Supplementary Information (SI) for Polymer Chemistry.
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Supporting information

Surfactant-free synthesis of polyethylene nanoparticles: toward more realistic model nanoplastics

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1. Kinetic study on radical emulsion polymerization of ethylene

Table S1 : Kinetics of radical emulsion polymerization of ethylene at 100 bar with an anionic or cationic initiator

Time (hours)	PC[a] (%)	ζ[b] (mV)	Z_{ave}[c] (nm)	PdI[d]	N_p[e] (mL^{-1})	D_n[f] (nm)	D_w/D_n[f]	D_{SAXS}[g] (nm)	σ[g]	T_m[h] (°C)	T_c[i] (°C)	X_c[i] (%)	M_n[k] (g mol^{-1})	M_w[k] (g mol^{-1})	$Đ$[k]
1*	0.3	-42	50	0.02	4.3x10^{13}	47	1.03	47	0.01	93	73	25	3 200	29 800	9.4
2*	0.6	-39	68	0.01	4.4x10^{13}	65	1.02	nd	nd	93	76	26	2 200	10 500	4.7
3*	1.2	-47	71	0.01	7.3x10^{13}	64	1.04	nd	nd	92	75	27	2 400	11 800	5.0
4*	2.0	-42	82	0.01	6.3x10^{13}	78	1.02	77	0.03	91	72	24	2 800	24 600	8.9
5*	1.9	-42	96	0.01	4.5x10^{13}	83	1.01	85	0.03	94	78	30	3 500	17 000	4.8
6*	1.3	-45	98	0.02	3.1x10^{13}	91	1.01	86	0.02	93	74	25	3 600	15 200	4.2
1**	0.7	36	46	0.03	1.6x10^{14}	41	1.09	44	0.08	90	74	20	2 900	8 200	2.8
2**	1.1	44	59	0.03	1.1x10^{14}	55	1.07	55	0.08	93	71	22	3 400	9 700	2.8
3**	1.3	43	54	0.04	1.7x10^{14}	46	1.07	52	0.06	90	67	23	3 400	9 900	2.9
4**	1.4	44	50	0.05	2.5x10^{14}	48	1.03	53	0.06	91	72	24	4 900	13 600	2.8
5**	1.5	38	58	0.05	1.7x10^{14}	49	1.02	nd	nd	92	71	25	3 200	12 100	3.8
6**	2.1	48	61	0.04	2.1x10^{14}	51	1.04	58	0.06	93	73	30	4 300	12 900	2.9

Synthesis conditions: *[APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 7.5 and **[AIBA] = 1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 8. [a] Polymer content, determined by gravimetry using equation (4), [b] Zeta potential of particles in deionized water, determined using equation (2), [c] Hydrodynamic diameter and polydispersity index determined by DLS, [d] Particle number, determined using equation (1), [e] Number-average diameter and associated dispersity, determined by TEM using equation (5), [f] Average diameter and log-normal standard deviation, determined by SAXS using equation (7), [g] Melting temperature, determined by DSC, [h] Crystallization temperature, determined by DSC, [i] Crystallinity, determined by DSC using equation (12), [j] Molar masses in number, in weight and dispersity, determined by HT-SEC.

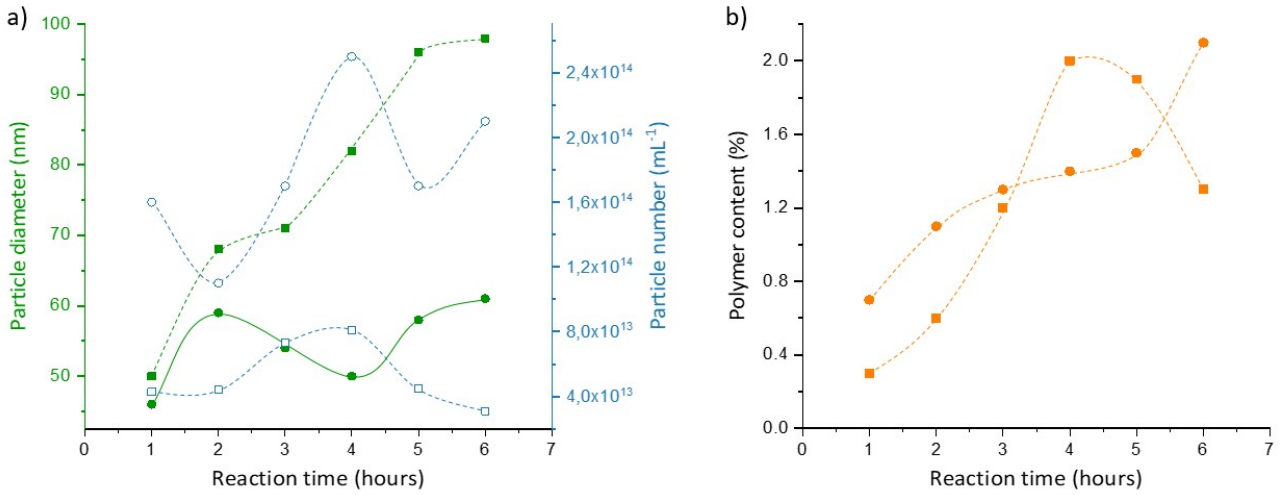

Figure S1 : Effect of reaction time on a) particle diameter (■ NPs APS and ● NPs AIBA), and particle number (□ NPs APS and ○ NPs AIBA), and b) on polymer content (■ NPs APS and ● NPs AIBA) during radical emulsion polymerization of ethylene using APS and AIBA as initiators, without surfactant. Synthesis conditions: (●, ○) [AIBA] = 1 g L^{-1}, 75 °C, $P_{ethylene}$ = 100 bar, 250 RPM, pH = 8; and (■, □) [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, $P_{ethylene}$ = 100 bar, 250 rpm-1, pH = 7.8

