Supporting Information

Porous Membranes from Acid decorated Block Copolymer Nano-objects via RAFT Alcoholic Dispersion Polymerization

Lakshmeesha Upadhyaya[a,c,d], Mona Semsarilar[a], Rodrigo Fernández-Pacheco[c], Gema Martinez[b,c], Reyes Mallada[c], André Deratani[a], Damien Quemener[a]

[a] Institut Européen des Membranes, IEM, UMR-5635, Université de Montpellier, ENSCM, CNRS, Place Eugène Bataillon, 34095 Montpellier cedex 5, France.

[b] Networking Research Centre on Bioengineering, Biomaterials and Nanomedicine, CIBER-BBN, 28029 Madrid, Spain

[c] Department of Chemical and Environmental Engineering and Aragon Nanoscience institute, Campus Río Ebro, C/ Mariano Esquillor s/n ,50018 Zaragoza, Spain

[d] Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

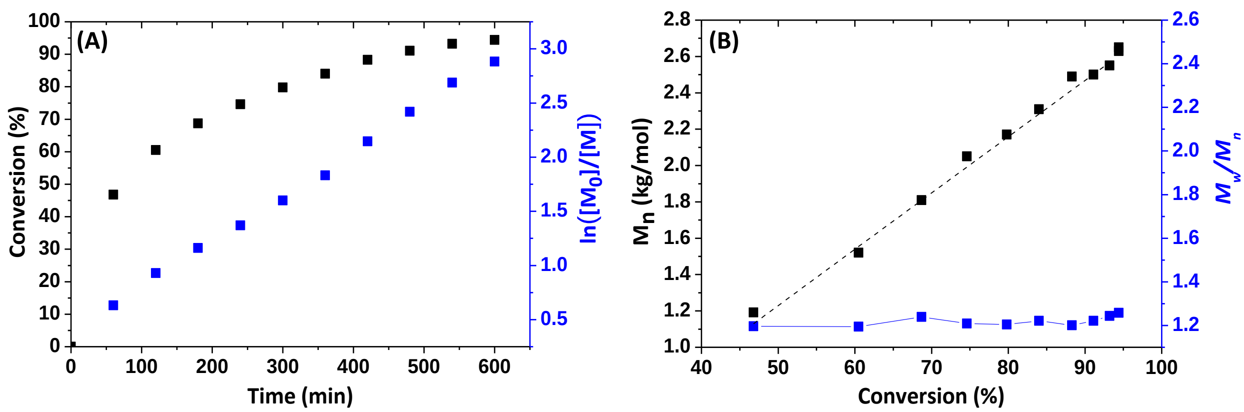

Figure S1. (A) [1]H NMR kinetic data obtained for RAFT dispersion polymerization of MAA at 10 w/w % solids in ethanol. The targeted block composition was $PMAA_{30}$. (B) Evolution of number- average molecular weight M_n and Polydispersity (M_w/M_n) with monomer conversion as judged by THF SEC (*vs.* PS calibration standards).

Table S1. Summary of diblock compositions, total solids content, conversion and degree of polymerization (DP), particle diameter and observed morphology for $PMAA_{27}$-$PMMA_y$.

Polymer composition	Solid Conc. (wt%)	Target DP	Conversion[a] (%)	Real DP	Hydrodynamic Diameter[b] (nm)	PDI[c]	Structure[d]
$PMAA_{27}$ $PMMA_{50}$	10	50	88.0	44	-	-	Soluble
$PMAA_{27}$ $PMMA_{75}$	10	75	97.3	73	32	0.08	S
$PMAA_{27}PMMA_{100}$	10	100	86.0	86	35	0.12	S
$PMAA_{27}$ $PMMA_{125}$	10	125	98.4	123	56	0.15	S
$PMAA_{27}$ $PMMA_{150}$	10	150	92.0	138	136	0.38	S
$PMAA_{27}$ $PMMA_{175}$	10	175	96.5	169	121	0.34	S+SW+V
$PMAA_{27}$ $PMMA_{200}$	10	200	93.0	186	195	0.12	S+SW+V
$PMAA_{27}$ $PMMA_{225}$	10	225	88.8	200	148	0.14	S+SW+V
$PMAA_{27}$ $PMMA_{250}$	10	250	87.2	218	118	0.12	V
$PMAA_{27}$ $PMMA_{275}$	10	275	90.1	248	152	0.18	V
$PMAA_{27}$ $PMMA_{300}$	10	300	89.6	269	169	0.15	V
$PMAA_{27}$ $PMMA_{50}$	12.5	50	74.0	37	-	-	Soluble
$PMAA_{27}$ $PMMA_{100}$	12.5	100	87.0	87	33	0.06	S
$PMAA_{27}$ $PMMA_{150}$	12.5	150	98.0	147	39	0.07	S
$PMAA_{27}$ $PMMA_{175}$	12.5	175	90.8	159	124	0.23	S+SW+V
$PMAA_{27}$ $PMMA_{200}$	12.5	200	88.0	176	132	0.24	S+SW+V
$PMAA_{27}PMMA_{225}$	12.5	225	88.8	200	134	0.18	S+SW+V
$PMAA_{27}$ $PMMA_{250}$	12.5	250	94.0	235	141	0.21	V
$PMAA_{27}$ $PMMA_{50}$	15	50	82.0	41	-	-	Soluble
$PMAA_{27}PMMA_{75}$	15	75	94.7	71	31	0.08	S
$PMAA_{27}$ $PMMA_{100}$	15	100	86.0	86	36	0.05	S
$PMAA_{27}$ $PMMA_{125}$	15	125	84.8	106	39	0.06	S
$PMAA_{27}$ $PMMA_{150}$	15	150	86.7	130	101	016	S+SW
$PMAA_{27}$ $PMMA_{175}$	15	175	86.2	151	112	0.21	S+SW
$PMAA_{27}$ $PMMA_{200}$	15	200	97.0	194	103	0.19	S+SW
$PMAA_{27}$ $PMMA_{225}$	15	225	92.8	209	162	0.39	W+V
$PMAA_{27}$ $PMMA_{250}$	15	250	92.0	230	126	0.09	V
$PMAA_{27}$ $PMMA_{50}$	20	50	92.0	46	-	-	Soluble
$PMAA_{27}$ $PMMA_{75}$	20	75	89.3	67	32	0.06	S
$PMAA_{27}$ $PMMA_{100}$	20	100	87.0	87	39	0.09	S

$PMAA_{27}PMMA_{125}$	20	125	92.0	115	69	0.18	S+SW
$PMAA_{27}$ $PMMA_{150}$	20	150	96.6	145	121	0.26	S+SW
$PMAA_{27}$ $PMMA_{200}$	20	200	86.0	172	121	0.36	S+SW
$PMAA_{27}PMMA_{225}$	20	225	87.1	196	138	0.38	S+SW
$PMAA_{27}$ $PMMA_{250}$	20	250	83.6	209	141	0.14	W+V
$PMAA_{27}$ $PMMA_{275}$	20	275	94.2	259	89	0.21	V
$PMAA_{27}$ $PMMA_{300}$	20	300	97.0	291	121	0.16	V
$PMAA_{27}$ $PMMA_{50}$	25	50	82.0	41	-	-	Soluble
$PMAA_{27}$ $PMMA_{75}$	25	75	92.0	69	32	0.03	S
$PMAA_{27}$ $PMMA_{100}$	25	100	89.0	89	36	0.09	S
$PMAA_{27}$ $PMMA_{125}$	25	125	84.8	106	86	0.28	S+SW
$PMAA_{27}$ $PMMA_{150}$	25	150	82.0	123	126	0.34	S+SW
$PMAA_{27}$ $PMMA_{200}$	25	200	93.5	187	182	0.32	S+SW
$PMAA_{27}$ $PMMA_{250}$	25	250	88.8	222	169	0.36	W+V
$PMAA_{27}$ $PMMA_{275}$	25	275	91.2	251	91	0.12	V
$PMAA_{27}$ $PMMA_{50}$	30	50	86.0	43	-	-	Soluble
$PMAA_{27}$ $PMMA_{75}$	30	75	89.3	67	28	0.12	S
$PMAA_{27}$ $PMMA_{100}$	30	100	92.0	92	32	0.13	S
$PMAA_{27}$ $PMMA_{125}$	30	125	87.2	109	85	0.18	S+SW
$PMAA_{27}$ $PMMA_{150}$	30	150	84.0	126	121	0.21	S+SW
$PMAA_{27}$ $PMMA_{200}$	30	200	92.5	185	136	0.23	S+SW
$PMAA_{27}$ $PMMA_{225}$	30	225	92.4	208	128	0.26	W+V
$PMAA_{27}$ $PMMA_{250}$	30	250	91.2	228	111	0.33	W+V
$PMAA_{27}$ $PMMA_{275}$	30	275	91.2	251	102	0.15	V
$PMAA_{27}$ $PMMA_{300}$	30	300	93.0	279	91	0.16	V

