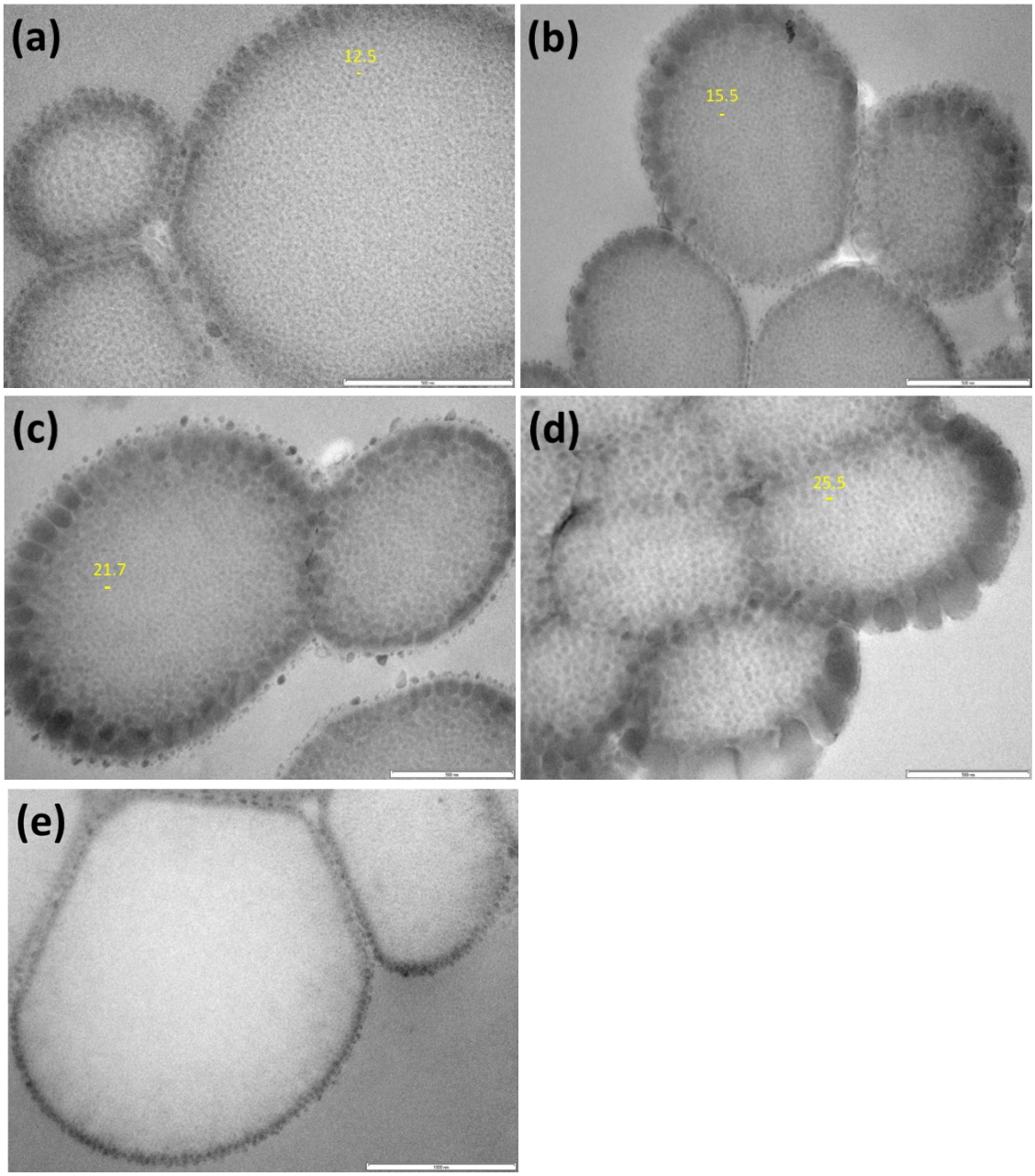
Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