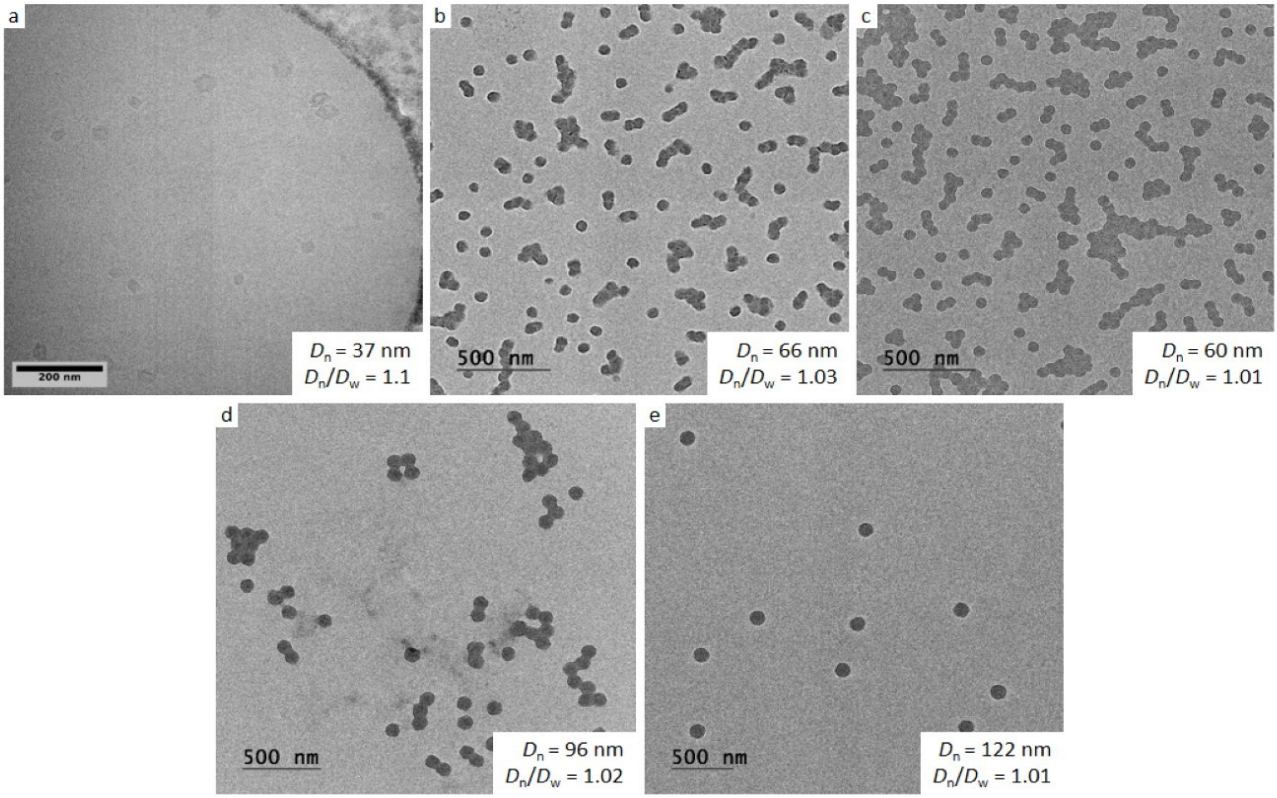

Figure S2: (Cryo)-TEM images of anionic PE nanoparticles obtained by radical emulsion polymerization with different ethylene pressures. a) 50 bar, b) 75 bar, c) 100 bar, d) 150 bar, e) 200 bar. Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 7.5

Goodness-of-fit parameters for SAXS analyses were calculated as follows:
The R_f factor was measure of model quality which is defined as

$$R_f = \frac{\sum_{i=1}^{N} ||I_{exp}(q)| - |I_{th}(q)||}{\sum_{i=1}^{N} |I_{exp}(q)|} \quad \text{(S1)}$$

Theoretical values of R_f range from 0 (perfect agreement of calculated and observed intensities) to infinity. R_f factors greater than 0.5 indicate very poor agreement between observed and calculated intensities. Models refining to $R_f < 0.05$ are often considered to be good. Weighted R_f factors R_w are also often used to track least-squares refinement, since the functions minimized are weighted according to estimates of the precision of the measured quantity. The weighted residuals are defined as:

$$R_w = \sqrt{\frac{\sum_{i=1}^{N} \left(\frac{||I_{exp}(q)| - |I_{th}(q)||}{\Delta I(q)}\right)^2}{\sum_{i=1}^{N} \frac{I(q)_{exp}^{2}}{\Delta I(q)^2}}} \quad \text{(S2)}$$

