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Compartmentalized nanoparticles in aqueous solution through hierarchical self-assembly of triblock glycopolymers

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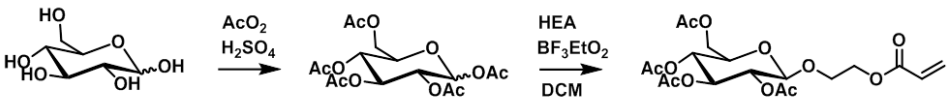
Supporting information



Scheme S1. Synthesis of glycosylated acrylate using D-glucose and 2-hydroxyethyl acrylate.

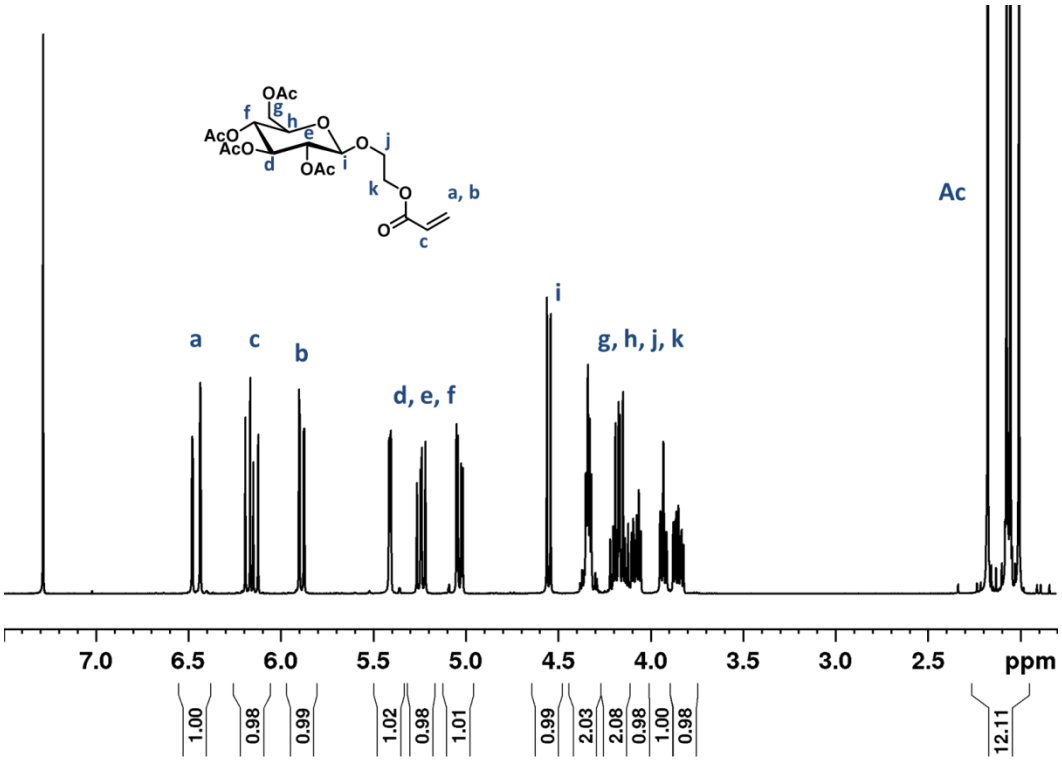


Figure S1. ^{1}H NMR of 2-(2′,3′,4′,6′-tetra-O-acetyl-D-glucosyloxy) ethyl acrylate (AcGlcEA) in $CDCl_3$

