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Polymer-encapsulation of iron oxide clusters using macroRAFT block copolymers as stabilizers: tuning of the particle morphology and surface functionalization

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SUPPORTING INFORMATION

Contents

1.1. Synthesis of RAFT and macroRAFT agents

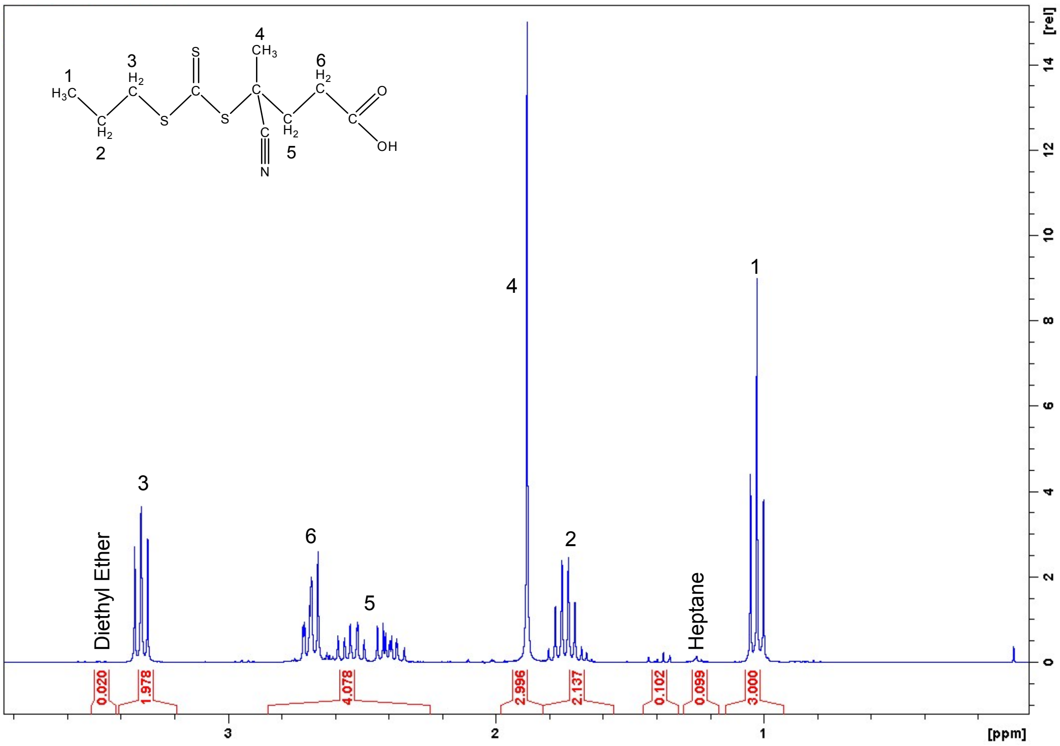


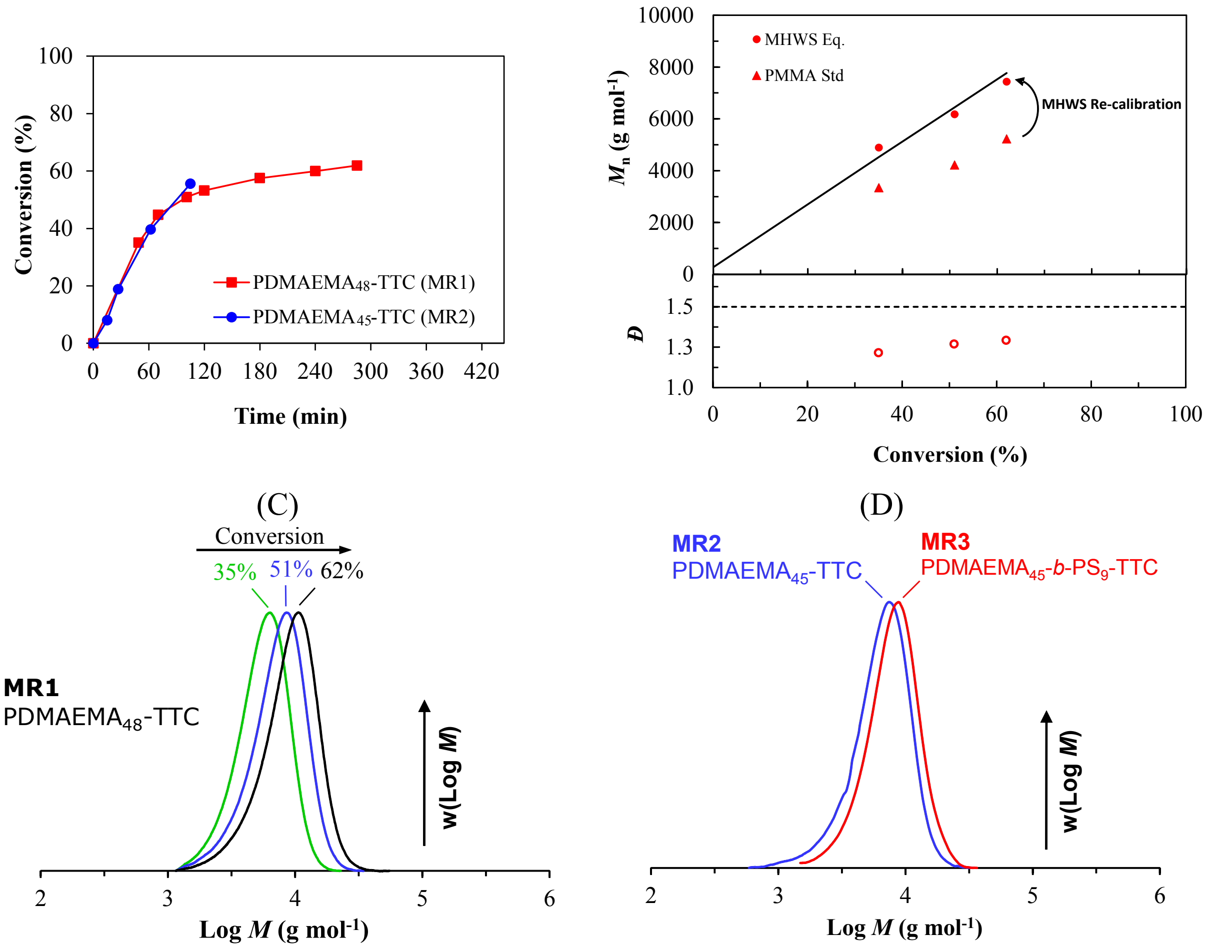
Figure S1 – ^{1}H NMR spectrum of the CTPPA RAFT agent.

Table S1 – Synthesis of hydrophilic and amphiphilic macroRAFT agents via RAFT polymerization in 1,4-Dioxane.

Exp.	**Structure**	**[Mon] (mol L^{-1})**	**[Mon]/ [RAFT]**	**[RAFT] / [Ini]**	**X (NMR) (%)**	**$M_{n,th}$[a] (g mol^{-1})**	**$M_{n,exp}$ (g mol^{-1})/$Đ$**	
							***THF-SEC*[b]**	***DMF-SEC*[c]**
MR1	PDMAEMA$_{48}$-TTC	1.2[a]	77	5	62	7800	7770/1.29	n.d.
MR2	PDMAEMA$_{45}$-TTC	1.2[a]	80	5	56	7300	6950/1.36	5300/1.33
MR3	PDMAEMA$_{45}$-*b*-PS$_9$-TTC	1.0[b]	30	3	27	7950	n.d.	6850/1.24
MR4	PAA$_{75}$-TTC	1.9[c]	81	9	92	5650	5950/1.19	n.d.
MR5	PAA$_{50}$-TTC	1.9[c]	80	9	62	3870	3650/1.11	n.d.
MR6	PAA$_{50}$-*b*-PS$_{10}$-TTC	0.9[b]	30	3	32	4880	5520/1.19	n.d.

[a] *Theoretical M_n calculated according to equation 1 (main text).*
Experimental number-average molar mass and dispersity determined either by: [b]SEC in THF based on either PDMAEMA (MR1 and MR2) or PMA (MR4 and MR5) calibration by using MWHS equations and conventional calibration using PS standards for MR6, or by [c]SEC in DMF using PS calibration.

(A) (B)



(C)

(D)

Figure S2 – (A-C) RAFT polymerization of DMAEMA in 1,4-dioxane using CTPPA as RAFT agent. Evolution of (A) monomer conversion versus time and (B) M_n and $Đ$ versus conversion (MR1). The straight line corresponds to the theoretical evolution of M_n with conversion. The triangles (□) correspond to M_n calculated from poly(methyl methacrylate) calibration and the circles to M_n (●) and $Đ$ (○) from PDMAEMA calibration using the MWHS parameters. (C) SEC-traces for PDMAEMA (run MR1, small-scale experiment for kinetic study) in THF using PDMAEMA calibration recalculated using the MHWS equations. (D) SEC-traces in DMF for the synthesis of PDMAEMA-*b*-PS (MR2 and MR3, scale-up experiments).