The interpretation of the parameters R_n and R_w can be summarized as:

- R_f, $R_w > 0.3$: questionable
- $0.1 > R_f$, $R_w > 0.3$: may be acceptable
- R_f, $R_w < 0.1$: believable

Table S2 : SAXS goodness-of-fit parameters for free-radical ethylene emulsion polymerization

$P_{ethylene}$ (bar)	R_f	R_w
50*	0.043556	0.091436
75*	0.091436	0.119614
100*	0.021452	0.013532
150*	0.013556	0.051321
200*	0.010065	0.057555
50**	0.039646	0.023999
75**	0.032639	0.033186
100**	0.039646	0.023999
150**	0.060087	0.049668
175**	0.008526	0.014610
200**	0.071856	0.063044

Synthesis conditions: *[APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 7.5 and **[AIBA] = 1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 8.

Table S3 : Successive seeding of surfactant-free PE latex at $P_{ethylene}$ = 100 bar

Latex	N_p^{i} [a] (mL^{-1})	N_p^{f} [b] (mL^{-1})	PC[c] (%)	ζ[d] (mV)	Z_{ave}[e] (nm)	PDI[e]	D_n[f] (nm)	D_w/D_n[f]	D_{SAXS}[g] (nm)	σ[g]	T_m[h] (°C)	T_c[i] (°C)	X_c[j] (%)	M_n[k] (g mol^{-1})	M_w[k] (g mol^{-1})	Đ[k]
0	0	$3.2x10^{13}$	5.2	-51	153	0.02	133	1.02	nd	nd	102	84	39	3 200	24 000	7.6
1	$1.2x10^{13}$	$1.2x10^{13}$	4.1	-47	197	0.03	151	1.11	nd	nd	99	81	36	1 200	17 400	14.9
2	$5.8x10^{12}$	$1.1x10^{13}$	3.9	-46	214	0.06	160	1.36	nd	nd	99	79	35	1 500	14 900	9.8
3	$4.5x10^{12}$	$1.1x10^{13}$	3.9	-47	197	0.12	129	1.52	nd	nd	98	79	37	1 300	13 200	10.2
4	$5.8x10^{12}$	$1.4x10^{13}$	3.8	-44	181	0.13	124	1.66	nd	nd	98	76	33	1 000	12 500	12.2
0′	0	$2.4x10^{13}$	4.6	-52	160	0.01	146	1.01	72	0.04	97	78	29	7 300	23 900	3.2
1′	$2.1x10^{13}$	$1.9x10^{13}$	5.3	-53	180	0.02	152	1.01	80	0.06	97	79	30	3 700	14 000	3.8
2′	$1.5x10^{13}$	$1.6x10^{13}$	5.6	-54	199	0.03	168	1.01	92	0.06	97	78	29	4 700	16 200	3.4
3′	$1.1x10^{13}$	$1.1x10^{13}$	4.5	-54	208	0.02	187	1.02	96	0.07	99	75	29	4 400	28 100	6.4

Synthesis conditions: Latex 0: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 150 bar, 75 °C, 250 RPM, 6 h, pH = 7.8, Latex 1-4: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8, $PC_{initial}$ = 2 %. Latex 0′: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 200 bar, 75 °C, 250 RPM, 6 h, pH = 7.8 and Latex 1′-3′: [APS] = 0.5 g L^{-1}, [$NaHCO_3$] = 0.5 g L^{-1}, $P_{ethylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8, $PC_{initial}$ = 4 %. [a] Initial particle number, determined using equation (1), [b] Final particle number, determined using equation (1), [c] Final polymer content, determined by gravimetry using equation (4), [d] Zeta potential of particles in deionized water using equation (2), [e] Hydrodynamic diameter and polydispersity index, determined by DLS, [f] Number average diameter and associated dispersity, determined by TEM using equation (5), [g] Average diameter and log-normal standard deviation, determined by SAXS using equation (7), [h] Melting temperature, determined by DSC, [i] Crystallization temperature, determined by DSC, [j] Crystallization rate, determined by DSC using equation (12), [k] Molar masses in number, in weight and dispersity, determined by HT-SEC.