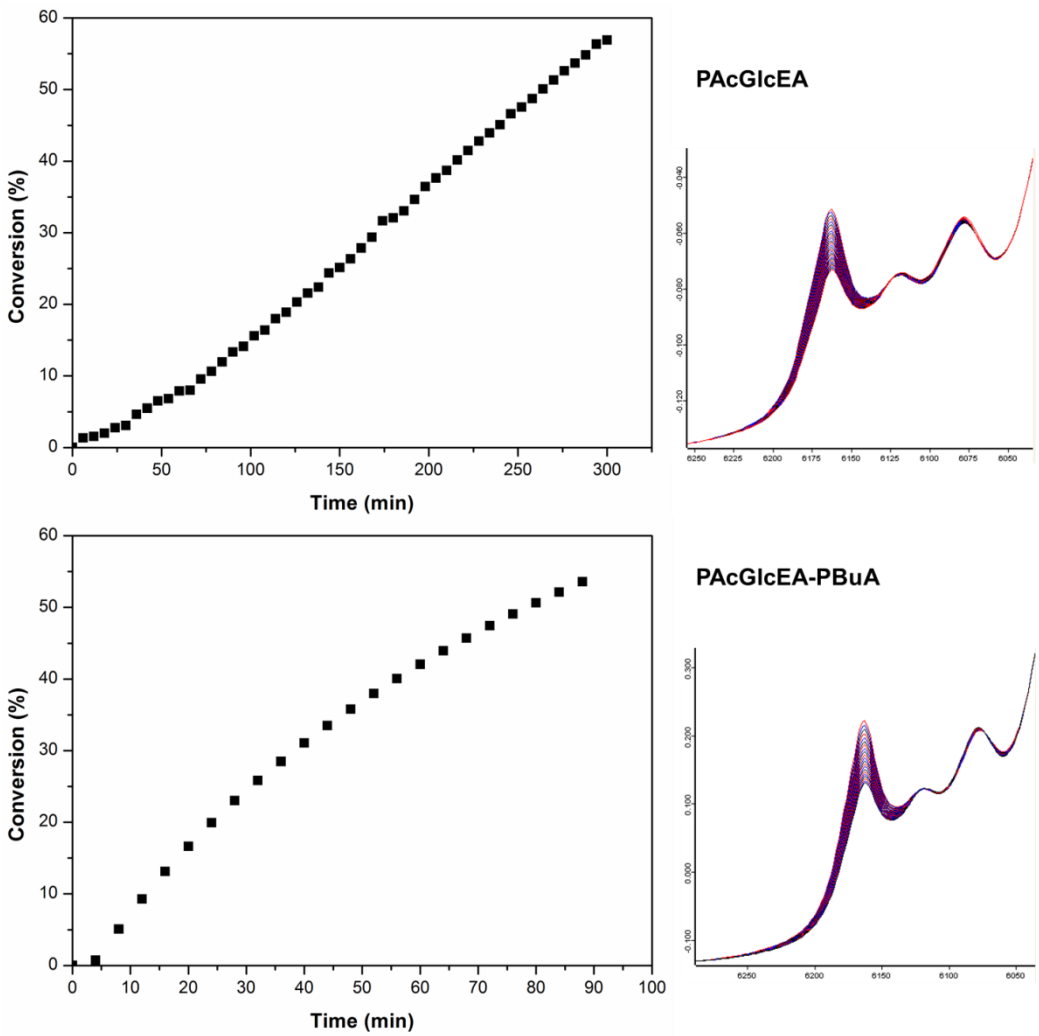


Figure S2. Monomer conversion over the course of the polymerization obtained by NIR spectroscopy. The integral of the vinylic peak at 6170 cm^{-1} was compared with the same integral at t = 0. Measurements were taken every 6 minutes (AcGlcEA polymerization) or every 4 minutes (BuA polymerization).