(A)

(B)

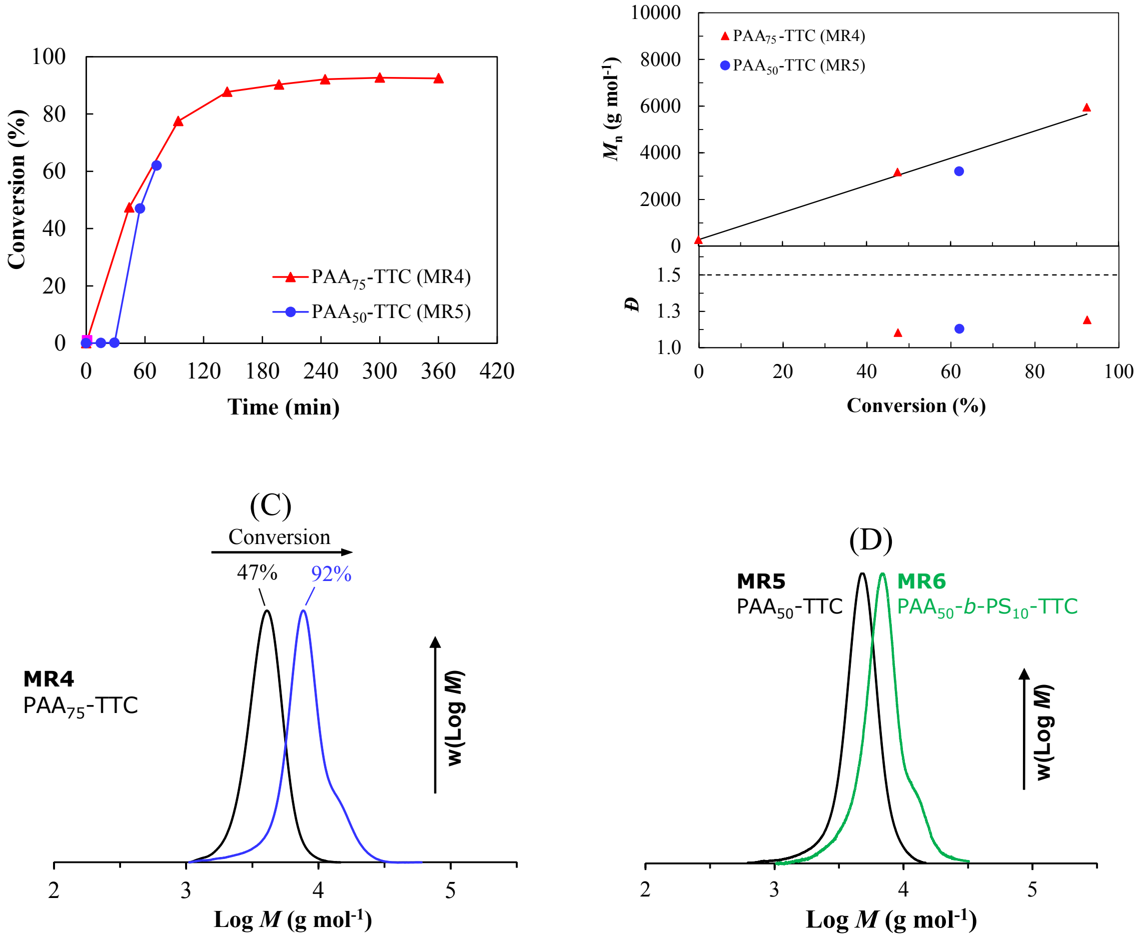
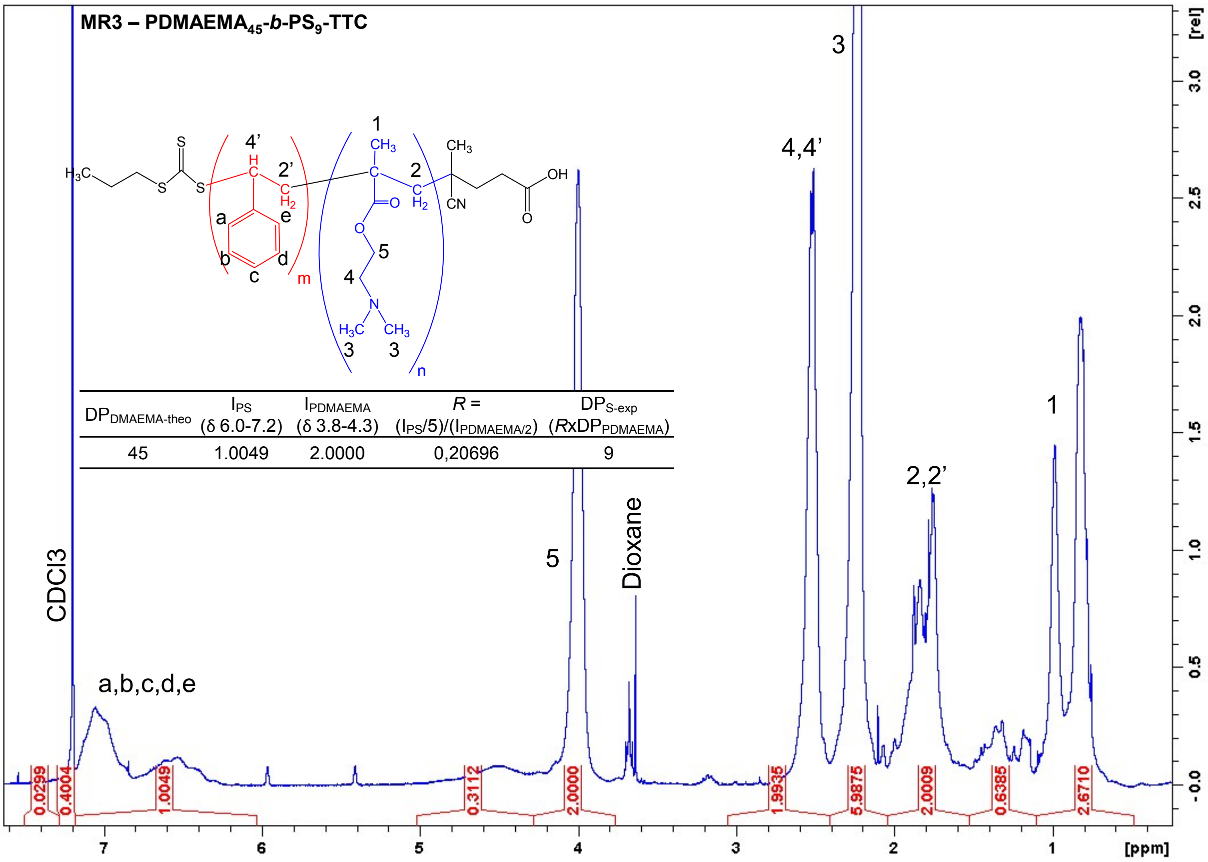


Figure S3 – (A-C) RAFT polymerization of AA in 1,4-dioxane using CTPPA as RAFT agent. Evolutions of (A) monomer conversion versus time and (B) Evolution of M_n and $Đ$ versus conversion (MR4) of the methylated samples using poly(methyl acrylate) calibration recalculated with the MWHS parameters. The straight line corresponds to the theoretical M_n. (C) SEC-traces in THF for PAA-TTC (run MR4, small scale for kinetic study). (D) SEC-traces in THF for the synthesis of PAA-*b*-PS (MR5 and MR6, scale-up experiments).



$DP_{DMAEMA\text{-}theo}$	I_{PS} (δ 6.0-7.2)	$I_{PDMAEMA}$ (δ 3.8-4.3)	*R* = $(I_{PS}/5)/(I_{PDMAEMA/2})$	$DP_{S\text{-}exp}$ (*R*x$DP_{PDMAEMA}$)
45	1.0049	2.0000	0,20696	9

Figure S4 – ^{1}H NMR spectrum of PDMAEMA$_{45}$-*b*-PS$_9$-TTC (MR3). Determination of the degree of polymerization of styrene via the relative integration of the PDMAEMA characteristic peak (5) and the aromatic peaks from PS (a, b, c, d, e).