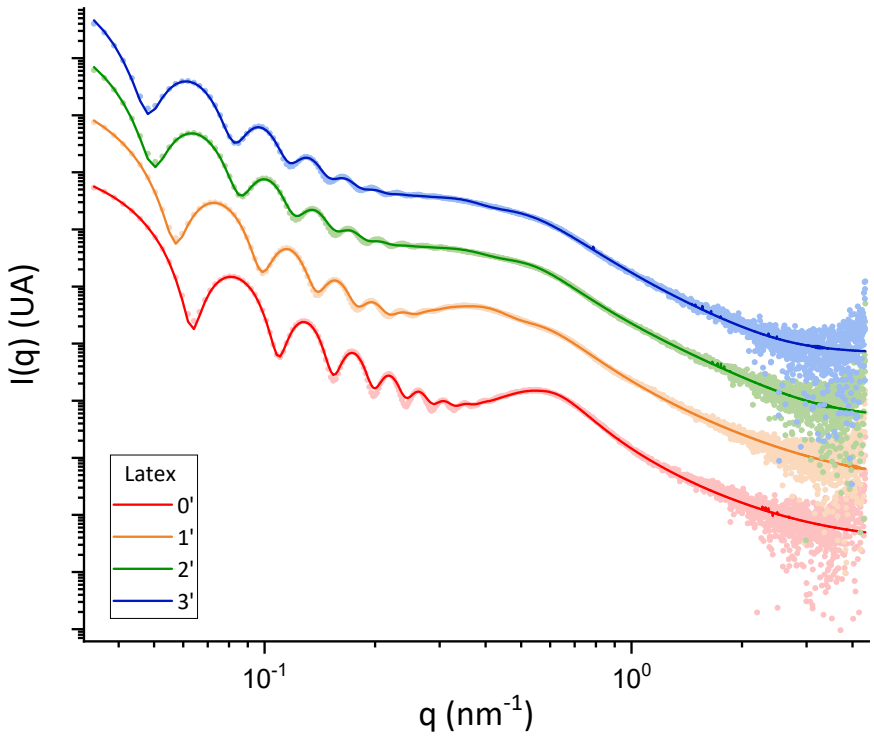

Figure S3: SAXS curves of anionic PE NPs obtained by successive latex seedings. Dashed lines represent raw datas, while solid lines correspond to fitted curves (a multiplicative factor was applied to the intensity for clarity). Synthesis conditions: Latex 0': [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 200 bar, 75 °C, 250 RPM, 6 h, pH = 7.8 and Latex 1'-3': [APS] = 0.5 g L^{-1}, [$NaHCO_3$] = 0.5 g L^{-1}, $P_{ehylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8, $PC_{initial}$ = 4 %

Table S4 : SAXS goodness-of-fit parameters for successive seeding of surfactant-free PE latex

Latex	R_f	R_w
0'	0.018509	0.036237
1'	0.025081	0.034454
2'	0.058907	0.053440
3'	0.063759	0.053137

Synthesis conditions: Latex 0': [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 200 bar, 75 °C, 250 RPM, 6 h, pH = 7.8 and Latex 1'-3': [APS] = 0.5 g L^{-1}, [$NaHCO_3$] = 0.5 g L^{-1}, $P_{ehylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8, $PC_{initial}$ = 4 %