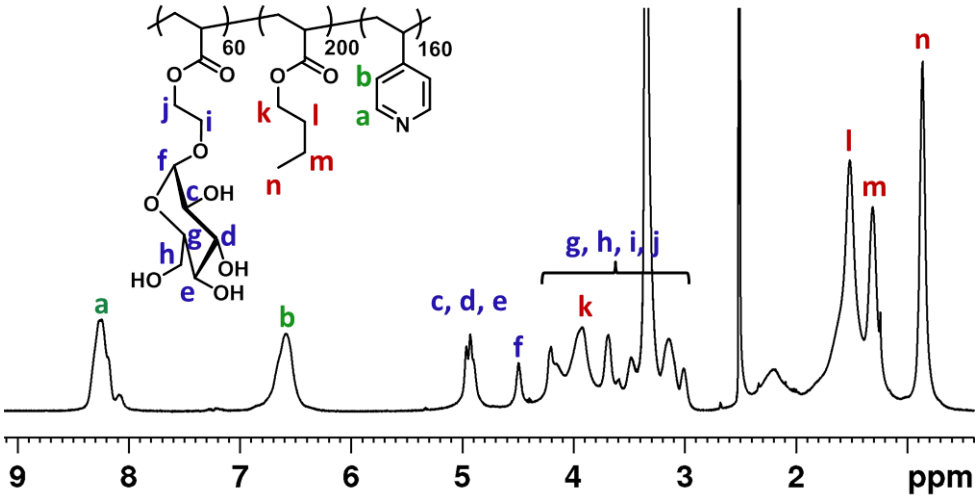


Figure S3. ^{1}H NMR of the purified triblock terpolymer obtained in DMSO-*d6* at 60°C.

