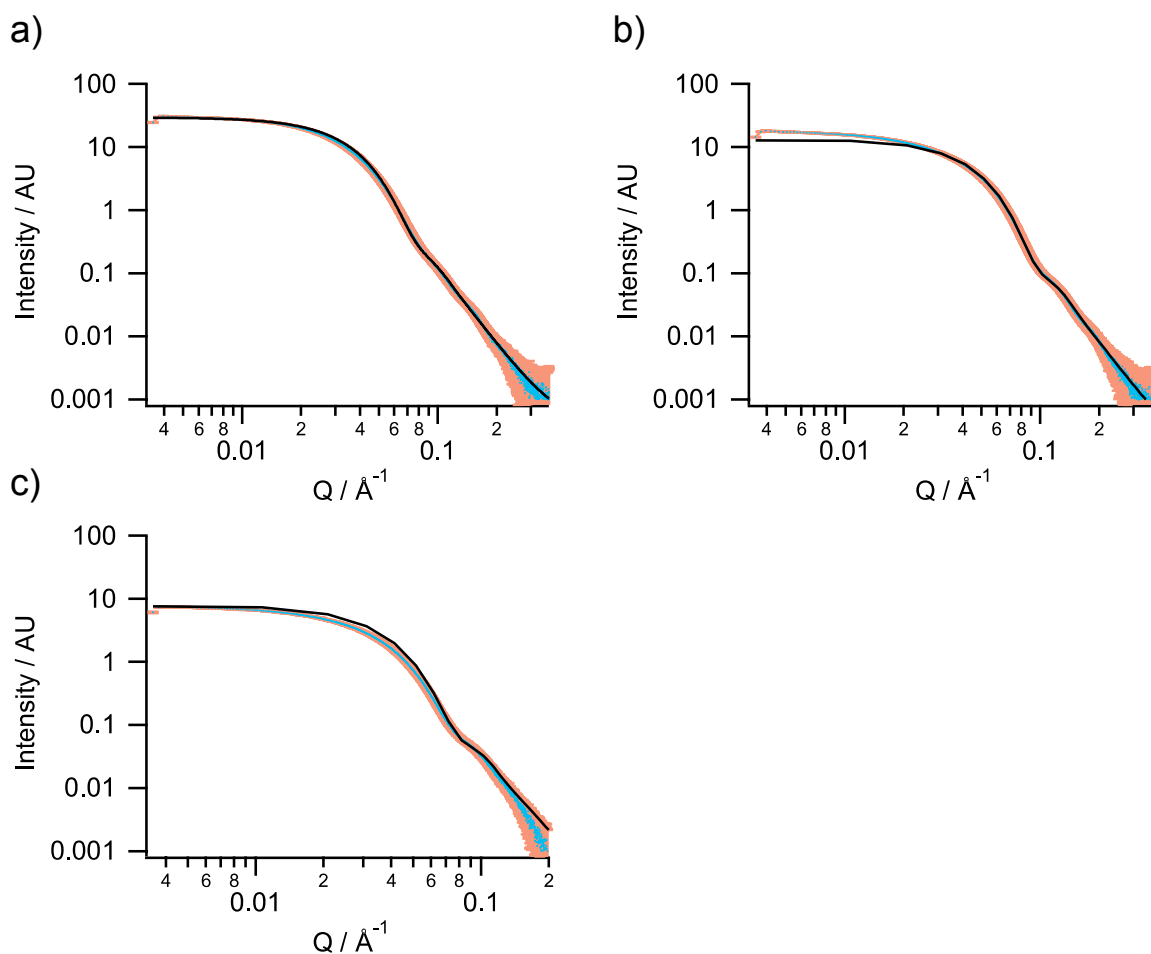
Figure S7: Small Angle X-ray Scattering (SAXS) from selected gold nanoparticles, synthesized using examples of different polymer architectures. (a) A PEGMA-DEAEMA-PEGMA triblock assumed to form classical spherical micelles, Polymer 3 (numbering as per Table 1); (b) a PEGMA-DEAEMA diblock assumed to form classical spherical micelles, Polymer 6; (c) a DEAEMA-PEGMA-DEAMEA triblock assumed to form flower micelles, Polymer 7. Plots show scattered intensity (cyan markers with light red error bars) versus momentum transfer, Q, together with fits (solid black line) to a sphere model.

Table S3: Sphere model fitting parameters for SAXS data, corresponding to solid black lines in Figure S4. Parameter names correspond to the SphereModel package on SANSView (see

No. of Polymer	R / Å	Dispersity	Scale	Background
P3	47	0.28	2.5×10^{-5}	4×10^{-4}
P6	40	0.23	2.2×10^{-5}	1×10^{-4}
P7	50	0.22	7.0×10^{-6}	1×10^{-4}

methods). Scattering length densities used are stated in Materials and Methods.

Table S4: Comparison of nanoparticle size including the polymer corona (hydrodynamic diameter from DLS) and including the gold core (from SAXS fits).

No. of Polymer	Architecture	Presumed structure	Overall diameter / nm (DLS)	Gold core diameter / nm (SAXS)
P3	BAB	Core-shell micelle	30.5	9.4
P6	AB	Core-shell micelle	28.0	8.0
P7	ABA	Flower micelle	30.5	10.0

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