[a] as judged by ^{1}H NMR
[b,c] measured by dynamic light scattering
[d] as judged by post mortem TEM analysis

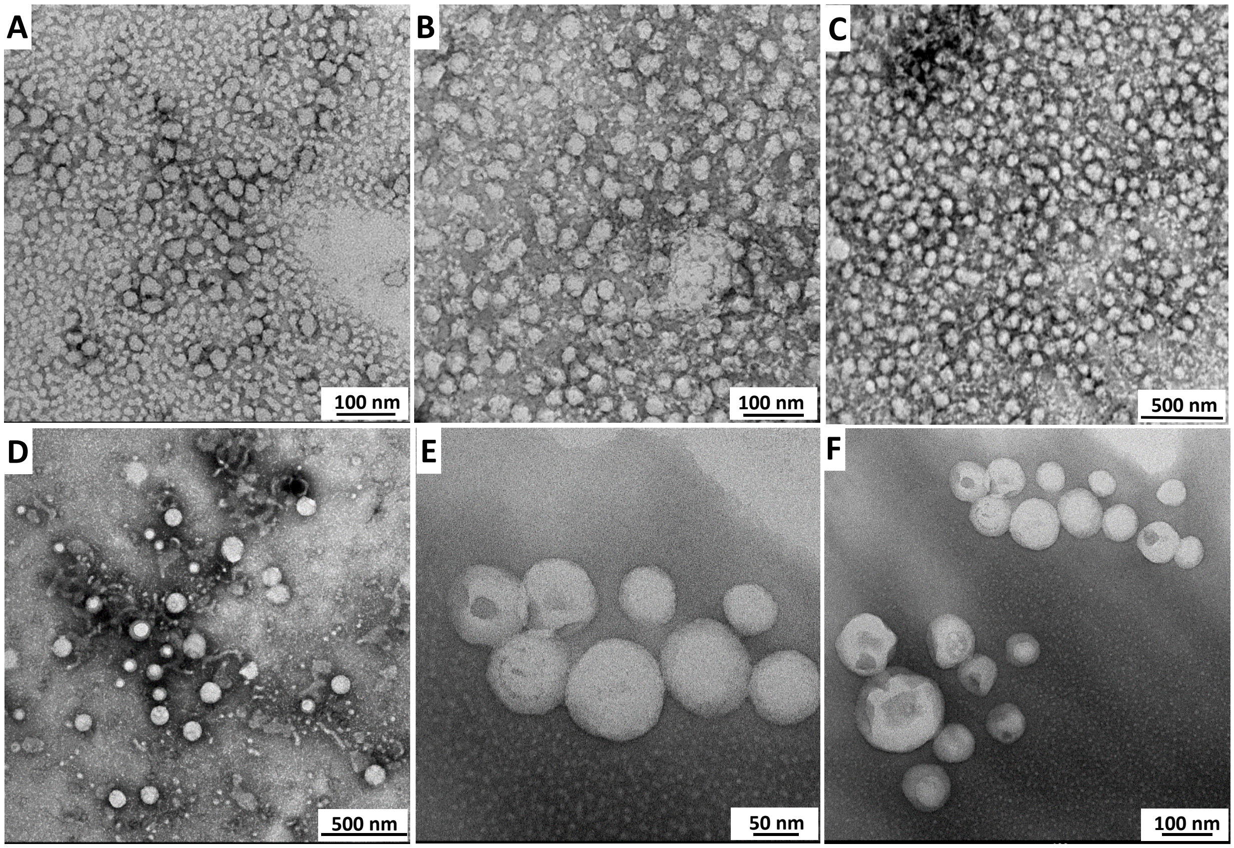

Figure S2. TEM images of $PMAA_{27}$-$PMMA_y$ at 10 w/w% total solids content where (A) y= 73; Spheres (B) y= 86; Spheres (C) y= 123; Spheres (D) y=169; Spheres + Short worms + Vesicles (E) y=218; Vesicles (F) y= 248; Vesicles.

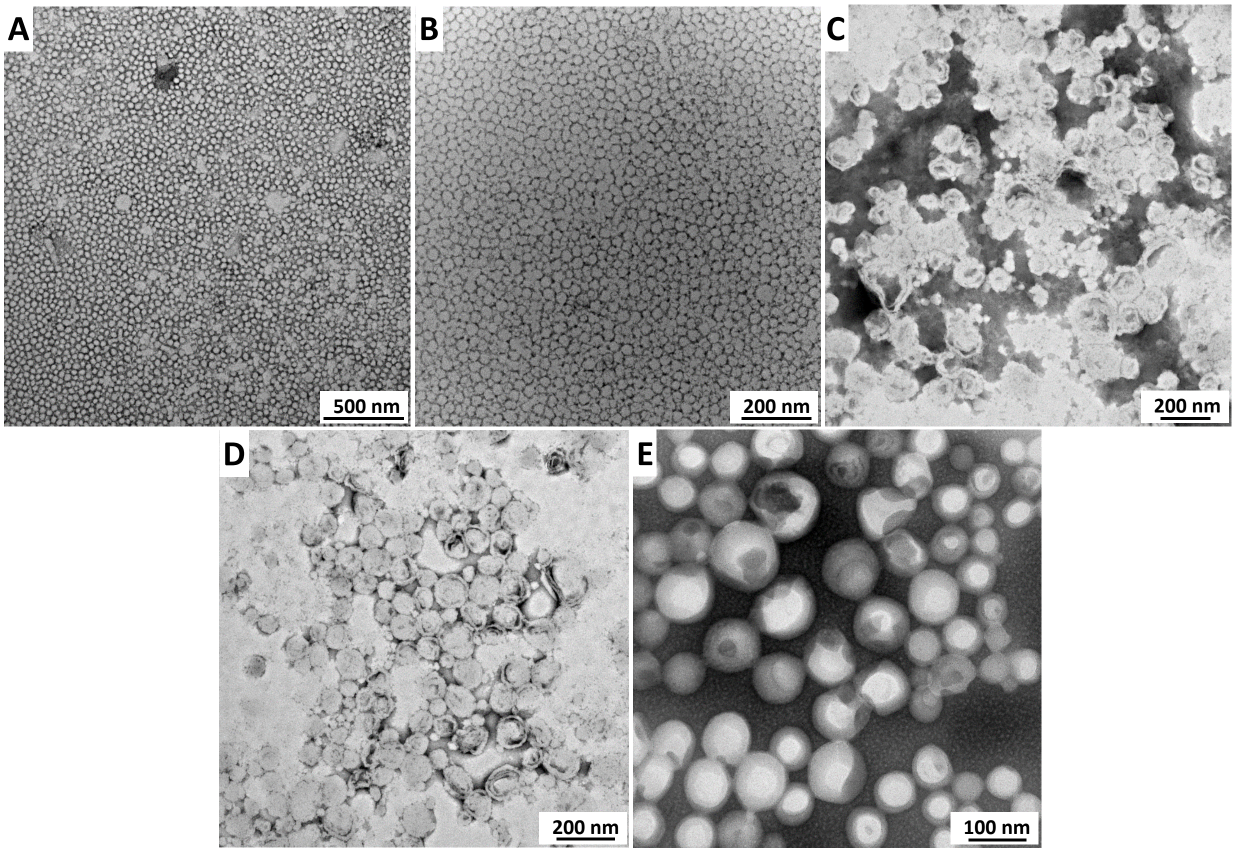

Figure S3. TEM images of $PMAA_{27}$-$PMMA_y$ at 12.5 w/w% total solids content where (A) y= 87; Spheres (B) y= 147; Spheres (C) y= 159; Spheres + Short worms + Vesicles (D) y=200; Spheres + Short worms + Vesicles (E) y=235; Vesicles.