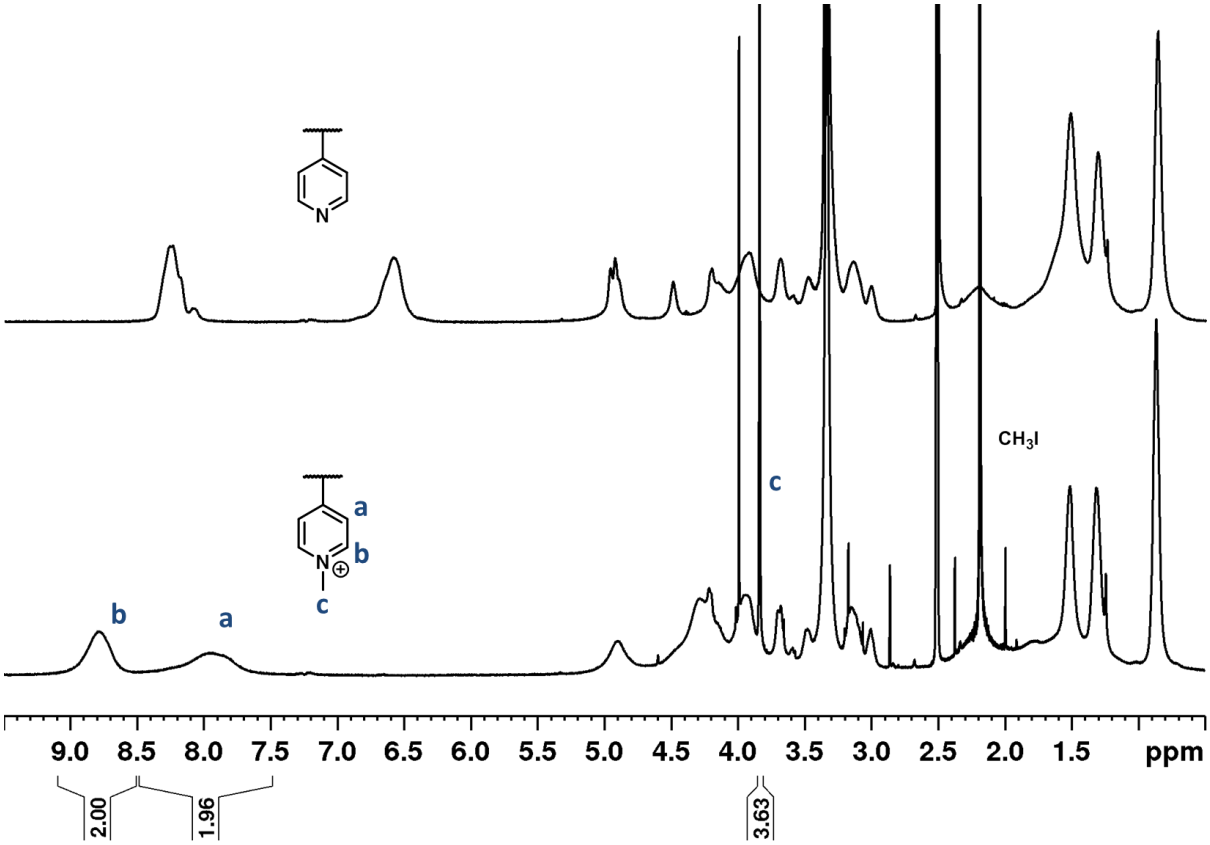


Figure S4. ^{1}H NMR showing successful methylation of P4VP functionalities obtained in DMSO-d6.

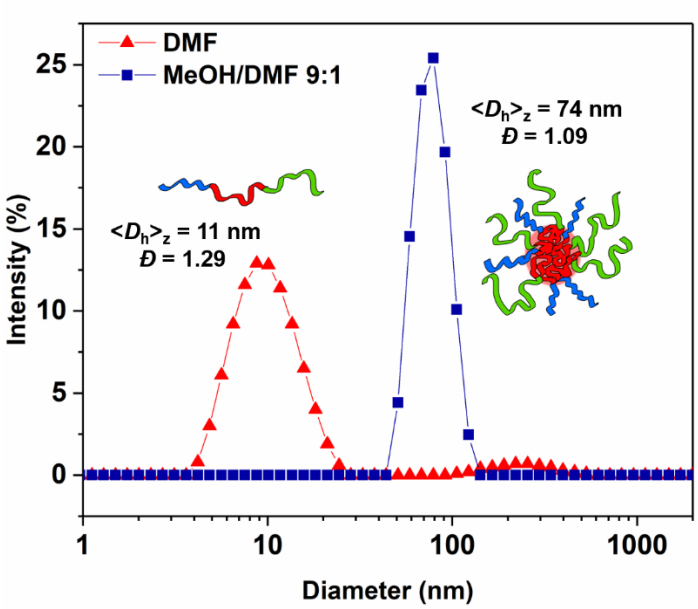


Figure S5. Size distribution by intensity of the sample in pure DMF and methanol/DMF 9:1 mixture showing the formation of micelles after addition of methanol. Viscosity and dielectric constant of the solvent mixture were taken from literature.[1] Concentration was 1 mg/mL.