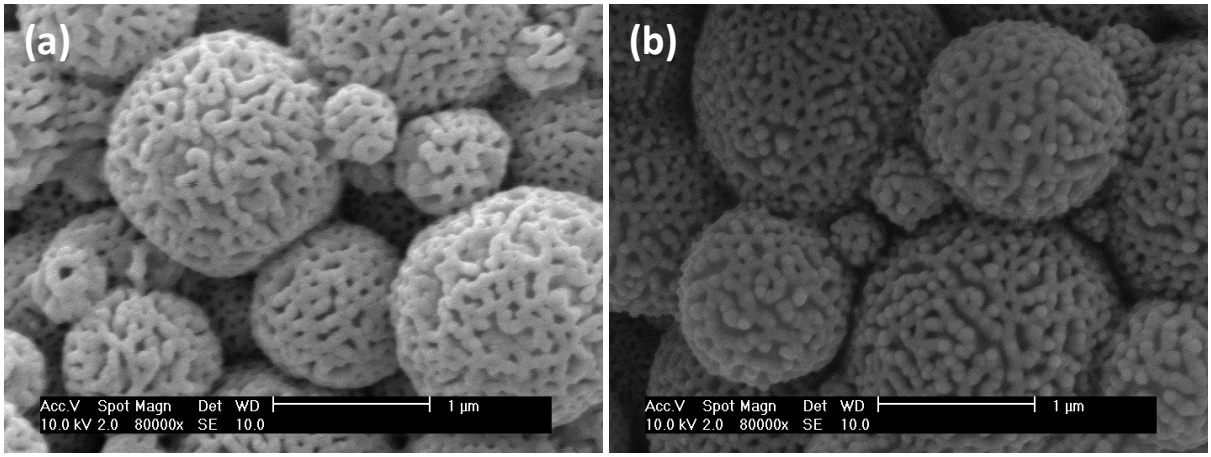


S1. TEM images of cross-sections (~80 nm in thickness) from the original PMMA-*b*-P4VP microparticles demonstrating a spherical internal morphology and increasing domain sizes (a-d). (a) M-V13.3, (b) M-V19.9, (c) M-V27.8, (d) M-V30.9, and the particles without internal structure (e) M-V9.1. The scale bar represents 500 nm, except (e) with 1000 nm.

S2. Internal structures of original PMMA-*b*-P4VP microparticles based on TEM analysis.

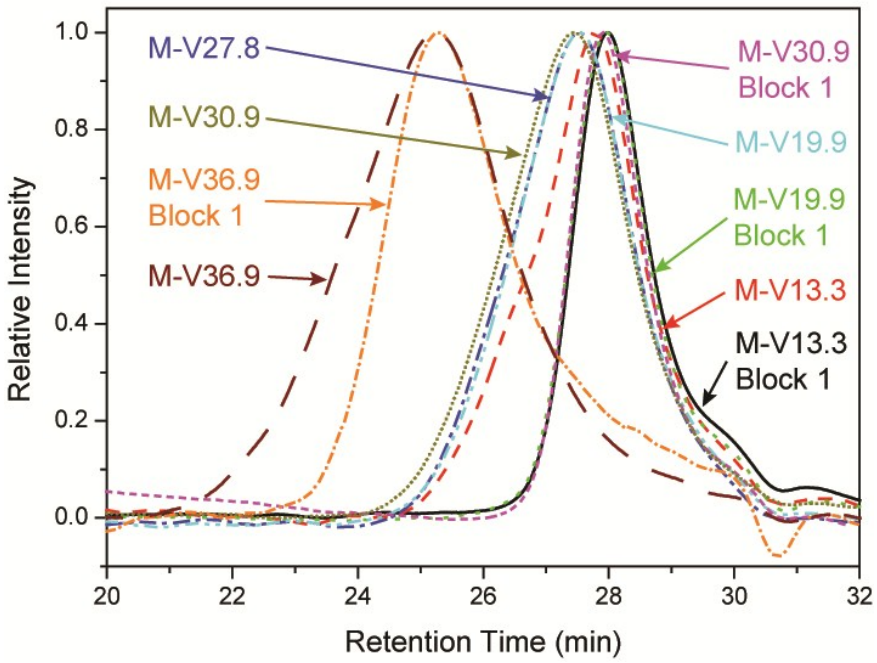
PMMA-P4VP	Morphology[a]	d^{P4VP} (nm)[b]	
		At centre	At periphery
M-V9.1	NON	--	--
M-V13.3	NON+SPH	12.5±1.3	--
M-V19.9	SPH (+coronal)	15.5±1.6	57.0±7.8
M-V27.8	SPH (+coronal)	21.7±2.1	60.9±12.6
M-V30.9	SPH (+coronal)	25.5±2.2	106.3±11.3
M-V36.9	SPH (+coronal)	60.4±9.0	116.4±7.3