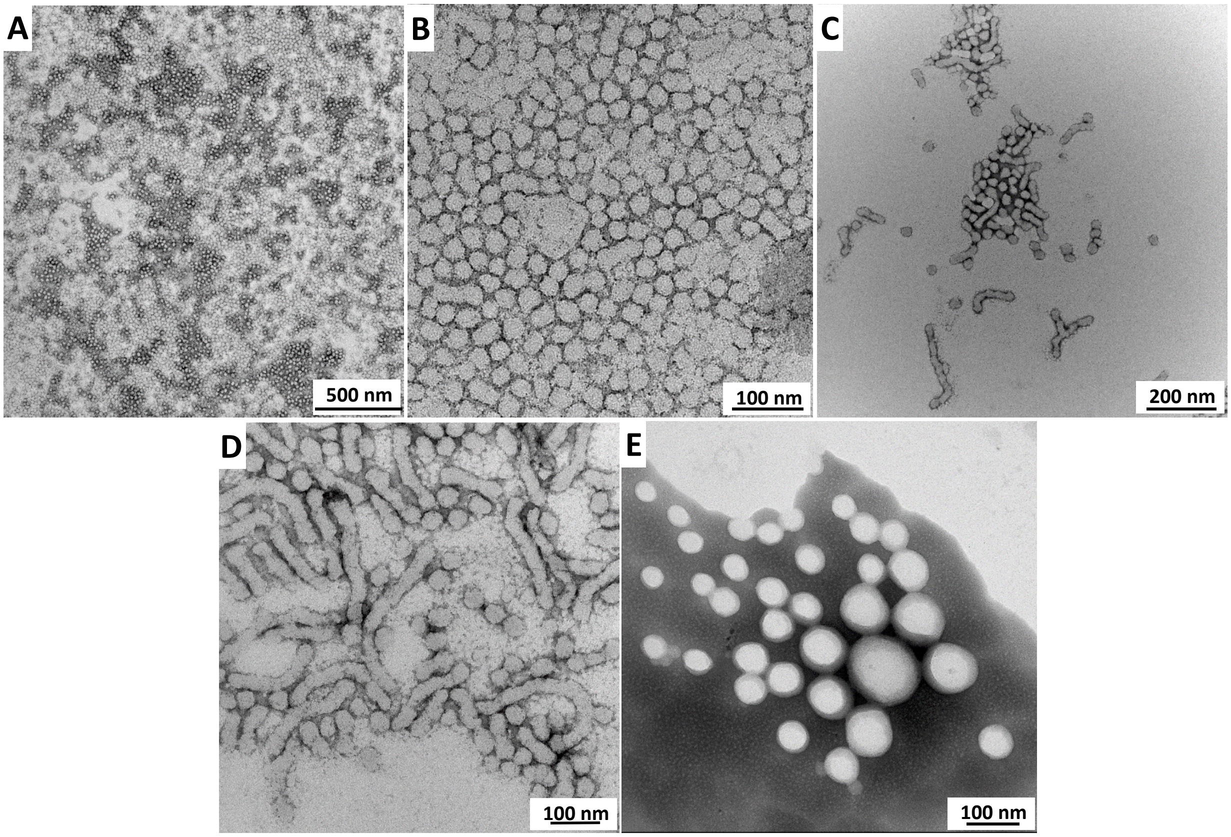

Figure S4. TEM images of $PMAA_{27}$-$PMMA_y$ at 15 w/w% total solids content where (A) y= 71; Spheres (B) y= 106; Spheres (C) y= 130; Spheres + Short worms (D) y=194; Spheres + Short worms (E) y=230; Vesicles.

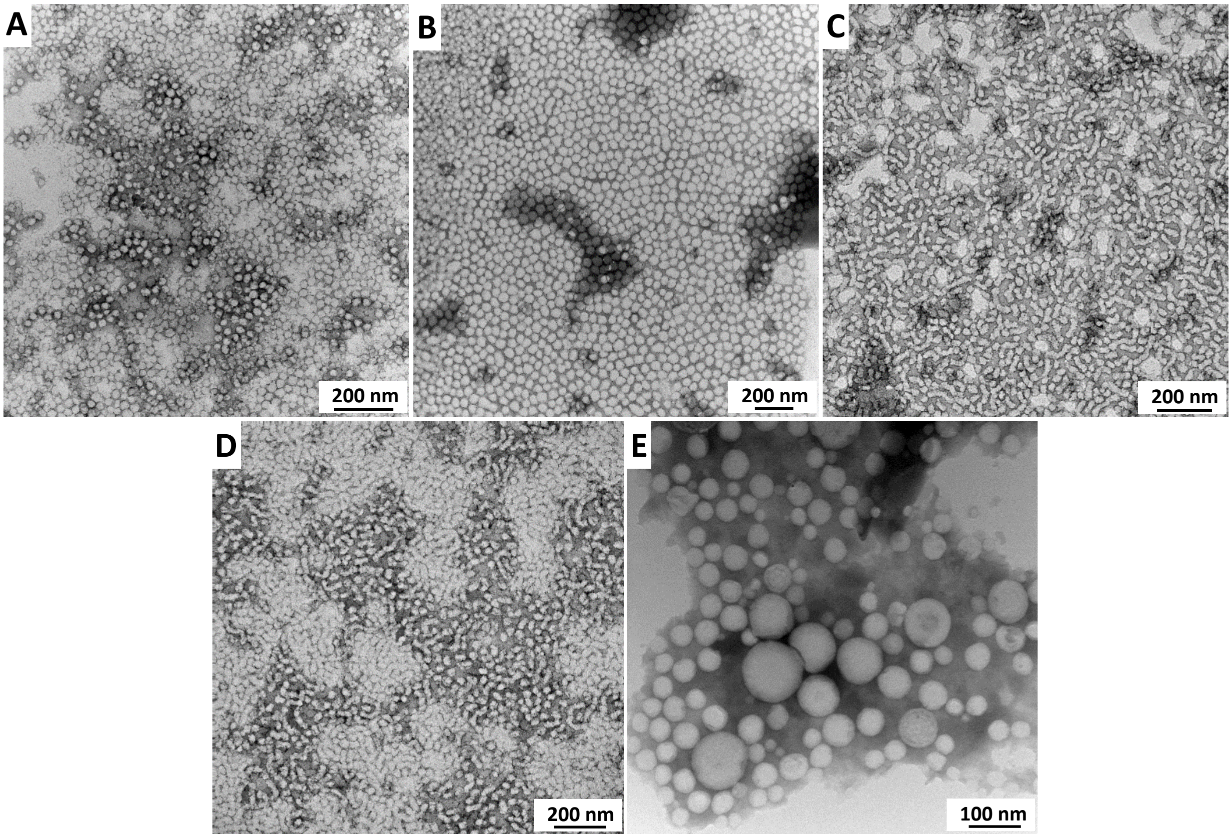

Figure S5. TEM images of $PMAA_{27}$-$PMMA_y$ at 25 w/w% total solids content where (A) y= 69; Spheres (B) y= 89; Spheres (C) y= 106; Spheres + Short worms (D) y=187; Spheres + Short worms (E) y=251; Vesicles.