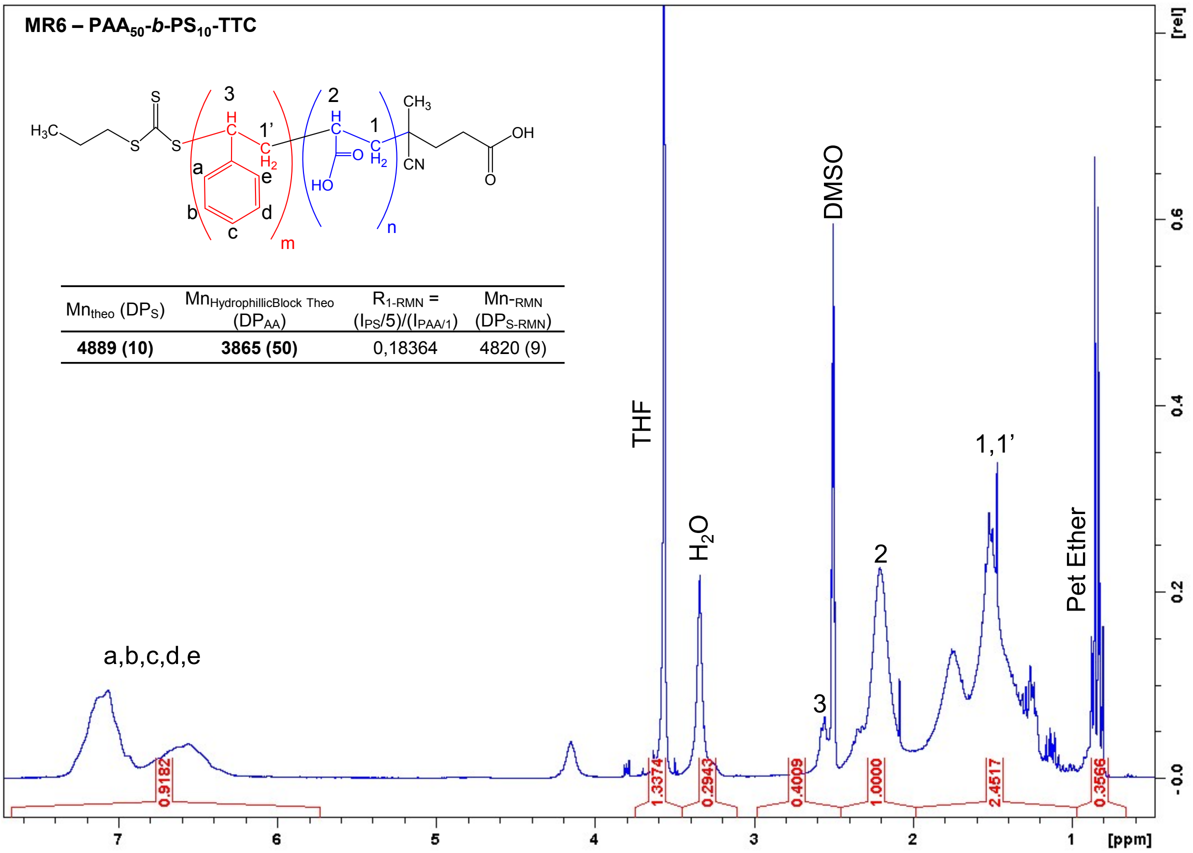


Figure S5 – ^{1}H NMR spectrum of PAA-*b*-PS-TTC (MR6). Determination of the degree of polymerization of styrene via the relative integration of the PAA characteristic peak (2) and the aromatic peaks from PS (a, b, c, d, e).

1.2. Clusters formation

Table S2 – Characteristics of the IO clusters prepared using amphiphilic macroRAFT agents as stabilizers.

Exp.	SC_{th} [a] (%)	$Z_{av\text{-}clusters}$ (nm)/PdI [b]	D_n (nm)/ D_w/D_n [c]	ω_{mag} (%) [d]	SC_{sep} (%) [e]
PDMAEMA@Clusters	2.67	184/0.10	71/1.58	87	2.00
PAA@Clusters	2.62	161/0.13	71/1.55	99	2.41

[a] *Theoretical solids content,* [b] *Determined by DLS,* [c] *Determined by statistical analysis of 1100-1300 particles from the TEM images,* [d] *Magnetic fraction after 10 min of magnetic separation,* [e] *Experimental solids content of the magnetic fraction after magnetic separation.*

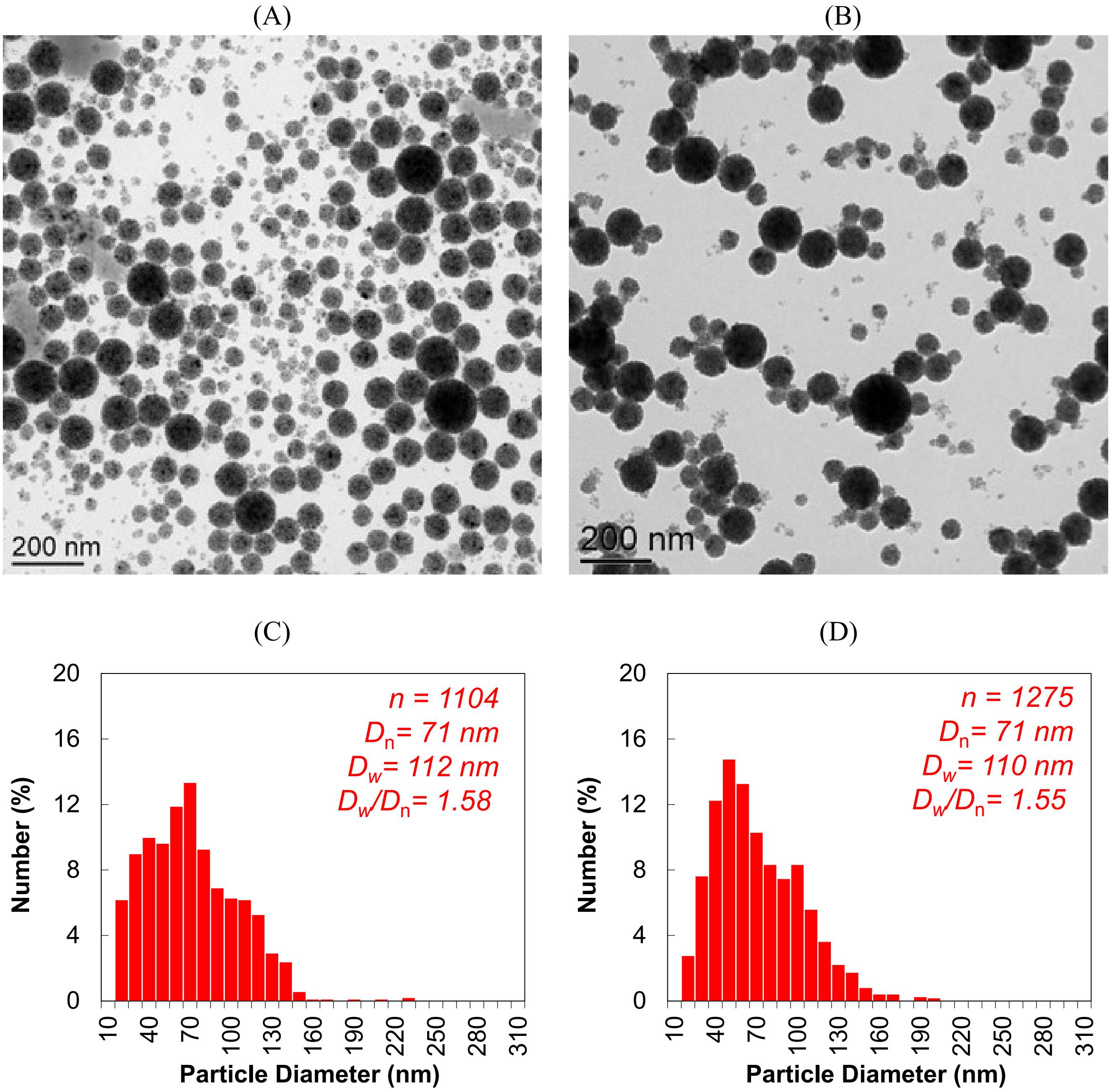


Figure S6 – TEM micrographs and number frequency size distribution histograms for (A, C) PDMAEMA@Clusters and (B, D) PAA@Clusters.

1.3. Synthesis and characterization of the magnetic latex particles (MLPs)

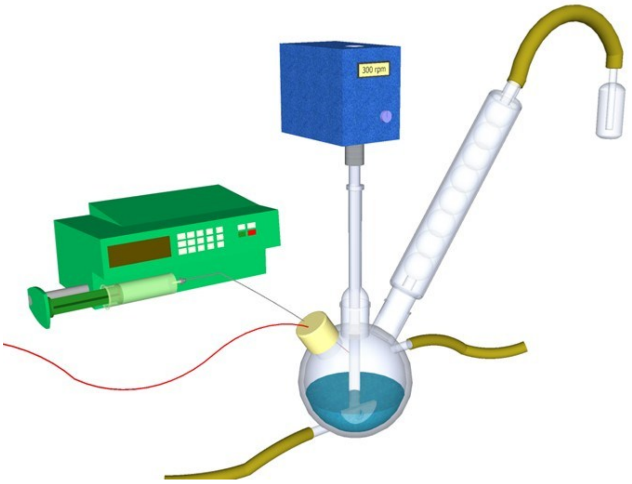


Figure S7 – Scheme illustrating the reaction system used for seeded emulsion polymerization.