[a]NON denotes non-structured, SPH denote sphere; [b]domain size determined by TEM, with at least 100 domains measured.



S3.
(a)
SEM

image of the porous from the sample M-sample after storage bench at room approximately one



particles produced V27.8. (b) The same in a glass vial on a temperature for year.

S4. GPC traces of the as-synthesised block copolymers listed in Table 1. Data for the reaction aliquots collected after the first PMMA block was polymerised but prior to injecting the second monomer are also included.

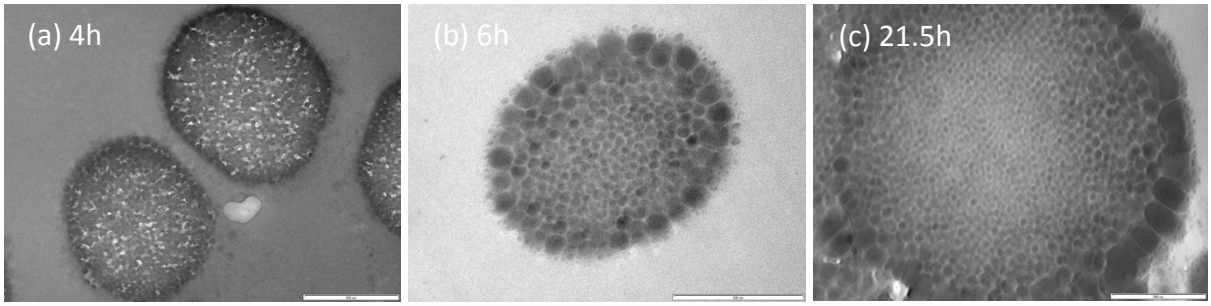
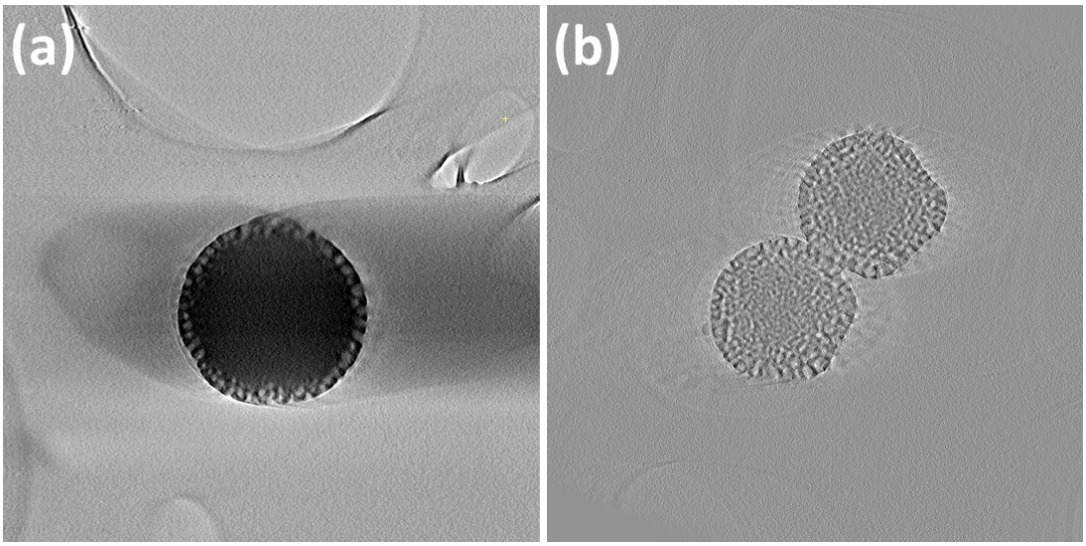
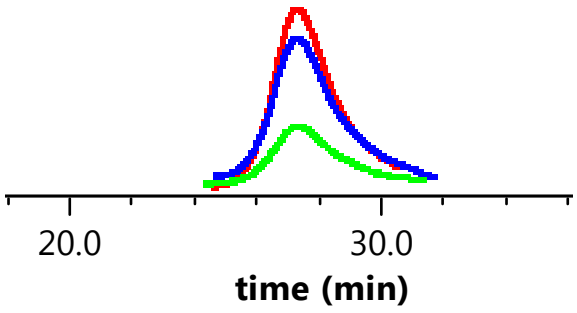