2. Radical emulsion copolymerization of ethylene with vinyl acetate

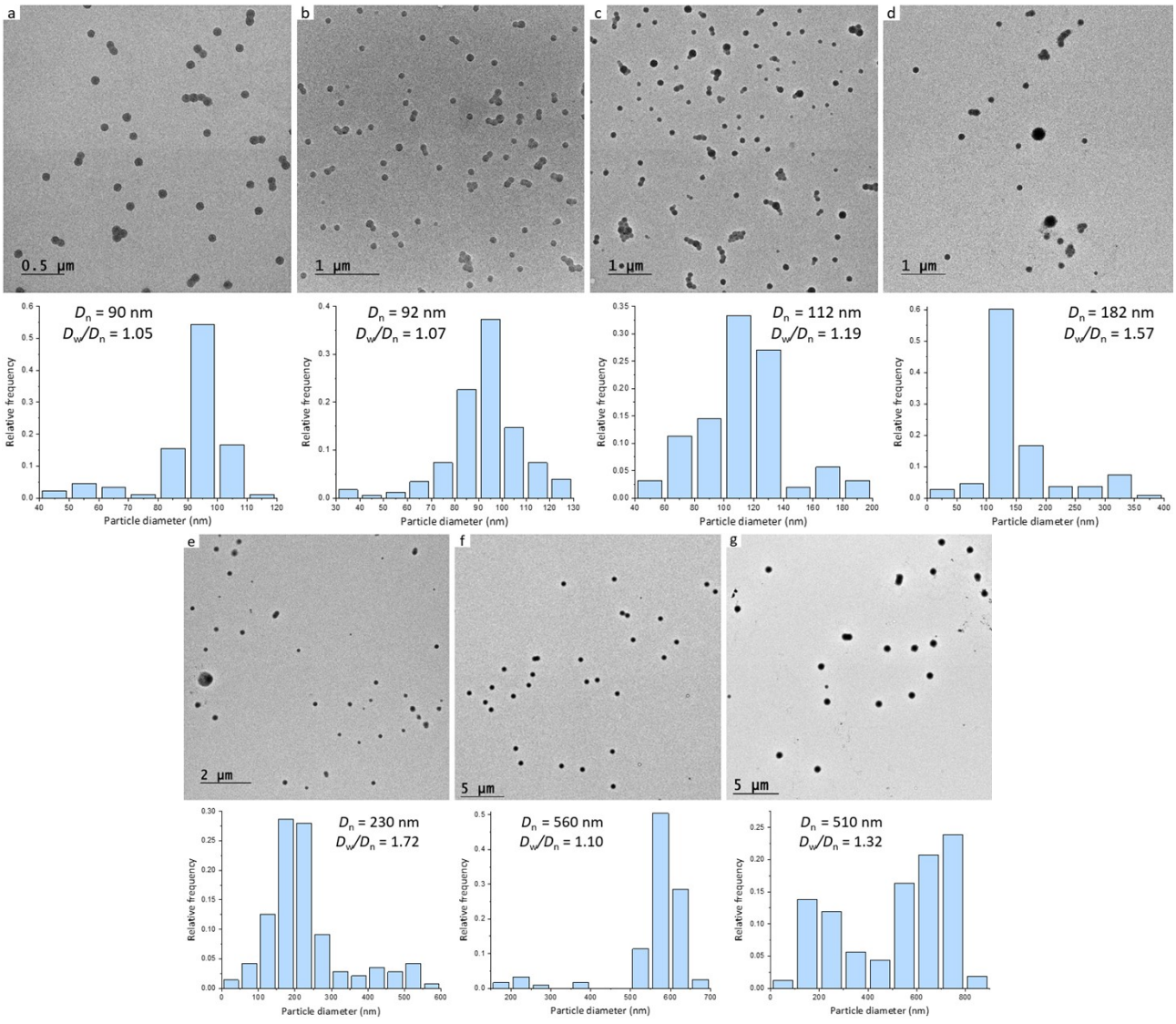

Figure S4 : TEM images of EVA copolymer nanoparticles obtained by radical emulsion copolymerization of ethylene and VAc with different VAc molar fractions. a) n_{VAc} = 1 mol%, b) n_{VAc} = 2 mol%, c) n_{VAc} = 6 mol%, d) n_{VAc} = 14 mol%, e) n_{VAc} = 17 mol%, f) n_{VAc} = 22 mol%, g) n_{VAc} = 27 mol%. Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] =1 g L^{-1}, $P_{ethylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8

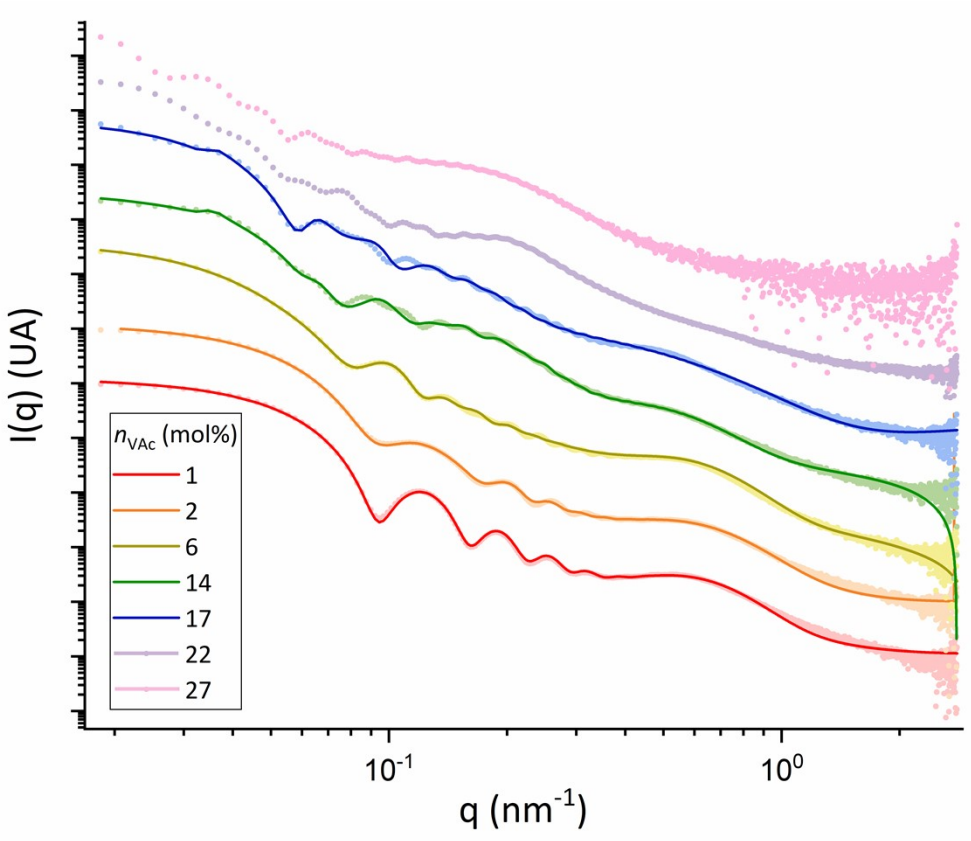

Figure S5 : SAXS curves of EVA copolymer nanoparticles obtained by radical emulsion polymerization with different VAc molar fractions. Dashed lines represent raw datas, while solid lines correspond to fitted curves (a multiplicative factor was applied to the intensity for clarity). Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 100 bar, 75 °C, 250 RPM, 4 h, pH = 7.8