Table S3 – Feeding conditions used during the semi-batch seeded emulsion polymerization of styrene using the PDMAEMA@Clusters and the PAA@Clusters as seeds.[a]

Exp	Initial Charge				Feed					Total
	Cluster (g)	Initiator (mg)	Sty (mg)	DVB (mg/wt%) [b]	Sty (g)	DVB (g/wt%) [c]	Onset time (min)	Endset time (min)	Rate ($g\,h^{-1}$)	DVB (wt%) [d]
1	15.0	8.2	63	-	1.64	-	35	275	0.41	0
2*	15.0	8.3	48	2.5/5	1.61	0.08/5	35	275	0.42	5
3	15.0	8.3	55	6.3/10	1.49	0.17/10	30	270	0.41	10
4	13.5	7.6	57	14.3/20	1.22	0.31/20	30	270	0.38	20
5	15.0	8.4	62	41.2/40	0.25	-	35	80	0.33	12
6	15.0	8.5	20	81.5/80	0.25	-	35	80	0.34	23
7	13.8	7.6	20	81.5/80	0.18	0.05/20	35	80	0.30	38
8*	15.0	8.2	20	80.6/80	0.23	0.06/20	35	80	0.38	36
9*	12.0	5.3	16	64.0/80	0.16	0.04/20	30	66	0.33	37
10	15.0	6.3	20	80.8/80	0.19	0.05/20	35	80	0.32	38
11	14.9	7.6	20	83.7/80	0.23	0.06/20	35	80	0.38	36
12*	14.8	5.8	20	80.0/80	0.19	0.05/20	35	80	0.32	38
13	14.9	5.8	21	83.2/80	0.19	0.05/20	35	80	0.32	38

*[a] VA-044 was used as initiator except for Exp 9-11 and Exp 12-13 where ACPA and APS were used, respectively. * Unstable latexes. [b, c, d] wt% of DVB based on overall monomer mass either in the [b] initial charge, [c] feed charge or [d] final. The PDMAEMA@Clusters were used as seeds for Exp 1-7 while Exp 8-13 were conducted with the PAA@Clusters.*

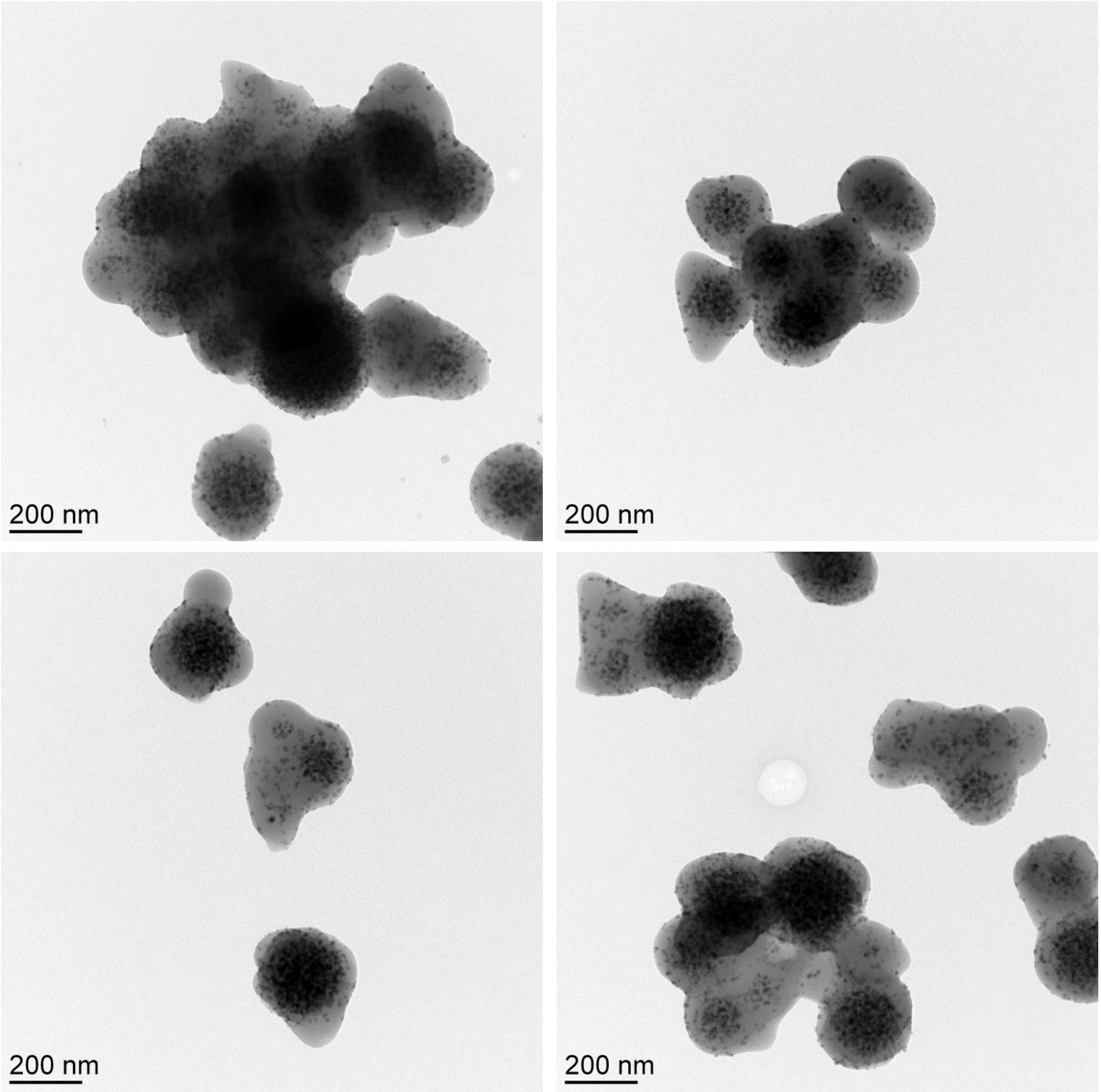


Figure S8 – TEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 5 wt% DVB and PC = 10% using the PDMAEMA@Clusters as seeds (Exp 2, Table 1 and Table S3). This latex got destabilized in the course of polymerization.

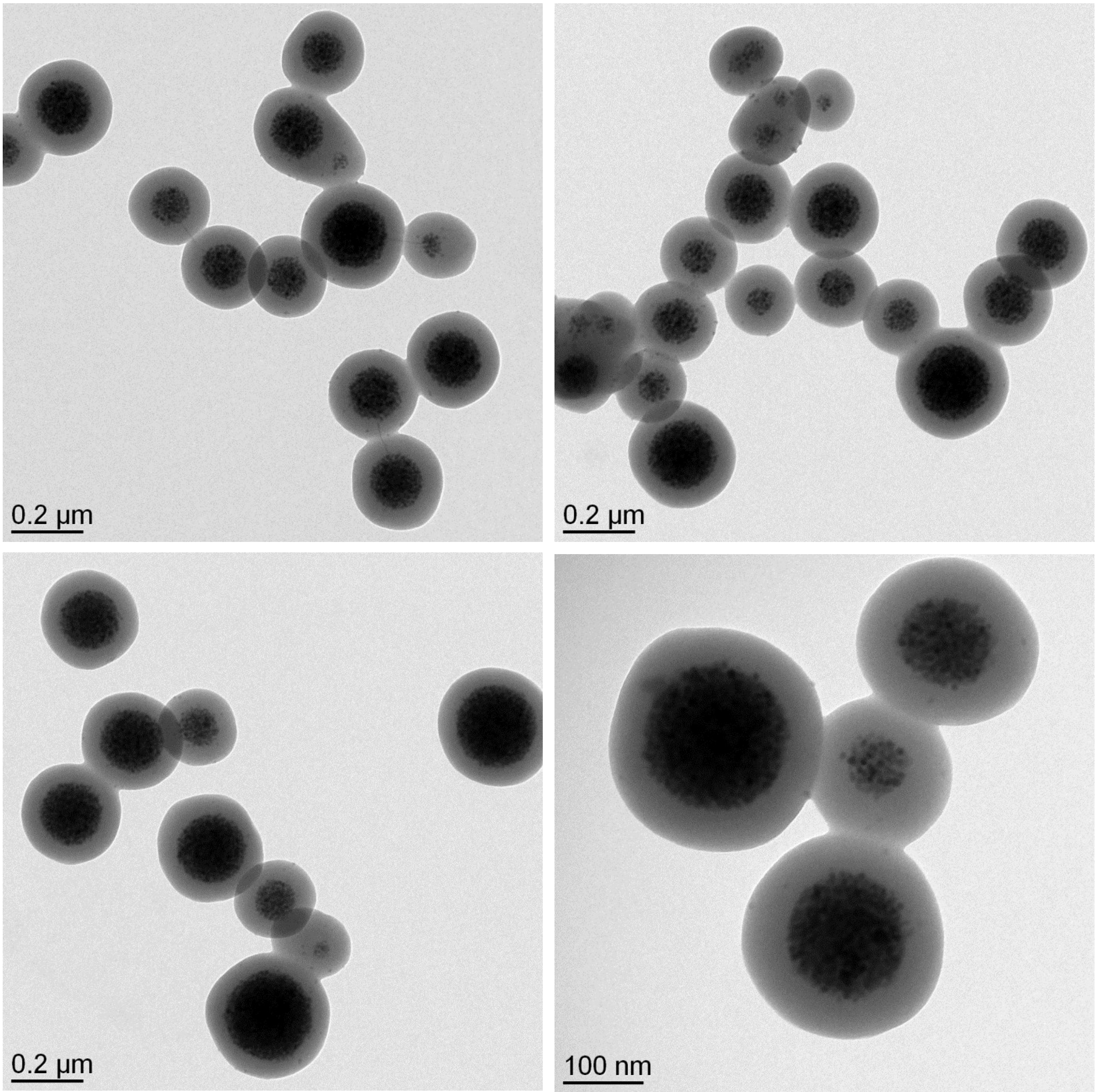


Figure S9 – TEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 10 wt% DVB and PC = 10% using the PDMAEMA@Clusters as seeds (Exp 3, Table 1 and Table S3).