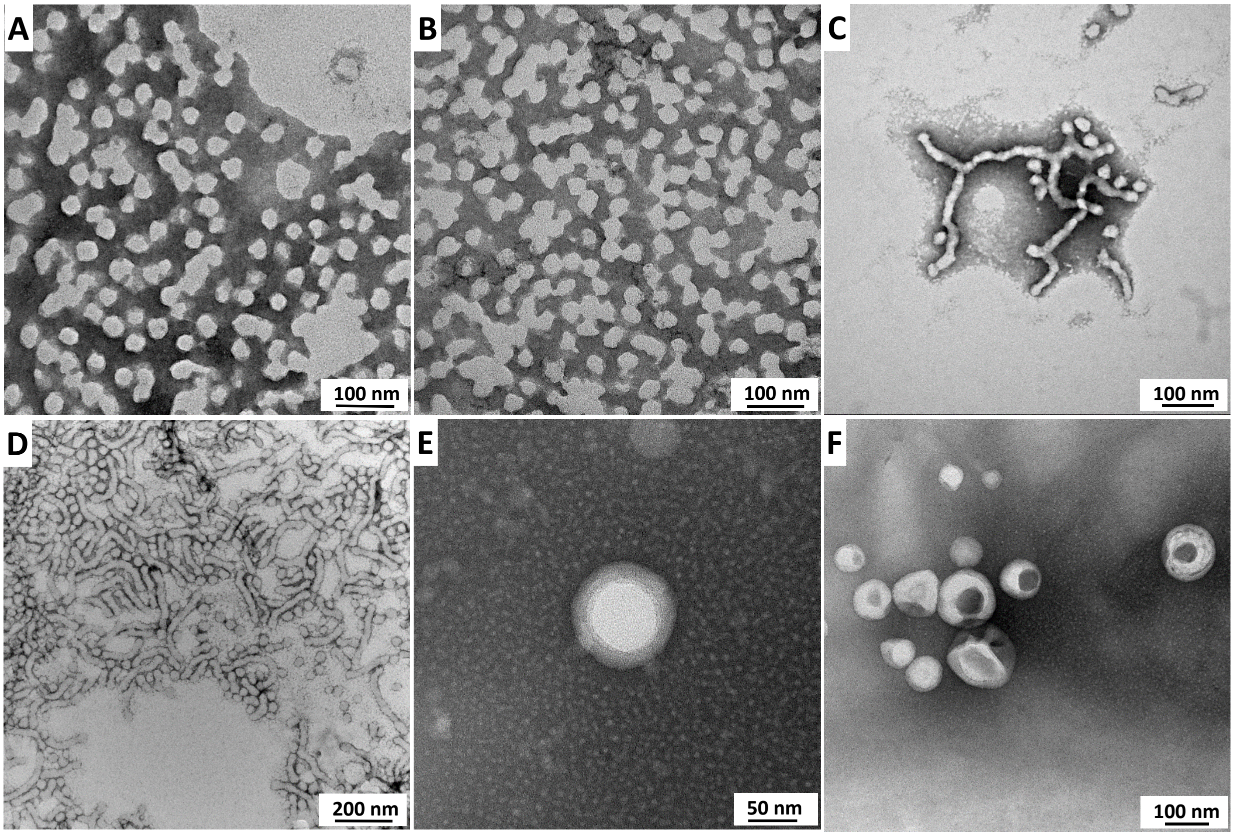

Figure S6. TEM images of $PMAA_{27}$-$PMMA_y$ at 30 w/w% total solids content where (A) y= 67; Spheres (B) y= 92; Spheres (C) y= 109; Spheres + Short worms (D) y=185; Spheres + Short worms (E) y=251; Vesicles (F) y= 279; Vesicles.

Table S2. Summary of diblock compositions, total solids content, conversion and degree of polymerization (DP), particle diameter and observed morphology for $PMAA_{47}$-$PMMA_{y}$

Polymer Composition	Solid Conc. (w/w %)	Target DP	Conversion[a] (%)	Real DP	Hydrodynamic Diameter[b] (nm)	PDI[c]	Structure[d]
$PMAA_{47}$ $PMMA_{75}$	10	75	96.0	72	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	10	125	96.8	121	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	10	150	94.6	142	-	-	Soluble
$PMAA_{47}$ $PMMA_{175}$	10	175	89.1	156	34	0.09	S
$PMAA_{47}$ $PMMA_{200}$	10	200	94.5	189	41	0.06	S
$PMAA_{47}$ $PMMA_{225}$	10	225	99.1	223	49	0.07	S
$PMAA_{47}$ $PMMA_{250}$	10	250	95.2	238	201	0.32	S+SW
$PMAA_{47}$ $PMMA_{275}$	10	275	98.5	271	217	0.29	S+SW
$PMAA_{47}$ $PMMA_{300}$	10	300	94.6	284	189	0.18	S+SW+V
$PMAA_{47}$ $PMMA_{325}$	10	325	98.7	321	247	0.26	S+SW+V
$PMAA_{47}$ $PMMA_{375}$	10	375	98.1	368	271	0.24	S+SW+V
$PMAA_{47}$ $PMMA_{75}$	12.5	75	92.0	69	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	12.5	150	96.6	145	-	-	Soluble
$PMAA_{47}$ $PMMA_{175}$	12.5	175	90.3	158	31	0.09	S
$PMAA_{47}$ $PMMA_{200}$	12.5	200	96.0	192	39	0.15	S
$PMAA_{47}$ $PMMA_{225}$	12.5	225	98.2	221	47	0.08	S
$PMAA_{47}$ $PMMA_{250}$	12.5	250	95.6	239	121	0.31	S+SW
$PMAA_{47}$ $PMMA_{275}$	12.5	275	97.8	269	149	0.38	S+SW
$PMAA_{47}$ $PMMA_{300}$	12.5	300	96.3	289	196	0.22	S+SW+V
$PMAA_{47}$ $PMMA_{400}$	12.5	400	94.5	378	201	0.28	S+SW+V
$PMAA_{47}$ $PMMA_{50}$	15	50	96.0	48	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	15	125	96.8	121	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	15	150	88.6	133	35	0.09	S
$PMAA_{47}$ $PMMA_{200}$	15	200	92.5	185	39	0.21	S
$PMAA_{47}$ $PMMA_{225}$	15	225	91.1	205	42	0.18	S
$PMAA_{47}$ $PMMA_{250}$	15	250	87.6	219	152	0.15	S+SW
$PMAA_{47}$ $PMMA_{275}$	15	275	92.7	255	141	0.36	S+SW
$PMAA_{47}$ $PMMA_{290}$	15	290	92.0	267	138	0.21	W
$PMAA_{47}$ $PMMA_{300}$	15	300	99.3	298	128	0.14	W
$PMAA_{47}$ $PMMA_{325}$	15	325	96.9	315	152	0.28	W+V

$PMAA_{47}$ $PMMA_{350}$	15	350	98.0	343	168	0.31	W+V
$PMAA_{47}$ $PMMA_{400}$	15	400	89.0	356	148	0.18	V
$PMAA_{47}$ $PMMA_{50}$	17.5	50	96.0	48	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	17.5	125	84.0	105	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	17.5	150	79.3	119	33	0.09	S
$PMAA_{47}$ $PMMA_{200}$	17.5	200	97.5	195	39	0.06	S
$PMAA_{47}$ $PMMA_{225}$	17.5	225	91.5	206	141	0.32	S+SW
$PMAA_{47}$ $PMMA_{250}$	17.5	250	99.6	249	167	0.35	S+SW
$PMAA_{47}$ $PMMA_{300}$	17.5	300	91.0	273	189	0.28	W
$PMAA_{47}$ $PMMA_{350}$	17.5	350	91.7	321	168	0.25	W+V
$PMAA_{47}$ $PMMA_{400}$	17.5	400	92.0	368	102	0.15	V
$PMAA_{47}$ $PMMA_{50}$	20	50	98.0	49	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	20	125	84.0	105	-	-	Soluble
$PMAA_{47}PMMA_{150}$	20	150	76.0	114	33	0.08	S
$PMAA_{47}$ $PMMA_{175}$	20	175	81.1	142	41	0.1	S
$PMAA_{47}$ $PMMA_{200}$	20	200	99.0	198	48	0.1	S
$PMAA_{47}$ $PMMA_{225}$	20	225	94.2	212	142	0.38	S+SW
$PMAA_{47}$ $PMMA_{275}$	20	275	89.0	245	168	0.34	S+SW
$PMAA_{47}$ $PMMA_{300}$	20	300	92.0	276	158	0.24	W
$PMAA_{47}$ $PMMA_{350}$	20	350	98.5	345	172	0.31	W+V
$PMAA_{47}$ $PMMA_{400}$	20	400	89.7	359	148	0.16	V
$PMAA_{47}$ $PMMA_{125}$	25	125	84.8	106	-	-	Soluble
$PMAA_{47}PMMA_{150}$	25	150	79.3	119	35	0.17	S
$PMAA_{47}$ $PMMA_{200}$	25	200	98.5	197	46	0.12	S
$PMAA_{47}$ $PMMA_{225}$	25	225	92.4	208	147	0.24	S+SW
$PMAA_{47}$ $PMMA_{250}$	25	250	96.4	241	173	0.21	S+SW
$PMAA_{47}$ $PMMA_{275}$	25	275	93.4	257	182	0.38	W
$PMAA_{47}$ $PMMA_{325}$	25	325	91.4	297	193	0.27	W
$PMAA_{47}$ $PMMA_{350}$	25	350	90.8	318	186	0.19	W+V
$PMAA_{47}$ $PMMA_{400}$	25	400	89.0	356	108	0.21	V
$PMAA_{47}$ $PMMA_{75}$	27.5	75	74.6	56	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	27.5	125	83.2	104	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	27.5	150	81.3	122	38	0.07	S
$PMAA_{47}$ $PMMA_{200}$	27.5	200	96.0	192	46	0.14	S
$PMAA_{47}$ $PMMA_{225}$	27.5	225	92.0	207	153	0.28	S+SW