The SAXS profiles display well-defined oscillations, characteristic of monodisperse systems. However, the positions of the scattering minima do not fit a single population, but rather suggest a mixture of monodisperse particle populations. The four curves corresponding to the lowest %VAc were therefore fitted using several monodisperse sphere form factors:

$$I(q,R,\Delta\eta) = N\frac{4}{3}\pi R^3 \frac{\Delta\eta^2}{(qR)^3} \quad \text{(S3)}$$

with N the number of particle (cm^{-3}), R is the sphere radius (nm) and $\Delta\eta$ scattering length density difference between particle and the solvent ($\Delta\eta = \eta_c - \eta_{sol}$ with: η_c= 9.25 x10^{10} cm^{-2} and η_{sol} = 9.44x10^{10} cm^{-2}). The results are presented in Table S3 below, where x_{nb} and x_v are the proportions of each population in number and volume, calculate using the formulas below:

$$x_{nb}^{i} = \frac{N_i}{\sum_i N_i} \times 100 \quad \text{(S4)}$$

$$x_{v}^{i} = \frac{N_i R_i^3}{\sum_i N_i R_i^3} \times 100 \quad \text{(S5)}$$

Table S5 : Characterization parameters of EVA nanoparticles based on SAXS curve fits

n_{Vac}[a] (mol%)	R[a] (nm)	N_{nb}[b] (%)	N_v[c] (%)	R_f[d]	R_w[d]
1	47.55	100	100	0.035757	0.029989
2	55.76	8.59	229.99	0.014423	0.016453
	45.27	33.44	62.43		
	18.67	578.97	7.59		
6	89.88	0.72	15.86	0.022735	0.023441
	60.95	8.00	54.88		
	45.36	6.63	18.73		
	16.02	84.65	10.53		
14	141.68	0.03	13.03	0.085609	0.10727
	123.37	0.06	15.65		
	66.56	0.82	34.17		
	50.52	0.70	12.76		
	12.04	98.40	24.38		

[a] Particle radius, [b] Number and [c] volume distributions, i.e. percentage that each size class occupies of the overall distribution, [d] Goodness-of-fit parameters

Table S6 : Influence of ethylene pressure on the synthesis of anionic EVA nanoparticles by surfactant-free radical emulsion polymerization of ethylene

C_{VAc} (mol L^{-1})	$P_{ethylene}$ (bar)	PC[a] (%)	Z_{ave}[b] (nm)	PDI[b]	D_n[c] (nm)	D_w/D_n[c]	n_{Vac}[d] (mol%)	T_m[e] (°C)	T_g[f] (°C)	X_c[g] (%)	M_n[h] (g mol^{-1})	M_w[h] (g mol^{-1})	$Đ$[h]	CI[i]
0.47	50	4.1	277	0.15	340	1.42	32.0	9	-10	2	1 700	13 900	7.9	5.3
	100	3.2	163	0.06	182	1.57	14.0	65	-20	19	1 900	17 900	9.5	3.5
	150	2.9	172	0.03	119	1.15	9.0	90	-29	22	2 500	23 100	9.4	1.6
	200	4.5	165	0.06	126	1.33	6.0	96	-29	32	2 400	28 000	11.9	1.4
0.12	50	1.2	95	0.07	nd	nd	1.8	93	-30	22	1 800	16 000	9	0.9
	100	1.0	118	0.03	94	1.04	1.5	90	-32	22	1 500	12 700	8	0.8
	150	2.4	137	0.01	115	1.02	0.4	96	-35	26	1 800	31 600	18	0.2
	200	4.1	170	0.01	138	1.20	0.5	100	-40	33	2 600	24 200	9	0.2

Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] =1 g L^{-1}, 75 °C, 250 RPM, 4 h, pH = 7.8. [a] Final polymer content, determined by gravimetry using equation (4), [b] Hydrodynamic diameter and polydispersity index, determined by DLS, [c] Number-average diameter and associated dispersity, determined by TEM using equation (5), [e] Vinyl acetate molar fraction in the copolymer, determined by ^{1}H NMR using equation (14), [f] Melting temperature, determined by DSC, [g] Crystallization temperature, determined by DSC, [i] Crystallization rate, determined by DSC using equation (12), [h] Molar masses in number, in weight and dispersity, determined by HT-SEC, [i] Carbonyl index, determined by FTIR using equation (13).