Fig. S5. TEM cross-sectional view of the sampling products during the chain extension of PMMA-P4VP (M-V41.2) at different time intervals. (a) 4 h, (b) 6 h and (c) 21.5 h.

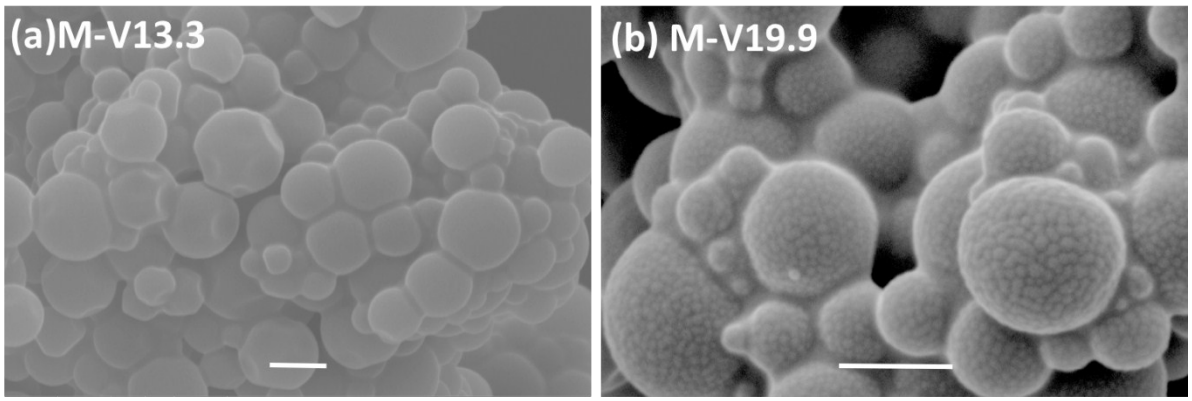


S6. GPC trace of sample M-V27.8 before (red) and after (blue and green) ethanol treatment.