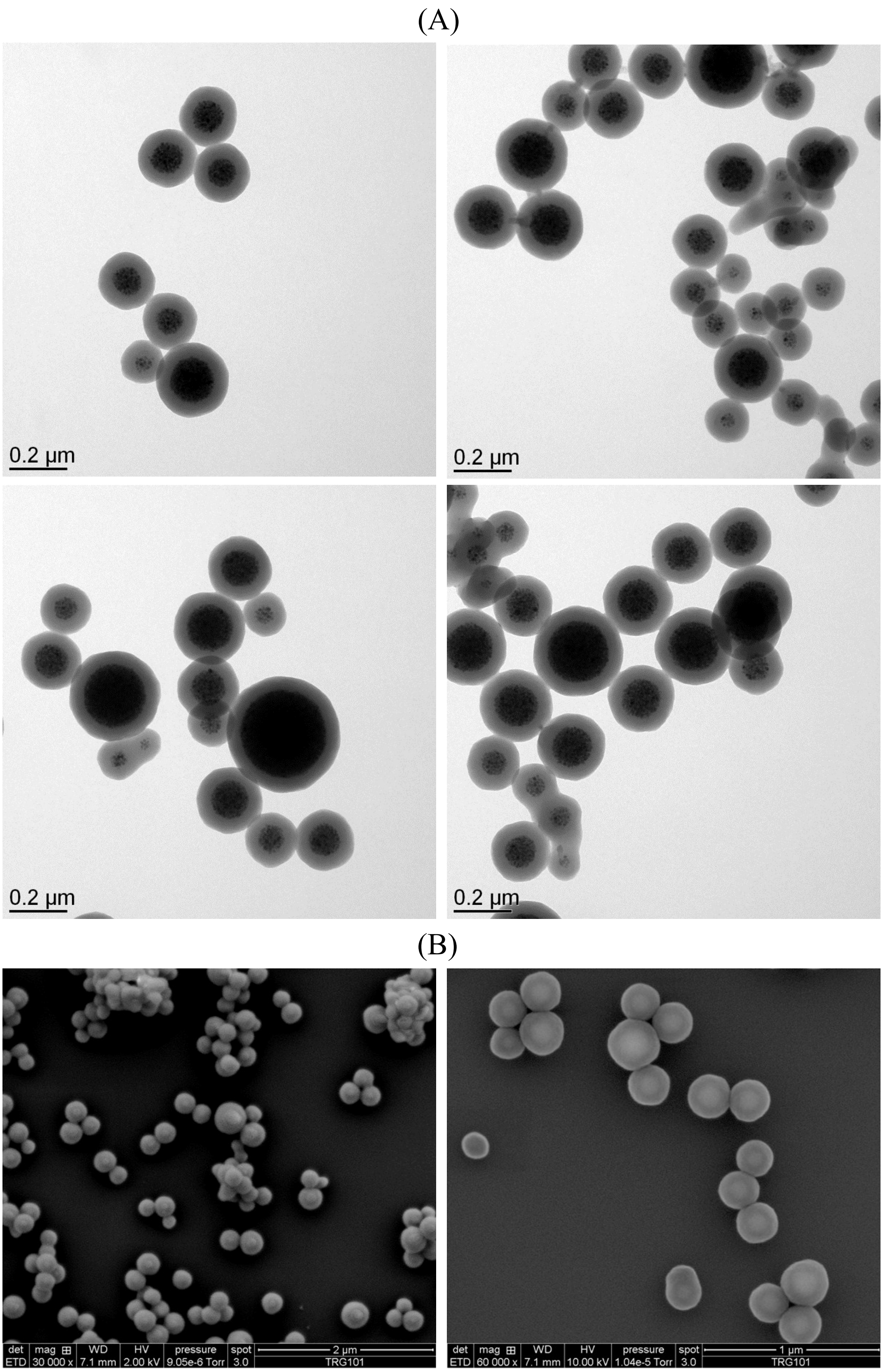


Figure S10 – (A) TEM and (B) SEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 20 wt% DVB and PC = 10% using the PDMAEMA@Clusters as seeds (Exp 4, Table 1 and Table S3).

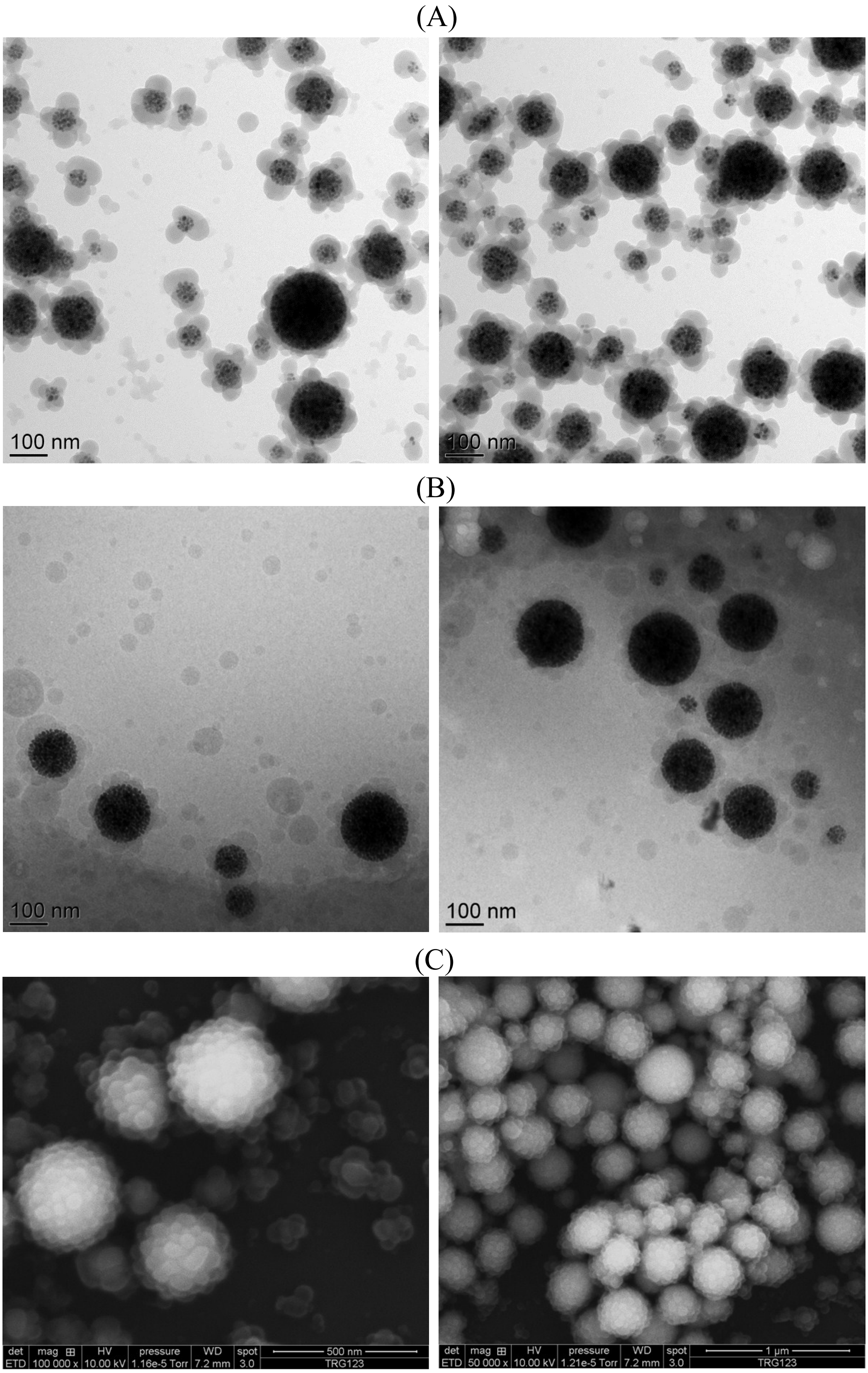


Figure S11 – (A) TEM, (B) Cryo-TEM and (C) SEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 12 wt% DVB and PC = 2.3% using the PDMAEMA@Clusters as seeds (Exp 5, Table 1 and Table S3).