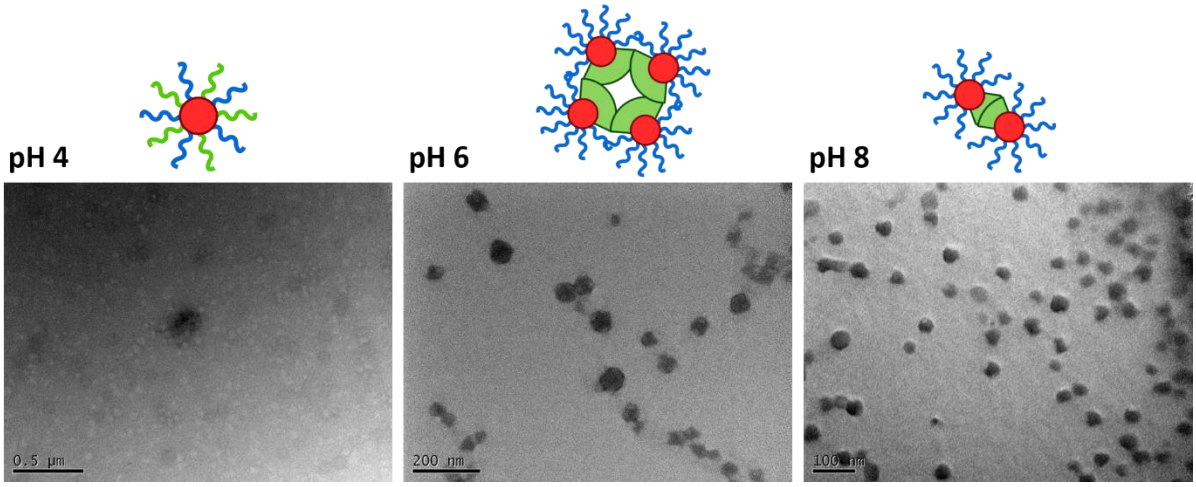


Figure S6. Unstained TEM micrograph of the particles in MilliQ water at pH of approximately 4, 6 and 8. When the P4VP block forms the corona the spherical particles are barely visible (pH 4). At pH 6 and 8 the solid-like P4VP domain appears dark and shows compartimentalization.

	Triblock with P4VP		Triblock with PQ4VP	
	$\langle D_h \rangle_z$ (nm)	***Đ***	**$\langle D_h \rangle_z$ (nm)**	***Đ***
pH ≈ 4	161	1.42	117	1.58
pH ≈ 6	146	1.27	93	1.44
pH ≈ 8	97	1.18	89	1.22

Table S1. Z-average diameter and polydispersity measured by DLS after dialysis for 24 hours against MilliQ water. pH was adjusted by addition of HCl and NaOH solution. Sample concentration was 1 mg/mL.