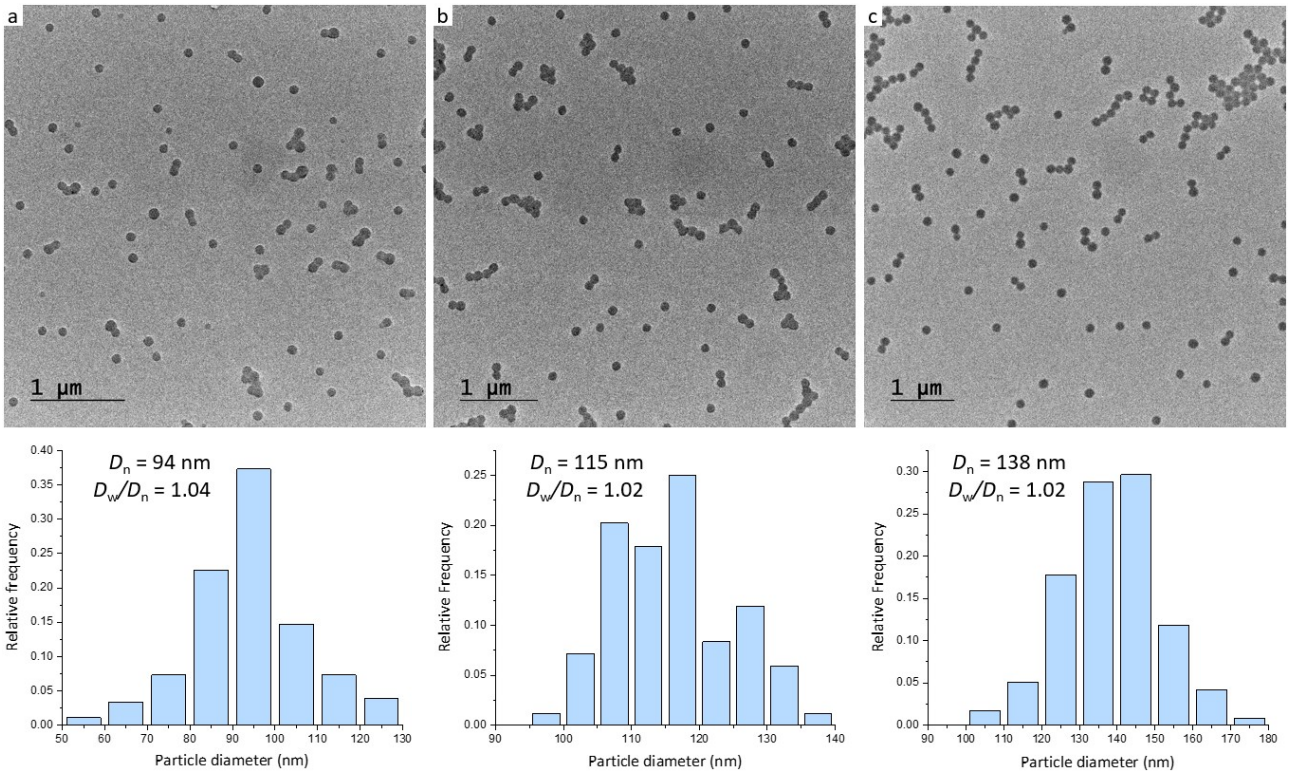

Figure S6: TEM images of EVA copolymer nanoparticles obtained by radical emulsion polymerization at different ethylene pressures. a) $P_{ethylene}$ = 100 bar, b) $P_{ethylene}$ = 150 bar, c) $P_{ethylene}$ = 200 bar. Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] =1 g L^{-1}, [VAc] = 0.12 mol L^{-1}, 75 °C, 250 RPM, 4 h, pH = 7.8

3. Radical emulsion copolymerization of ethylene with carbon monoxide

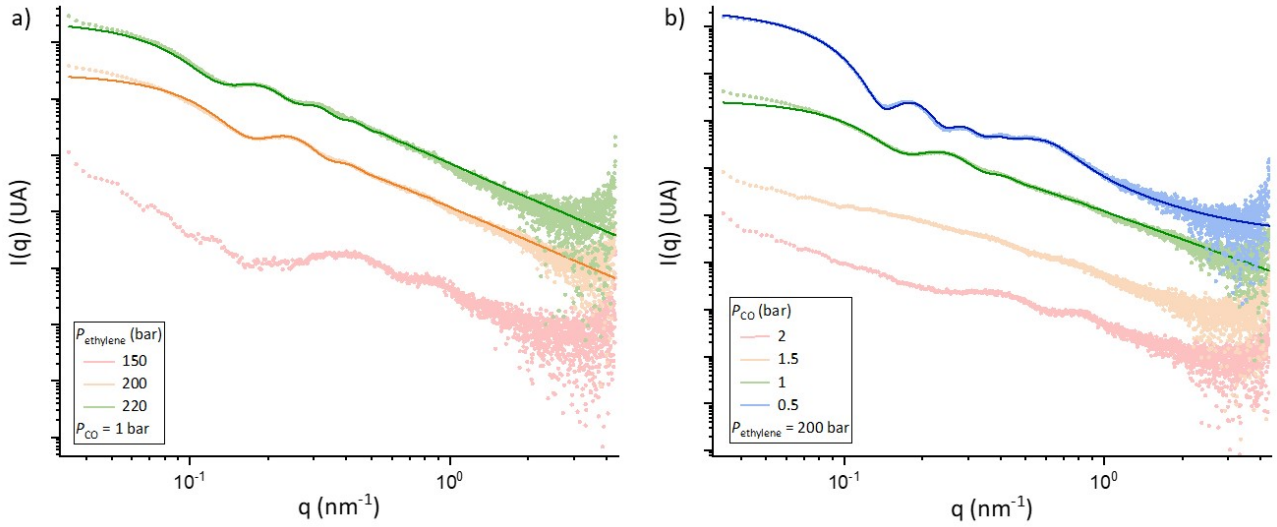

Figure S7 : SAXS curves of ECO copolymer nanoparticles obtained by radical emulsion polymerization with a) different ethylene pressures and b) different carbon monoxide pressures. Dashed lines represent raw datas, while full lines correspond to fitted curves (a multiplicative factor was applied to the intensity for clarity). Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, 250 RPM, 6 h, pH = 7.8