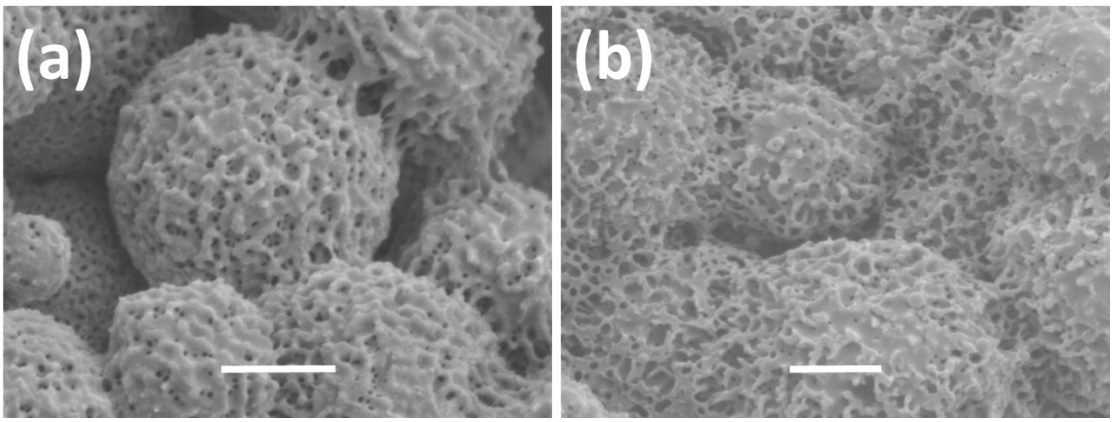
S7. Videos formed by Tilt TEM mapping of porous microparticles at varied tilt angels and each video is formed by ~90 TEM images at varied tilt angels with 1 degree increments. (a) M-V13.3, (b) M-V19.9, (c) M-V27.8, (d) M-V30.9, (e) M-V36.9.
(Refer to video links)



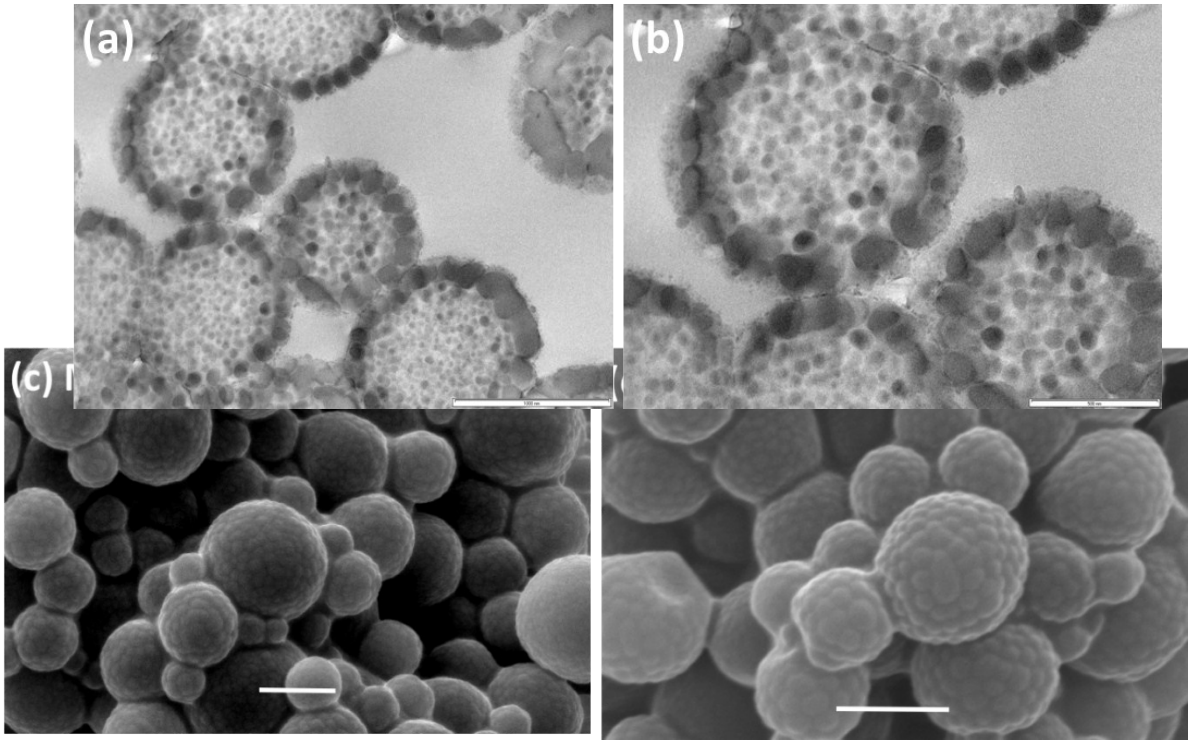
S8. 3D tomographic reconstruction of porous microparticles**.** A slice through near-centre from SIRT tomographic reconstruction of a porous microparticle from samples with varied P4VP mole fractions is presented. (a) M-V13.3, with pores only developed on the sub-surface layers, (b) M-V30.9, with pores that clearly have penetrated throughout the microparticle.