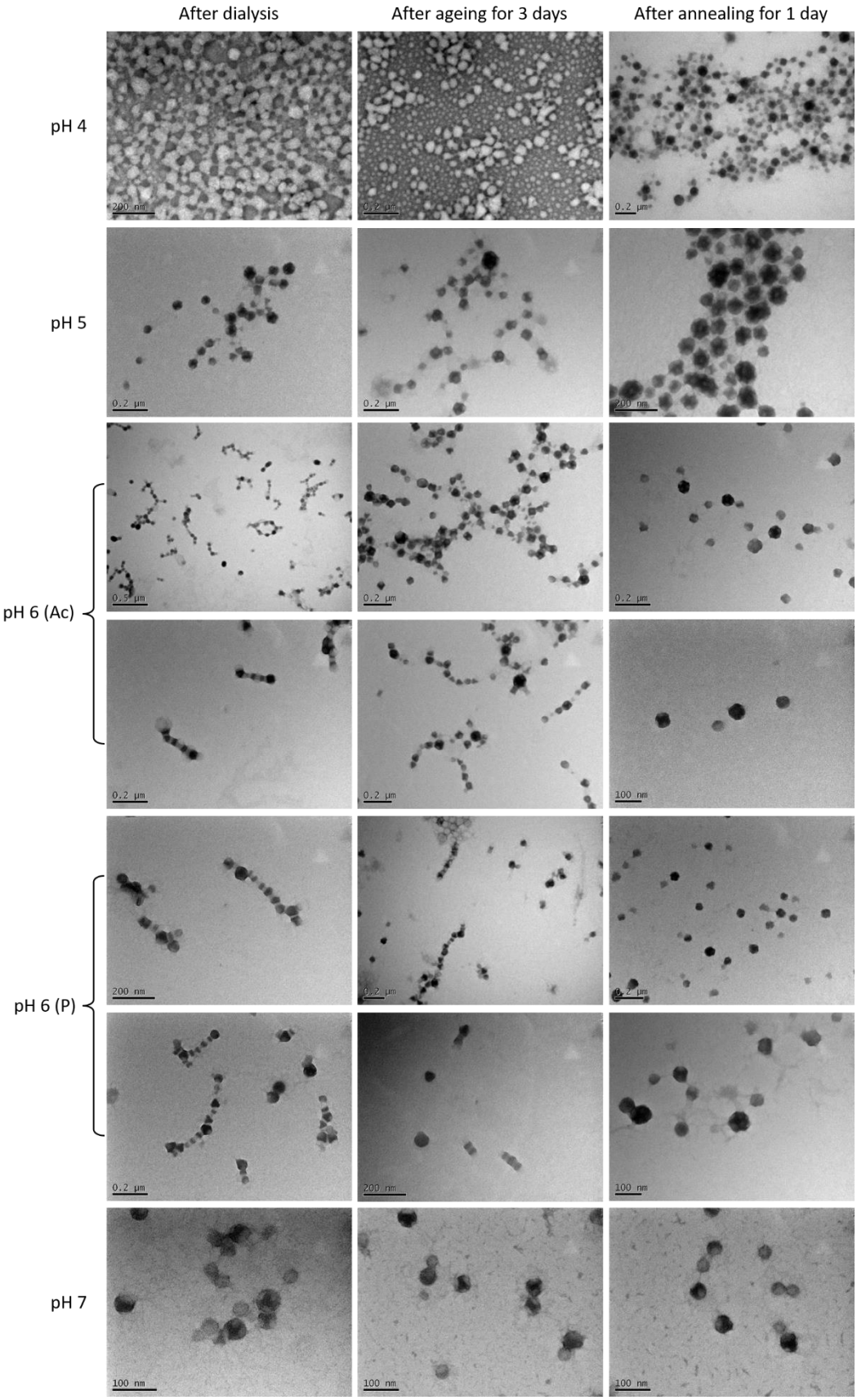


Figure S7. Additional TEM micrographs of nanoparticles in 5 mM sodium acetate (pH 4 to 6) or KH_2PO_4 buffer (pH 6, 7) fresh after 1-day dialysis (left), after ageing for 3 days at room temperature (middle) and after annealing for 1 day at 45°C (right).

	After dialysis for 1 day		After aging for 3 days		After annealing for 1 day	
	$\langle D_h \rangle_z$ (nm)	*Đ*	$\langle D_h \rangle_z$ (nm)	*Đ*	$\langle D_h \rangle_z$ (nm)	*Đ*
pH 3[a]	113	1.23	108	1.25	102	1.26
pH 4[a]	165	1.38	180	1.32	197	1.31
pH 5[a]	252	1.28	248	1.11	238	1.16
pH 5.5[a]	176	1.35	190	1.08	192	1.09
pH 6[a]	185	1.28	171	1.12	149	1.39
pH 6[b]	202	1.32	169	1.08	152	1.34
pH 6.5[b]	136	1.21	145	1.12	132	1.10
pH 7[b]	173	1.33	183	1.29	198	1.18
pH 8[b]	140	1.29	126	1.29	136	1.16

Table S2. Z-average diameter and polydispersity measured by DLS after dialysis for 24 hours, ageing for 3 days or annealing at 45°C for one day. Dialysis solvent was 5 mM sodium acetate buffer (a) or 5 mM potassium dihydrogenphosphate buffer (b). pH was adjusted by addition of HCl and NaOH solution. Sample concentration was 1 mg/mL.

	pH 6		pH 8	
Buffer concentration	$\langle D_h \rangle_z$ (nm)	*Đ*	$\langle D_h \rangle_z$ (nm)	*Đ*
5 mM	185	1.28	140	1.29
21 mM	157	1.25	132	1.24
37 mM	165	1.38	120	1.42

Table S3. Z-average diameter and polydispersity measured by DLS after increasing the strength of the buffer. An appropriate amount of 100 mM sodium acetate (pH 6) or dihydrogenphosphate (pH 8) buffer was slowly added to the colloidal solution in 5 mM buffer. The measurements show the stability of the particles up to a buffer concentration of 37 mM.