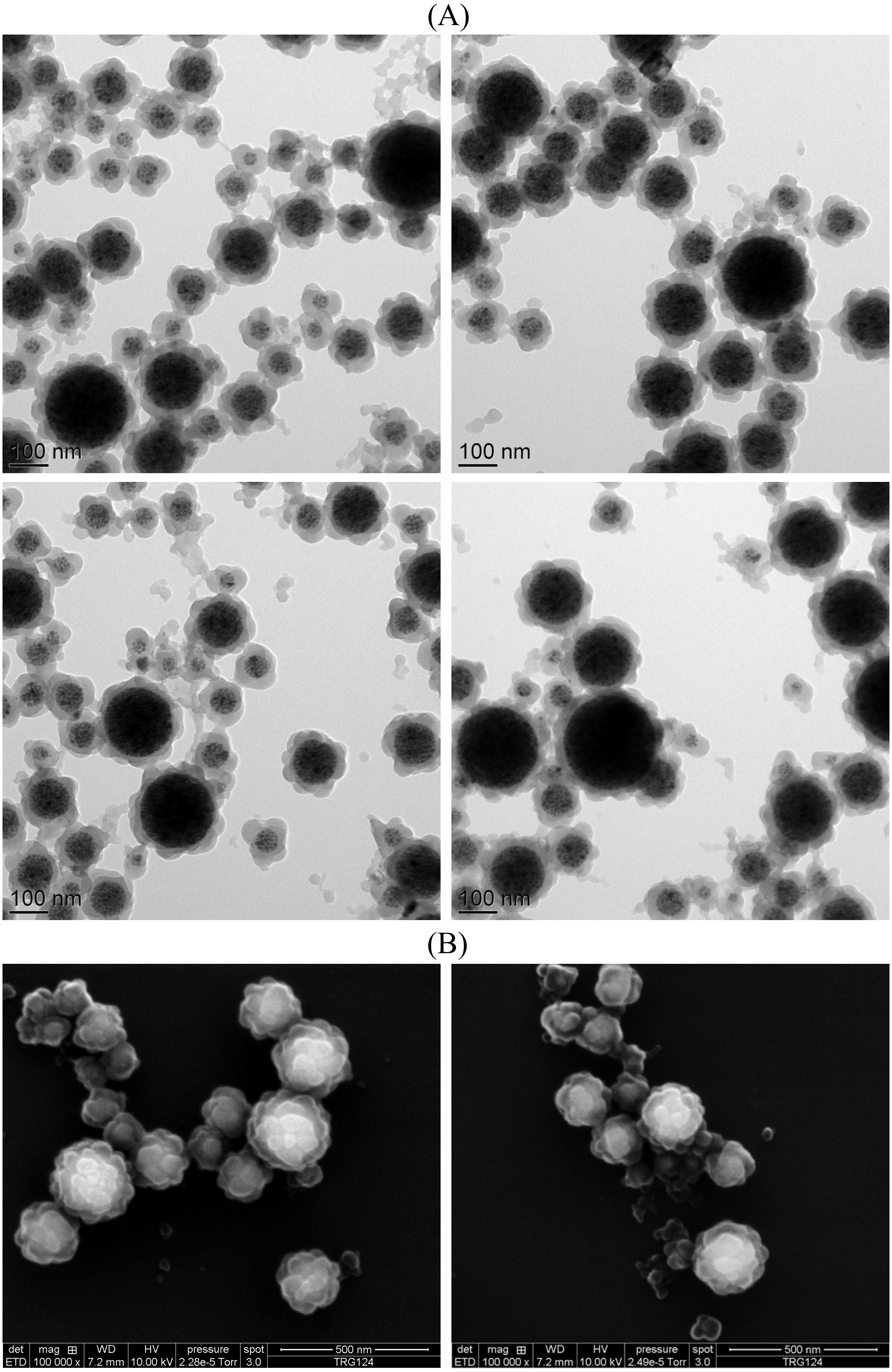


Figure S12 – (A) TEM and (B) SEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 23 wt% DVB and PC = 2.3% using the PDMAEMA@Clusters as seeds (Exp 6, Table 1 and Table S3).

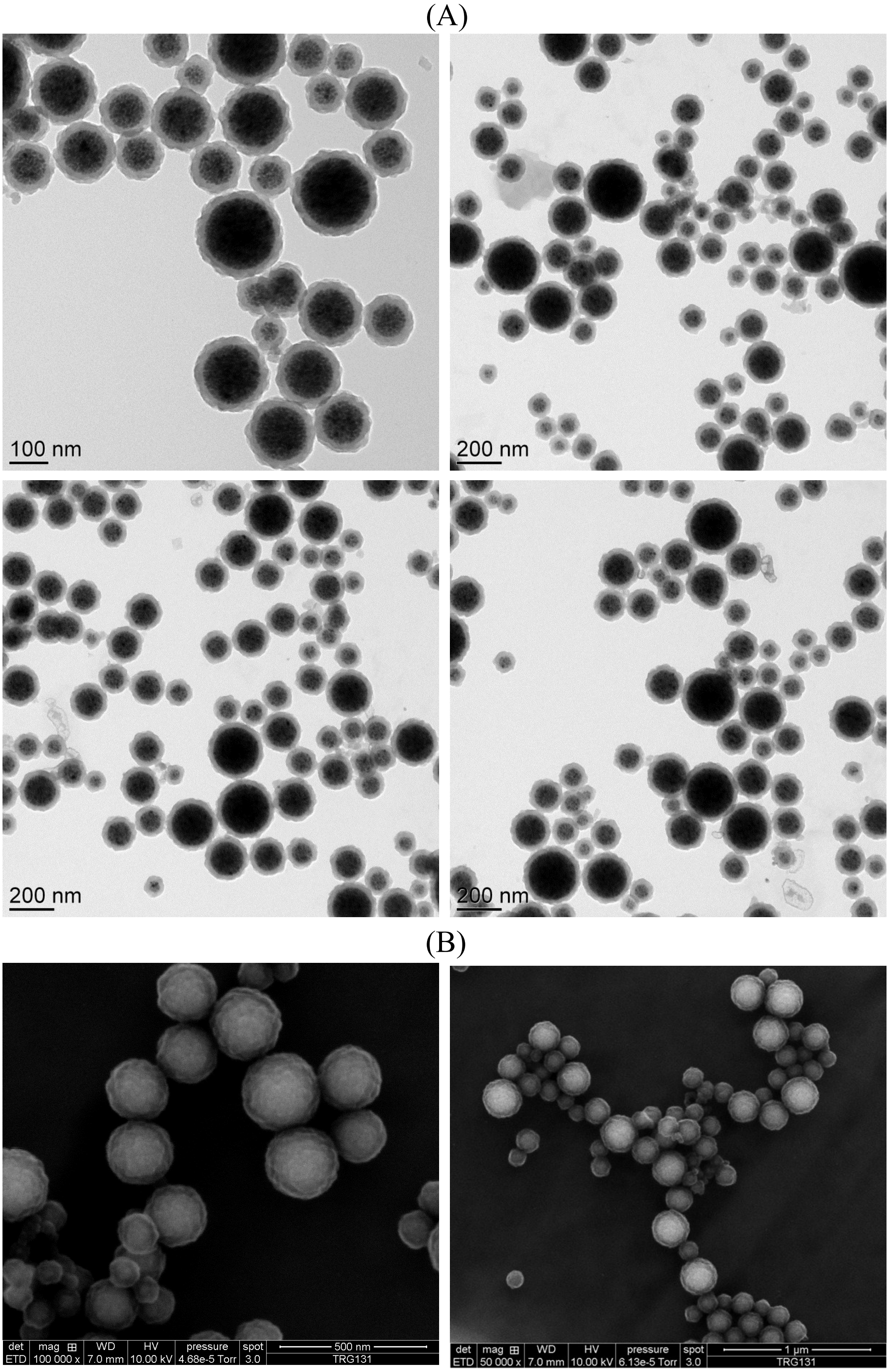


Figure S13 – (A) TEM and (B) SEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene with 38 wt% DVB and PC = 2.5% using the PDMAEMA@Clusters as seeds (Exp 7, Table 1 and Table S3).