$PMAA_{47}$ $PMMA_{275}$	27.5	275	93.1	256	176	0.23	W
$PMAA_{47}$ $PMMA_{350}$	27.5	350	90.0	315	193	0.32	W+V
$PMAA_{47}$ $PMMA_{400}$	27.5	400	89.7	359	128	0.16	V
$PMAA_{47}$ $PMMA_{100}$	30	100	61.0	61	-	-	Soluble
$PMAA_{47}$ $PMMA_{125}$	30	125	84.0	105	-	-	Soluble
$PMAA_{47}$ $PMMA_{150}$	30	150	78.0	117	41	0.10	S
$PMAA_{47}$ $PMMA_{175}$	30	175	80.0	140	43	0.09	S
$PMAA_{47}$ $PMMA_{225}$	30	225	84.0	189	47	0.12	S
$PMAA_{47}$ $PMMA_{250}$	30	250	82.0	205	129	0.29	S+SW
$PMAA_{47}$ $PMMA_{275}$	30	275	88.3	243	171	0.31	S+SW
$PMAA_{47}$ $PMMA_{300}$	30	300	86.3	259	198	0.28	W
$PMAA_{47}$ $PMMA_{325}$	30	325	91.1	296	187	0.32	W
$PMAA_{47}$ $PMMA_{350}$	30	350	91.7	321	168	0.21	W+V
$PMAA_{47}$ $PMMA_{400}$	30	400	92.2	369	120	0.12	V

[a] as judged by ^{1}H NMR
[b,c] measured by dynamic light scattering
[d] as judged by post mortem TEM analysis

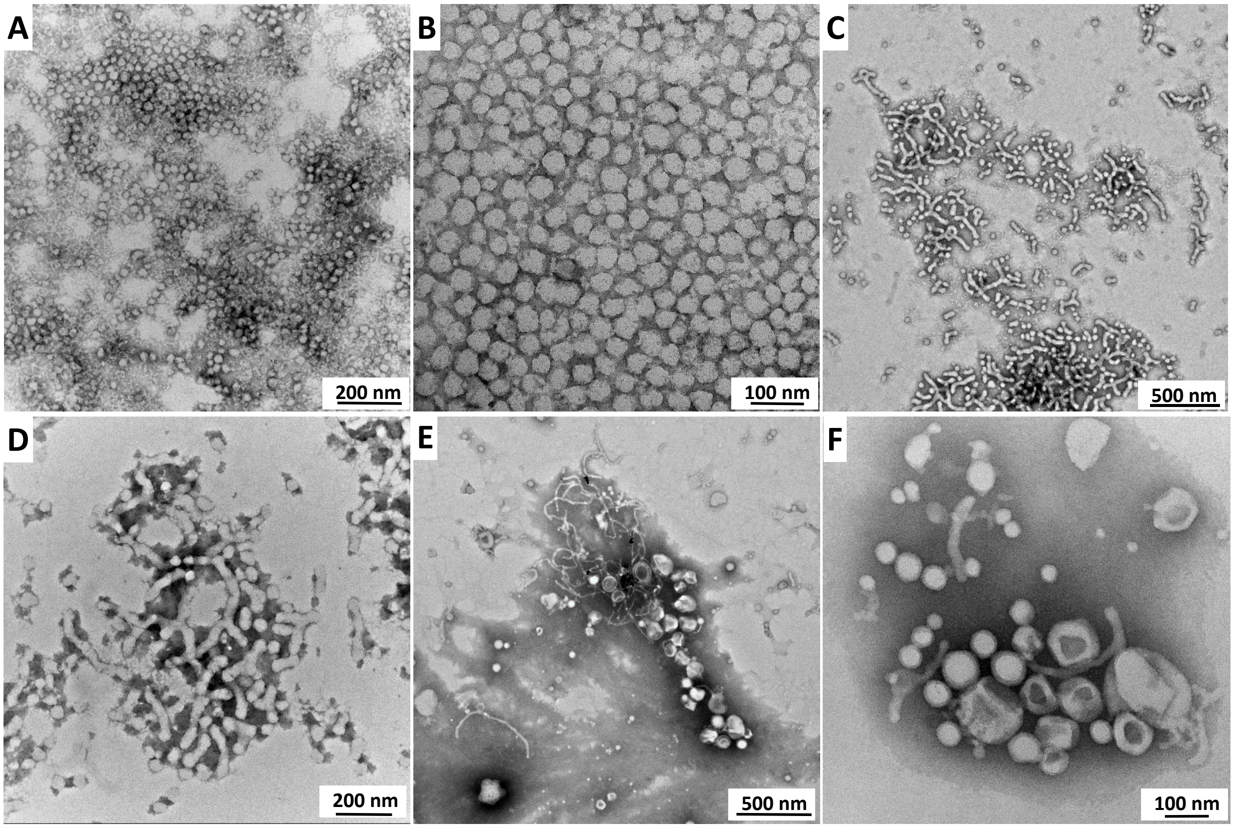

Figure S7. TEM images of $PMAA_{47}$-$PMMA_y$ at 10 w/w% total solids content where (A) y= 156; Spheres (B) y= 223; Spheres (C) y= 238; Spheres + Short worms (D) y=271; Spheres + Short worms (E) y=284; Spheres + Short worms + Vesicles (F) y= 368; Spheres + Short worms + Vesicles.