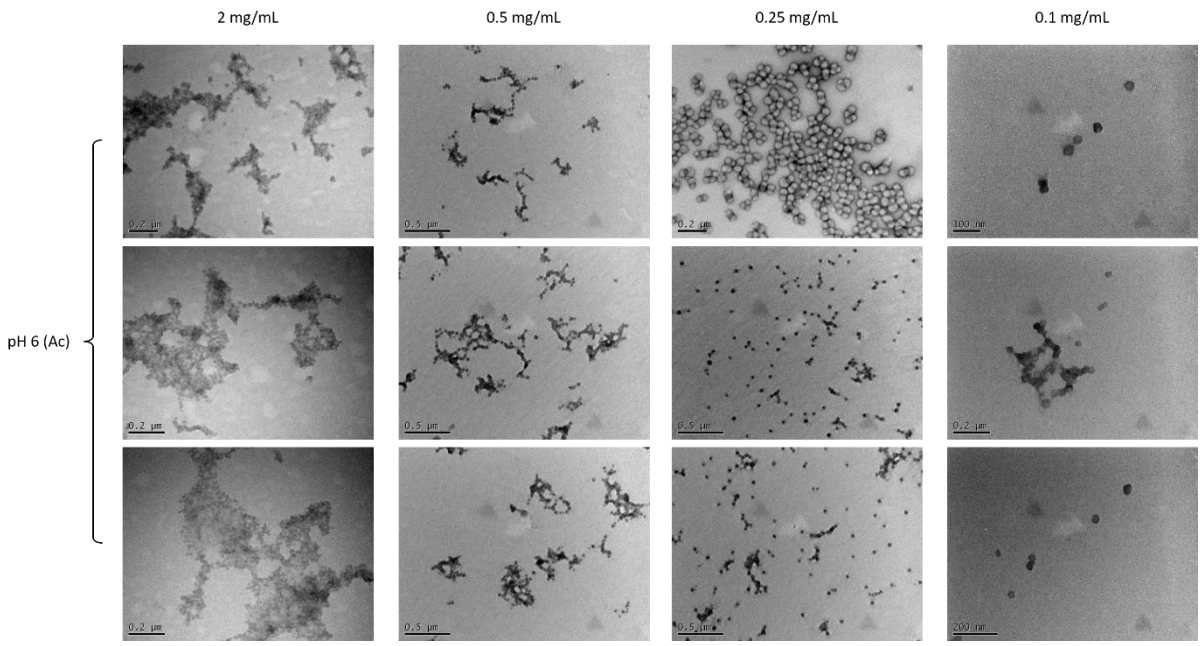


Figure S8. Additional TEM micrographs of nanoparticles in 5 mM sodium acetate at pH 6 prepared using different concentration of primary particle solution after dialysis for 24 hours.

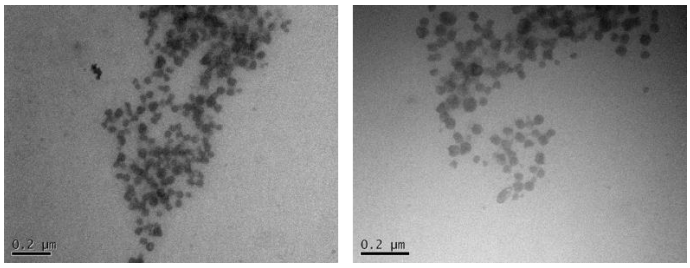


Figure S9. TEM micrographs of nanoparticles at pH 6 prepared at a concentration of 0.1 mg/mL (in 5 mM sodium acetate buffer) and subsequently concentrated to approximately 0.5 mg/mL.

	$\langle D_h \rangle_z$ (nm)	*Đ*
2 mg/mL	554	1.43
0.5 mg/mL[a]	288	1.31
0.25 mg/mL[a]	156	1.18
0.1 mg/mL[a]	141	1.22

Table S4. Z-average hydrodynamic diameter and polydispersity measured by DLS after dialysis for 24 hours. a) The sample in MeOH/DMF 9:1 was diluted with MeOH to the concentration specified before dialysis against 5 mM sodium acetate buffer at pH 6 for one day.

1. C. S. Yang, Y. Sun, Y. He and P. S. Ma, *J Chem Eng Data*, 2008, **53**, 293-297.