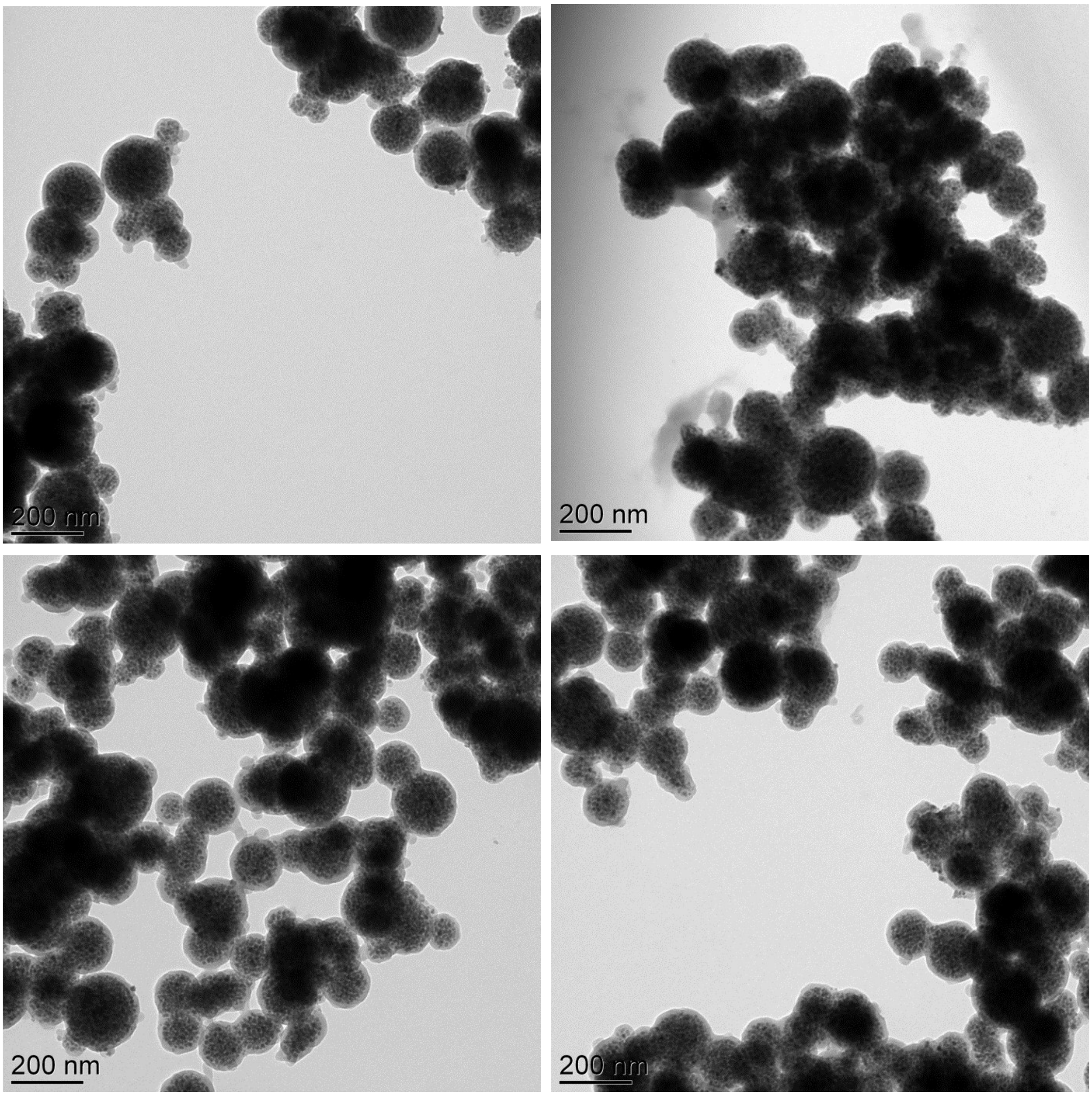


Figure S14 – TEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene at pH 7.5 using ACPA as initiator at 70 ºC and the PAA@Clusters as seeds (Exp 9, Table 2 and Table S3). Note that this latex was unstable.

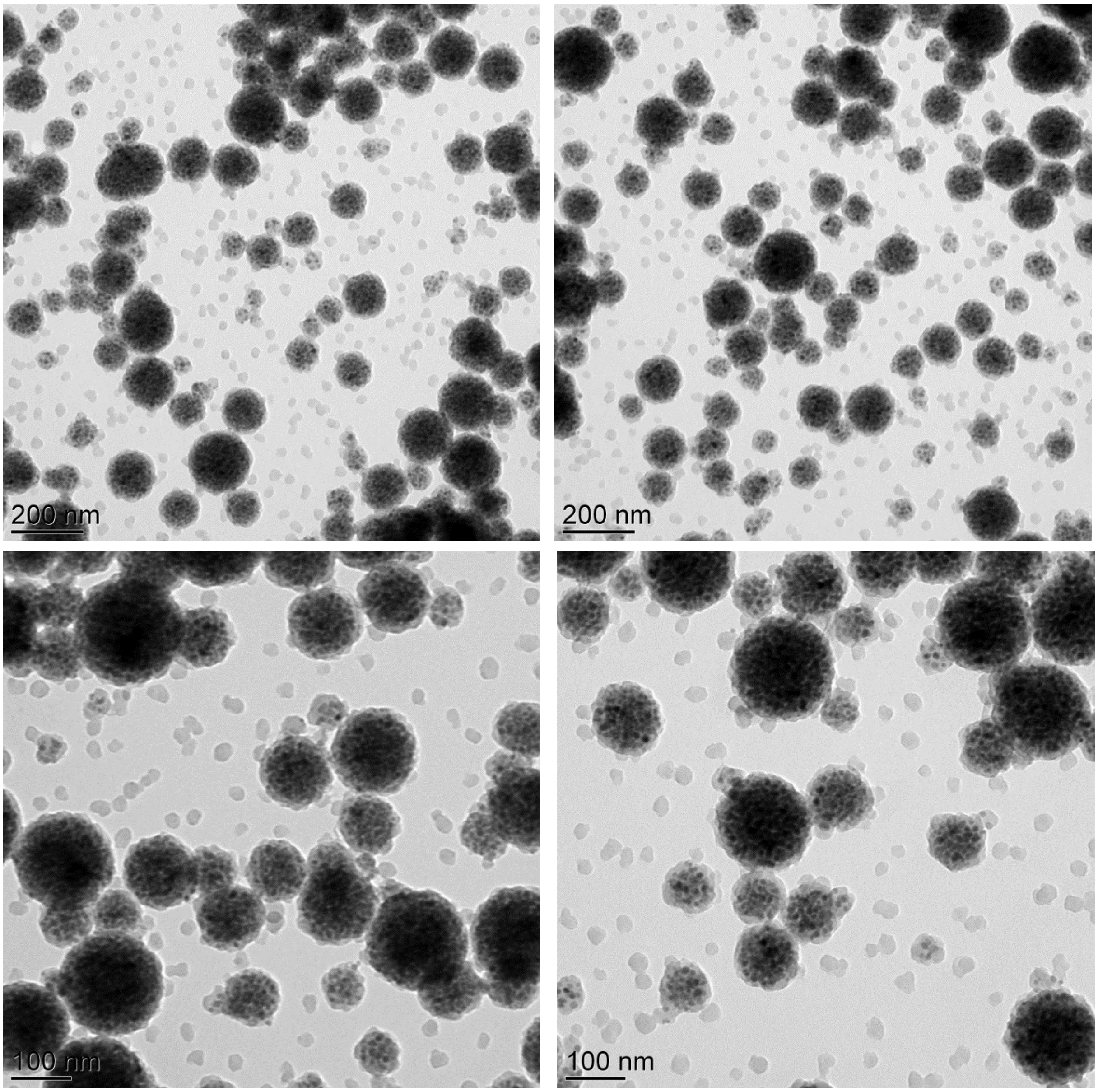


Figure S15 – TEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene at pH 9.6 using ACPA as initiator at 70 ºC and the PAA@Clusters as seeds (Exp 10, Table 2 and Table S3).

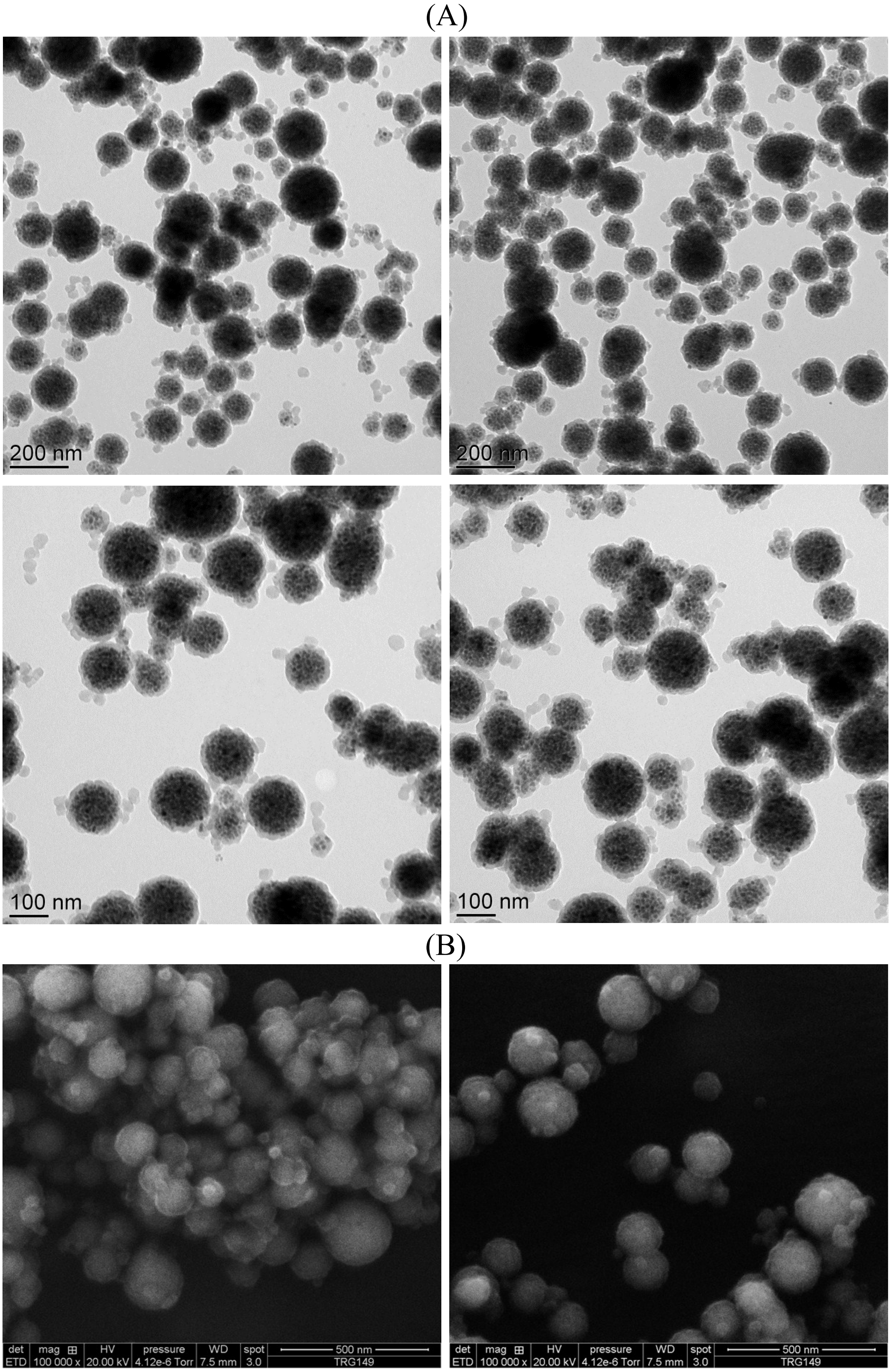


Figure S16 – (A) TEM and (B) SEM images of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene at pH 9.6 using ACPA as initiator at 80 ºC and the PAA@Clusters as seeds (Exp 11, Table 2 and Table S3).