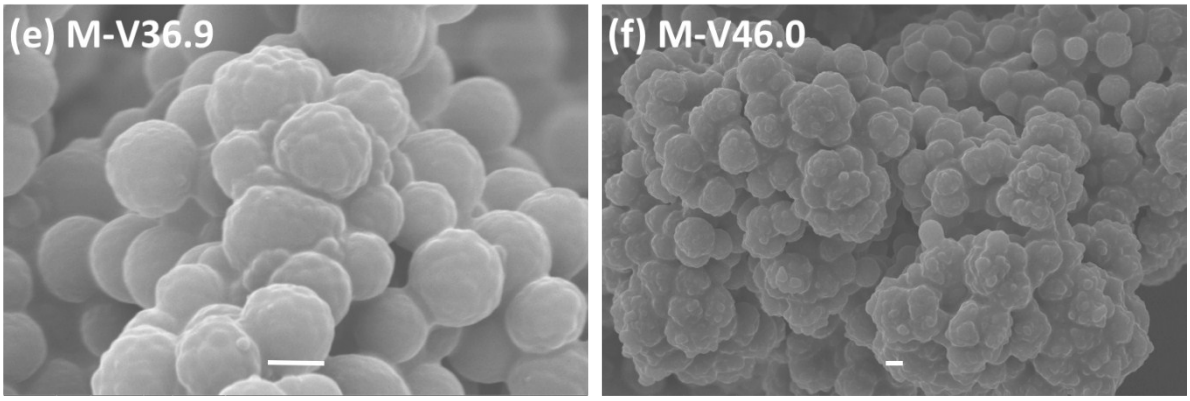


S9. SEM image of M-V36.4 demonstrating interparticle fusion at higher proportions of P4VP. Scale bar in both is 250 nm.