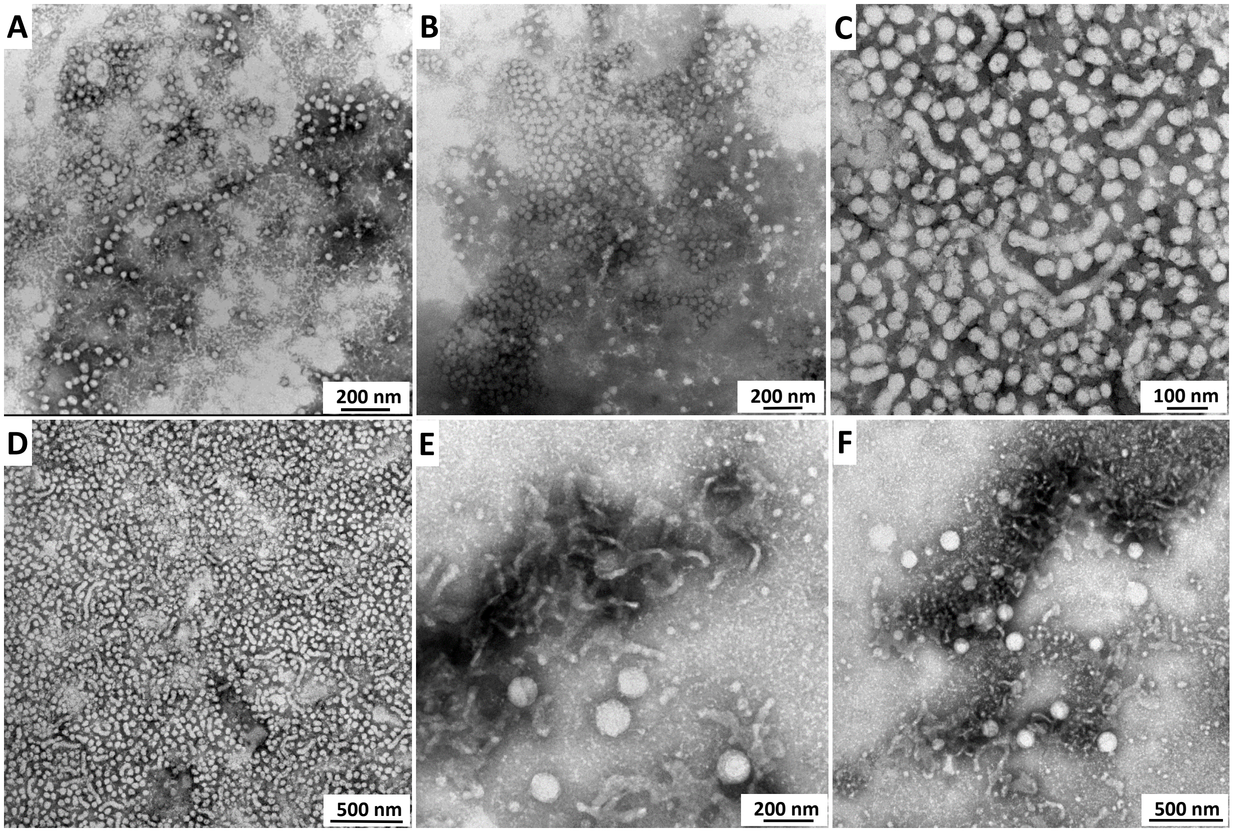

Figure S8. TEM images of $PMAA_{47}$-$PMMA_y$ at 12.5 w/w% total solids content where (A) y= 158; Spheres (B) y= 221; Spheres (C) y= 239; Spheres + Short worms (D) y=269; Spheres + Short worms (E) y=289; Spheres + Short worms + Vesicles (F) y= 378; Spheres + Short worms + Vesicles.

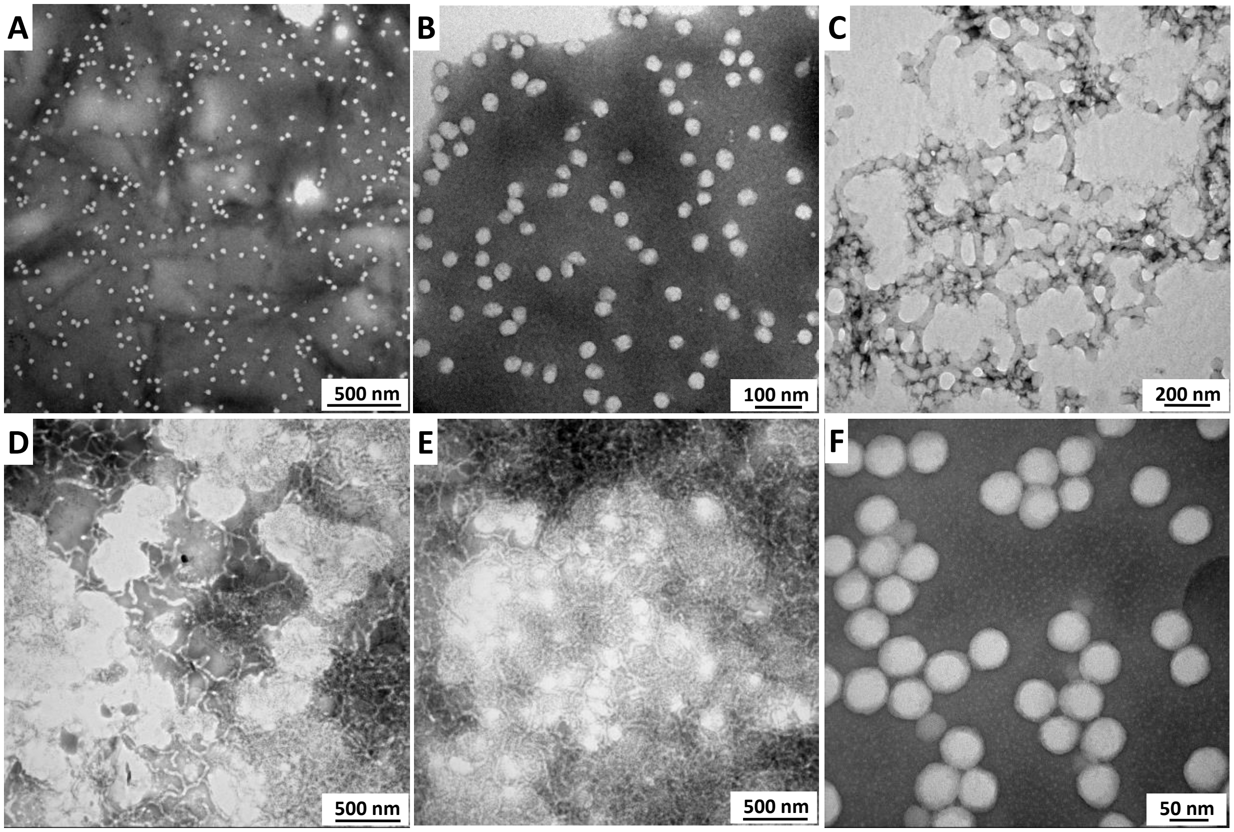

Figure S9. TEM images of $PMAA_{47}$-$PMMA_y$ at 15 w/w% total solids content where (A) y= 133; Spheres (B) y= 205; Spheres (C) y= 219; Spheres + Short worms (D) y=315; Worms + Vesicles (E) y=343; Worms + Vesicles (F) y= 356; Vesicles.