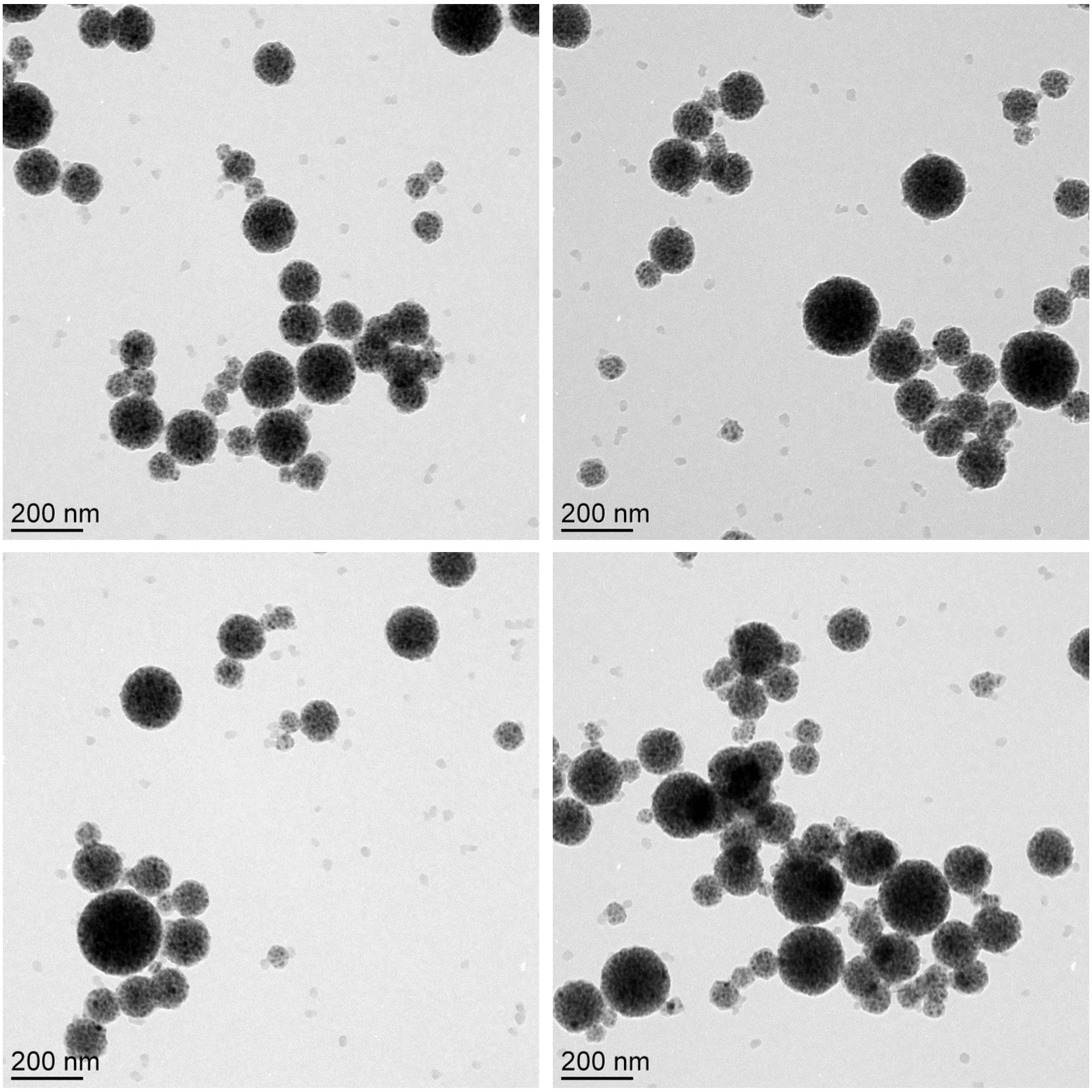


Figure S17 – (A) TEM of magnetic latex particles prepared via seeded semi-batch emulsion polymerization of styrene at pH 7.3 using APS as initiator at 75 ºC with $NaHCO_3$ and the PAA@Clusters as seeds (Exp 13, Table 2 and Table S3).

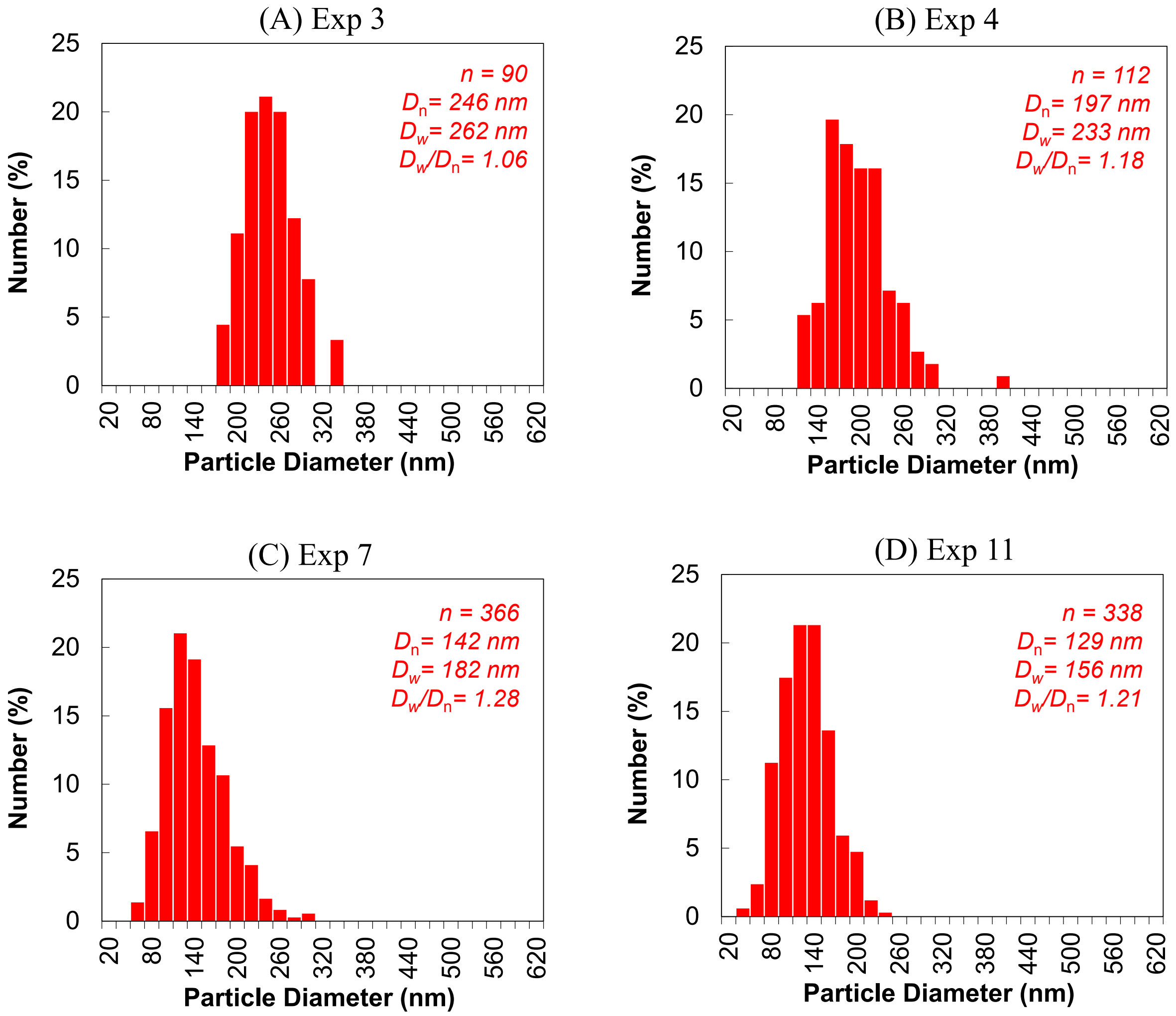


Figure S18 – Number frequency size distribution histograms of the magnetic latex particles prepared via seeded semi-batch emulsion polymerization (Exp 3, 4 and 7 in Table 1, and Exp 11 in Table 2).