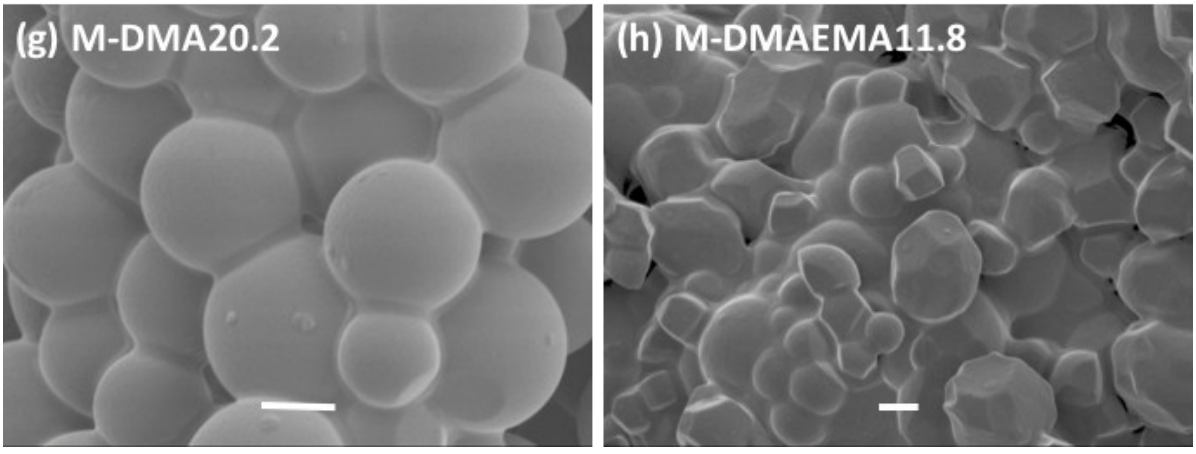


S10. TEM images of sections in the cross-(~80 nm thickness) of the original M-V36.9 (200k-b-133k) microparticles. Scale bar is 1000 nm in (a) and 500 nm in (b).





S11. SEM images of original microparticles prior to swelling/de-swelling, fabricated using RAFT dispersion polymerisation in $scCO_2$. PMMA-*b*-P4VP microparticles (a) M-V13.3, (b) M-V19.9, (c) M-V27.8, (d) M-V30.9, (e) M-V36.9, (f) M-V46.0, (g) M-DMA20.2 (PMMA-*b*-



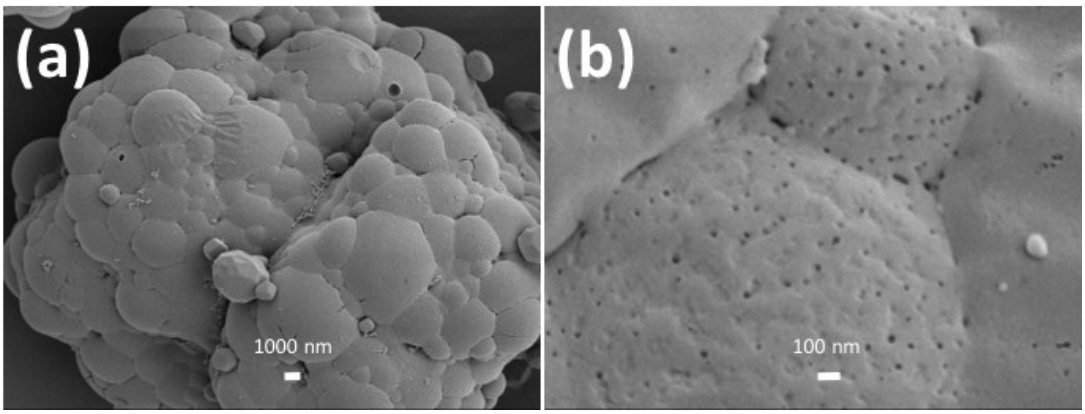
PDMA) and (h) M-DMAEMA11.8 (PMMA-*b*-PDMAEMA). Scale bar 1000 nm.

S12. Specific surface areas, pore structure parameters of the porous BCP microparticles.

Samples	S_{BET}	V_{total}	V_{meso}	V_{micro}	Pore width (N_2 Ads)[a]	Pore width[b] (TEM)	Pore width[c] (SEM)

	(m^2/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)	(nm)						(nm)	(nm)
M-V13.3	11	0.069	0.052	0	20.1	--	--	--	--	--	21.2±1.7	37.3±5.8
M-V19.9	77.7	0.45	0.38	0.0029	21.6	37	50.3	--	--	--	40.2±6.1	74.2±8.3
M-V27.8	91.3	0.69	0.53	0.0017	25.2	37	50.3	68.4	86.2	117.2	54.5±8.9	112.7±14.6
M-V30.9	87.9	0.59	0.45	0.0038	25.2	37	50.3	68.4	86.2	117.2	85.8±16.4	168.8±26.5

[a]Pore width at centre of the characteristic multiple regular peaks from the pore size distributions in **Fig 5b**; [b,c]Surface pores



S13. SEM images of M-DMAEMA11.8 swollen with ethanol showing significant inter-particle fusion (a) and (b) at high magnification.