Table S7 : SAXS goodness-of-fit parameters for ethylene-carbon monoxide copolymers

P_{CO} (bar)	P_{ETH} (bar)	R_f	R_w
0.5	200	0.03078	0.03336
1	200	0.03829	0.01953
1.5	200	0.09476	0.07046
2	200	0.14937	0.10036
1	150	0.03078	0.03336
1	220	0.09476	0.07065

Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, 75 °C, 250 RPM, 6 h, pH = 7.8

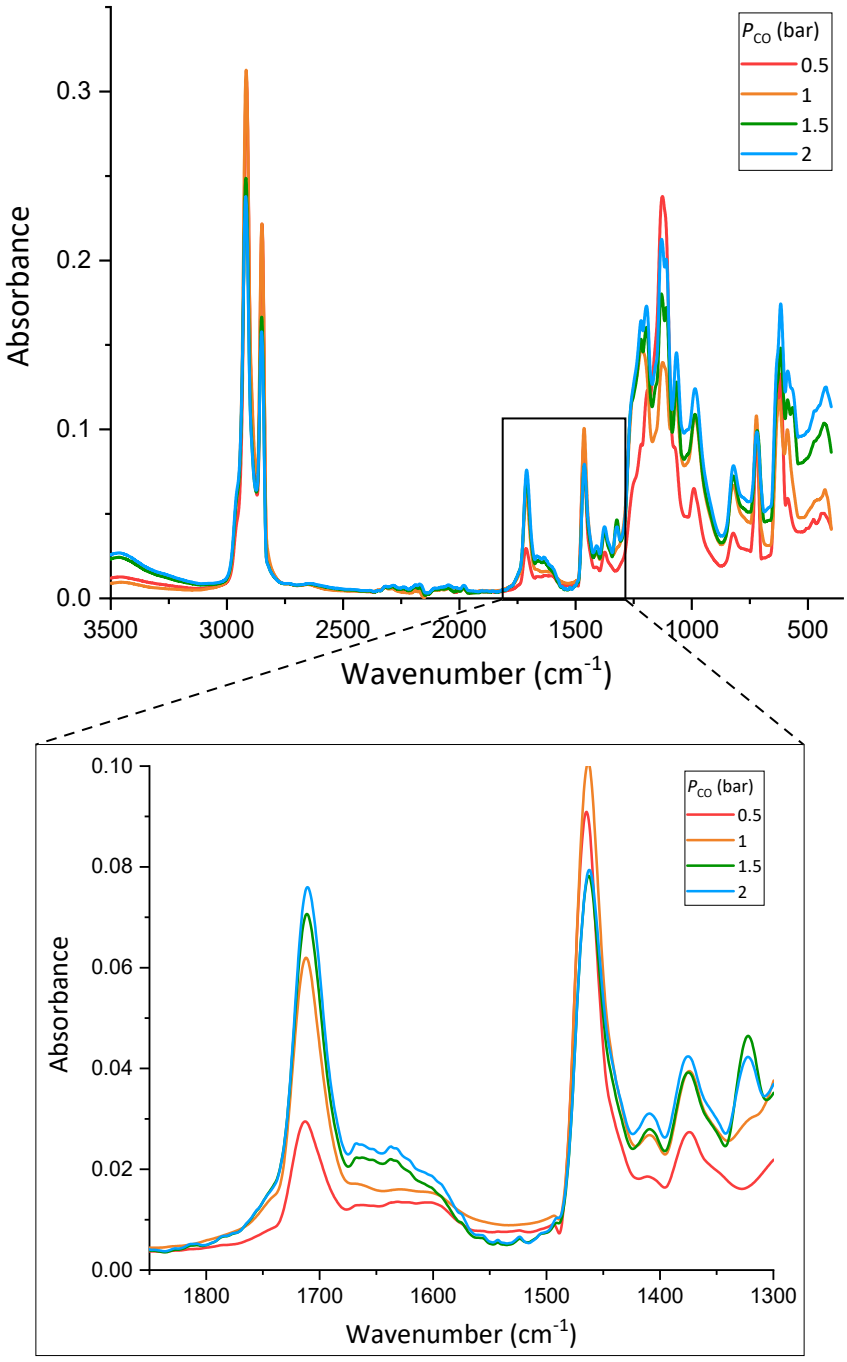

Figure S8: FTIR spectra of ECO copolymers obtained by surfactant-free radical emulsion copolymerization of ethylene and CO at different CO pressures. Synthesis conditions: [APS] = 1 g L^{-1}, [$NaHCO_3$] = 1 g L^{-1}, $P_{ethylene}$ = 200 bar 75 °C, 250 RPM, 6 h, pH = 7.8