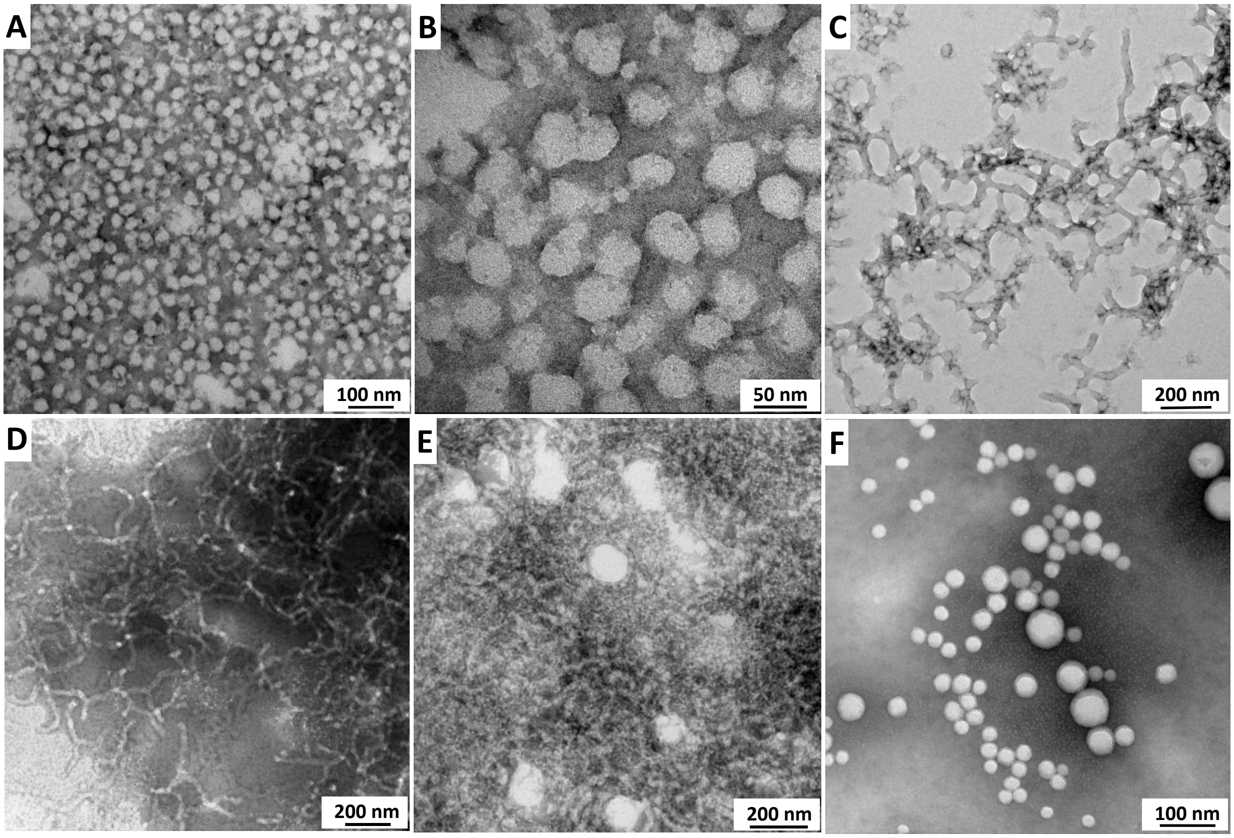

Figure S10. TEM images of $PMAA_{47}$-$PMMA_y$ at 17.5 w/w% total solids content where (A) y= 119; Spheres (B) y= 195; Spheres (C) y= 206; Spheres + Short worms (D) y=273; Worms (E) y=321; Worms + Vesicles (F) y= 368; Vesicles.

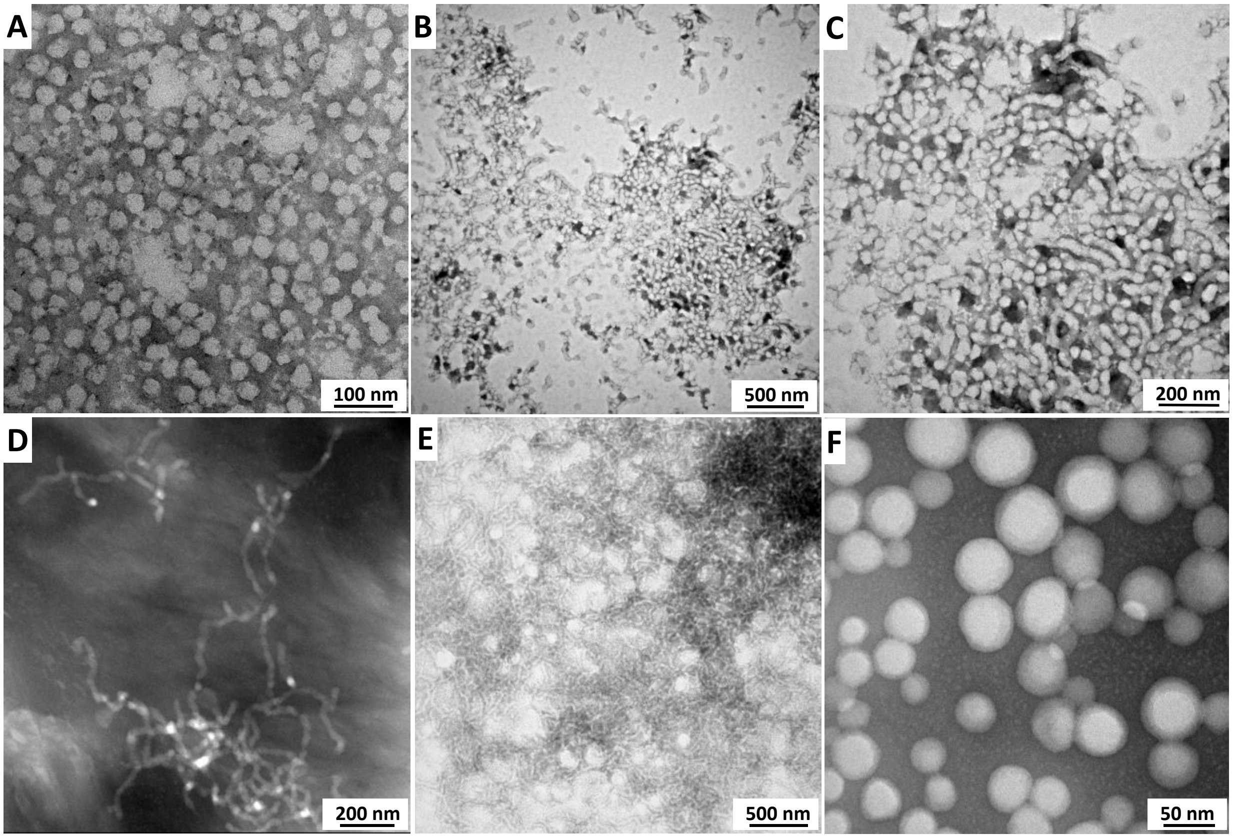

Figure S11. TEM images of $PMAA_{47}$-$PMMA_y$ at 25 w/w% total solids content where (A) y= 119; Spheres (B) y= 208; Spheres + Short worms (C) y= 241; Spheres + Short worms (D) y=257; Worms (E) y=318; Worms + Vesicles (F) y= 356; Vesicles.

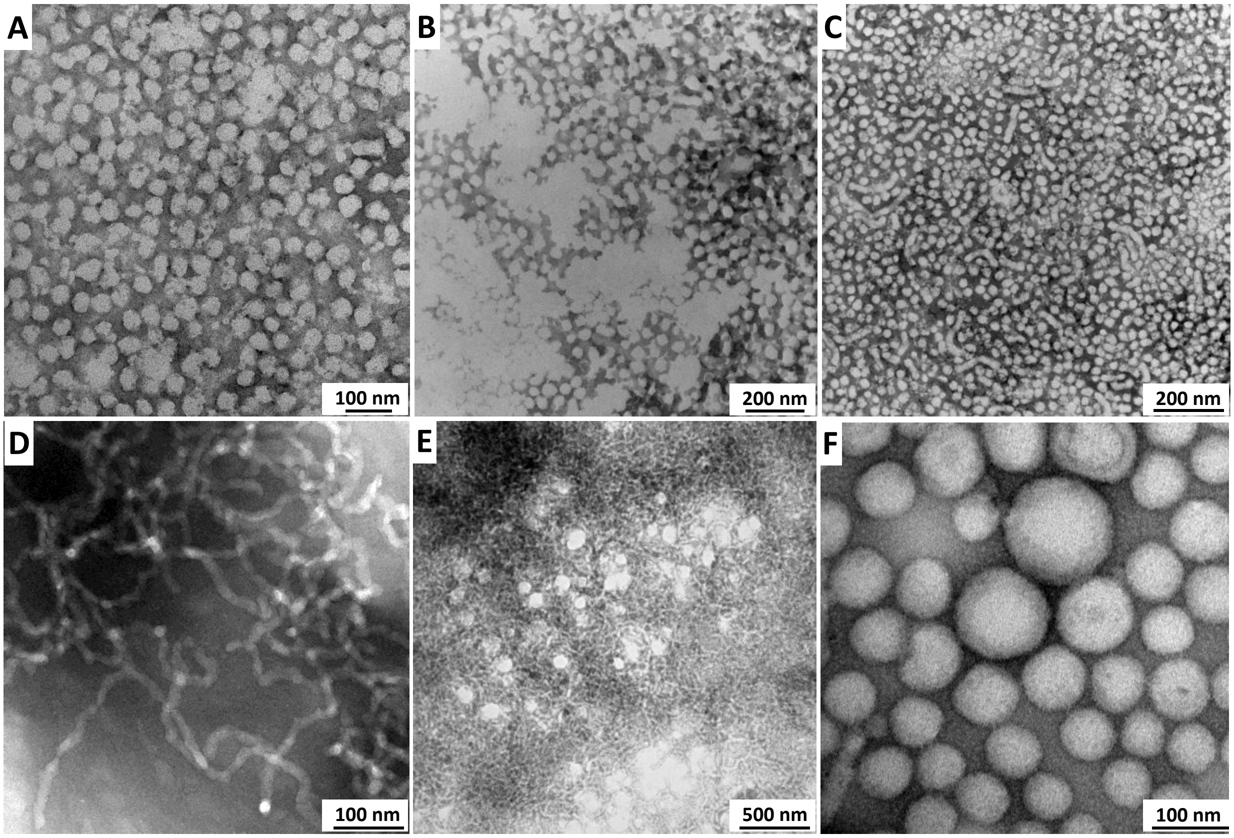

Figure S12. TEM images of $PMAA_{47}$-$PMMA_y$ at 27.5 w/w% total solids content where (A) y= 122; Spheres (B) y= 192; Spheres (C) y= 207; Spheres + Short worms (D) y=256; Worms (E) y=315; Worms + Vesicles (F) y= 359; Vesicles.

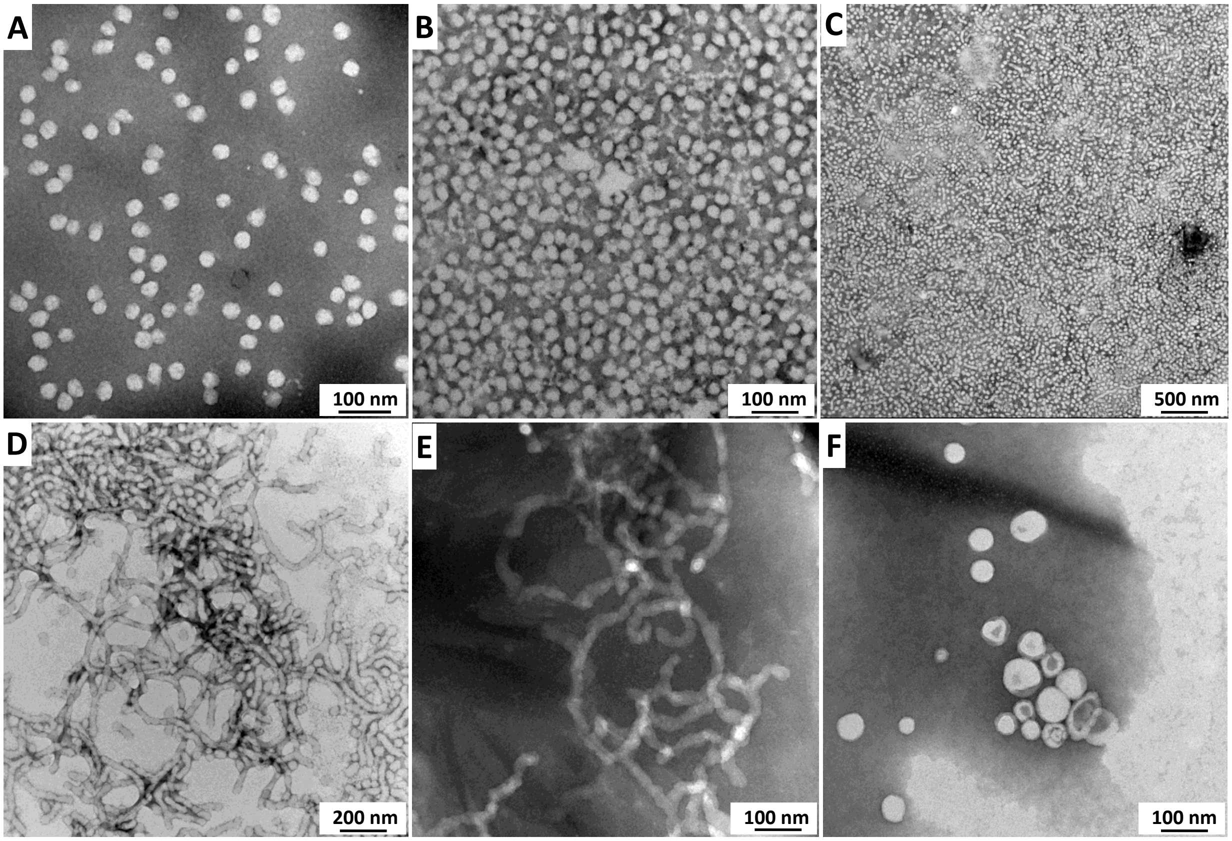

Figure S13. TEM images of $PMAA_{47}$-$PMMA_y$ at 30 w/w% total solids content where (A) y= 117; Spheres (B) y= 189; Spheres (C) y= 205; Spheres + Short worms (D) y=243; Spheres + Short worms (E) y=259; Worms (F) y= 369; Vesicles.

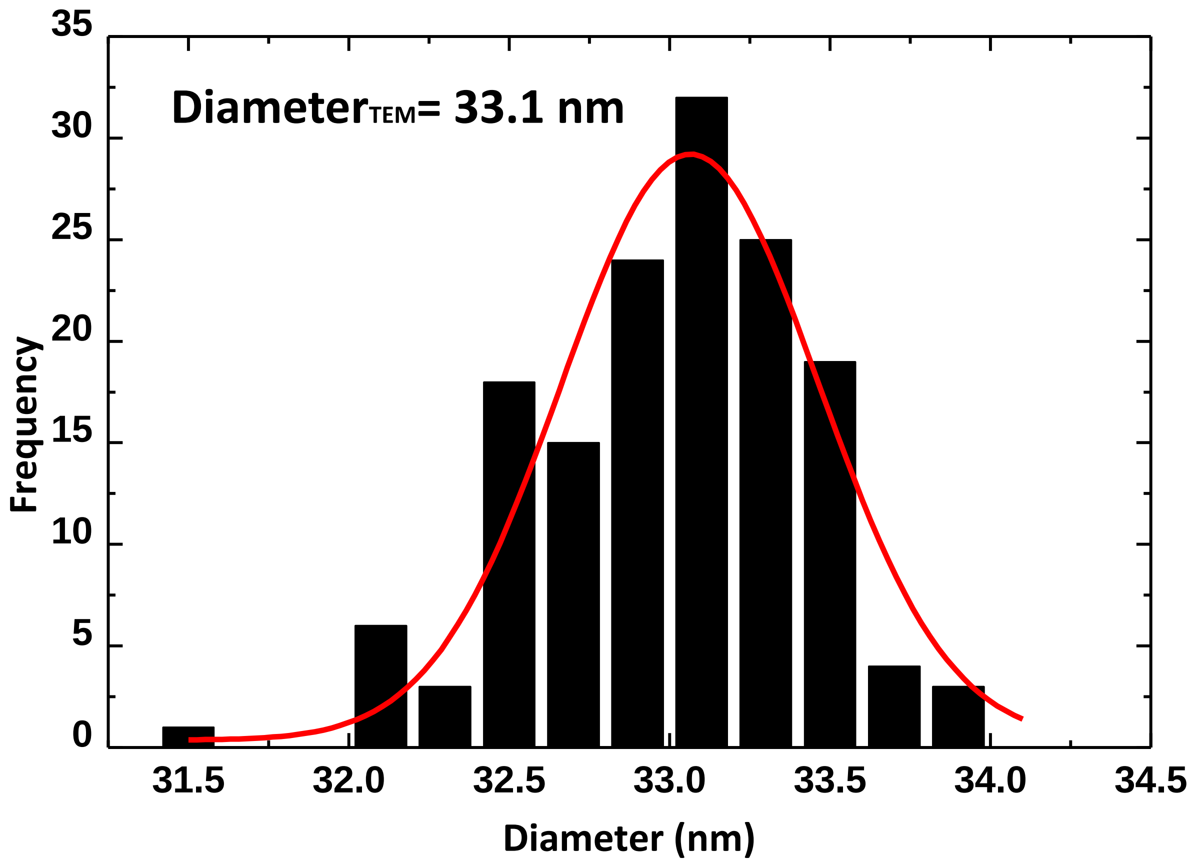

Figure S14. Particle diameter calculated from TEM image using ImageJ software for $PMAA_{27}$-$PMMA_{106}$ spherical particles prepared at 15 w/w %. The TEM image of the particle is presented in Fig. S4B.

Flux and permeability

According to Darcy's law the volumetric flux could be calculated as following equation

$Flux\ (J_V) = V_P/(t * S)$ (L. h^{-1}.m^{-2}) **Eqn (S1)**

$Permeability\ (L_P) = J_v/\ \Delta P$ (L. h^{-1}.m^{-2}.bar^{-1}) **Eqn (S2)**

Where V_p = Permeate volume, t = Time, S = Surface area and ΔP= pressure difference.