Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis and Characterization of Gradient Morphology Polymeric Nanoparticles

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Electronic Supplementary Information

X-Ray Photoelectron Spectroscopy (XPS)

XPS samples were prepared by freeze-drying the liquid latex samples immediately after sampling from the reactor (samples were taken at different times during the synthesis). Samples were first frozen using liquid nitrogen. Water was then removed by sublimation under vacuum at a pressure of 0.05 mbar at -80°C. Freeze-drying prevented coalescence/coagulation of the nanoparticles in the presence of water and preserved their shape, which was necessary in order to accurately monitor their morphology using XPS. The powder-like nanoparticles were subsequently cast on an adhesive grid for XPS analysis. X-Ray Photoelectron Spectroscopy analysis was performed under incident conditions, the X-ray penetration depth being lower than 5 nm (ultrathin layer method).

A Kratos Axis ULTRA XPS incorporating a 165 mm hemi-spherical electron energy analyzer was used. The incident radiation was monochromatic A1 X-rays (1486.6 eV) at 225W (15 kV, 15 mA). Survey (wide) scans were taken at analyzing pass energy of 160 eV and multiplex (narrow) higher resolution scans at 20 eV. Survey scans were carried out over 1360-0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow higher resolution scans were run with 0.2 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0 10^9 Torr and during sample analysis 1.0 10^8 Torr. The experimental data were analyzed using the software Advantage.

Dynamic Light Scattering (DLS)

DLS was used to measure the hydrodynamic diameter of the nanoparticles in the form of the Z-average value. Directly after sampling, 1 drop of latex (approx. 250 mg) was diluted in Milli-Q water for DLS analysis (Malvern Zetasizer). The count rate was kept between 100 and 500 kcps by using highly diluted samples, typically translucent solutions.

Transmission Electron microscopy (TEM)

An FEI Tecnai G2 20 TEM operating at 200 kV was used to characterise the morphology and shape of the nanoparticles. Samples were prepared by diluting the final latexes in water. 1 drop of the diluted latex was deposited on a Formvar coated copper grid and left to dry. The samples were then stained for 1 h using a vapour of osmium tetroxide (OsO_4) at 2 wt %. Staining was used to improve the visibility of the particle on the grid.

Size-Exclusion Chromatography (SEC)

SEC was performed on the samples after freeze-drying (without purification) in order to determine the molecular weights (MWs) and molecular weight distributions. THF was used as the eluent (40 °C, 1.0 mL/min) with an injection volume of 50 µL. A Shimadzu modular system consisting of a DGU-12A solvent degasser, LC-10AT pump, CTO-10A column oven and an ECR 7515-A refractive index detector, and a Polymer Laboratories 5.0 µm bead-size guard column (50 x 7.8 mm^2), followed by four 300 x 7.8 mm^2 linear Phenogel columns (10^5, 10^4, 10^3 and 500 Å). The SEC was calibrated using PS and PMMA standards with MWs ranging from 500 to 10^6 g mol^{-1}.

Differential Scanning Calorimetry (DSC)

The analysis of the thermal properties of the different latexes was made using a TA Instruments Q20 series differential scanning calorimeter. Latex samples were first freeze-dried in order to remove water and residual monomers and obtain powder-like materials. 10 mg of each latex were analysed using DSC. Prior to the actual measurement, a first heating scan (melting of the polymer powder) above the T_g of the materials was conducted in all cases in order to achieve optimal contact between the material and the heated pan. That step was essential to perform quantitative measurements, as per previously established procedures. The second heating ramp was the actual measurement used for the characterization of the different polymer phase transitions. The heating ramp was fixed at 10°C / min for all scans, and cooling was performed at 20 °C/min.

Gas Chromatography

Monomer conversions of the PFEP MMA/S system were monitored by gas chromatography (See equation 1). Instantaneous conversions were determined using a Shimadzu GC-17A gas chromatograph with an AT-WAX column (Alltech 30 m, 0.25 mm i.d., film thickness 0.25 µm) and H_2 as carrier gas (66 mL/min) with a isothermal temperature program of 7 min at 100 °C. BuOH was used as internal standard.

$$\text{Conversion (\%)} = 100 \times \frac{1 - m_{residual\ monomer}}{m_{monomer}} \tag{1}$$

Recipe for the seed latexes

The reactor initially contained a solution of SDS in water (0.1 g in 27.225 g, 0.37 wt %). 5 wt % of the pre-emulsified monomer were taken from the feed / near tank depending on the type of synthesis process. 0.23 g of APS in 1.1 g of water were then added into the reactor to initiate the polymerization (30 min at 75 °C under nitrogen bubbling). The resulting seed latexes had a particle diameter (Z-Average) of 31 nm for PMMA, 36 nm for PS, 26 nm for PS-stat-PMMA and 35 nm for the core-shell PS-PMMA system.

Recipes for the homogeneous particles (semi-batch emulsion polymerization)

The far tank emulsion was progressively fed into the near tank at 0.190 mL min^{-1} while the near tank was fed into the reactor at 0.380 mL min^{-1} (same overall feed time of approx. 3 h for both tanks). The initiating solution (APS in water) was continuously fed into the reactor (over 3 h) maintained at a temperature of 80°C.

Table 1: PMMA nanoparticles

Chemical	Feed Tank (g)	Initiator Tank (g)	Reactor (g)
MMA	46.83	-	PMMA seed latex (31 nm)
S	-	-	
APS	-	0.13	
Water	16.54	7.7	
SDS	0.3	-	

Table 2: PS nanoparticles

Chemical	Feed Tank (g)	Initiator Tank (g)	Reactor (g)
MMA	-	-	PS seed latex (36 nm)
S	46.83	-	
APS	-	0.13	
Water	16.54	7.7	
SDS	0.3	-	

Table 3: PS-stat-PMMA nanoparticles

Chemical	Tank (g)	Initiator Tank (g)	Reactor (g)
MMA	23.46	-	PS-stat-PMMA seed latex (26 nm)
S	23.37	-	
APS	-	0.34	
Water	16.54	7.7	
SDS	0.3	-	

Recipes for the core-shell particles (sequential semi-batch emulsion polymerization)

The reactor initially contained the PS seed latex. Styrene was first fed into the reactor at 0.190 mL min^{-1} for 1.5h. MMA was then fed into the reactor at 0.190 mL min^{-1} for 1.5h. Two initiating solutions (APS in water) were fed into the reactor maintained at a temperature of 80°C.

Table 4: PS-PMMA Core-shell nanoparticles

Chemical	1st Tank (g)	1st Initiator Tank (g)	2nd Tank (g)	2nd Initiator Tank (g)	Reactor (g)
MMA	-	-	23.46	-	PS seed latex (35 nm)
S	23.37	-	-	-	
APS	-	0.07	-	0.07	
Water	8.27	3.85	8.27	3.85	
SDS	0.13	-	0.17	-	

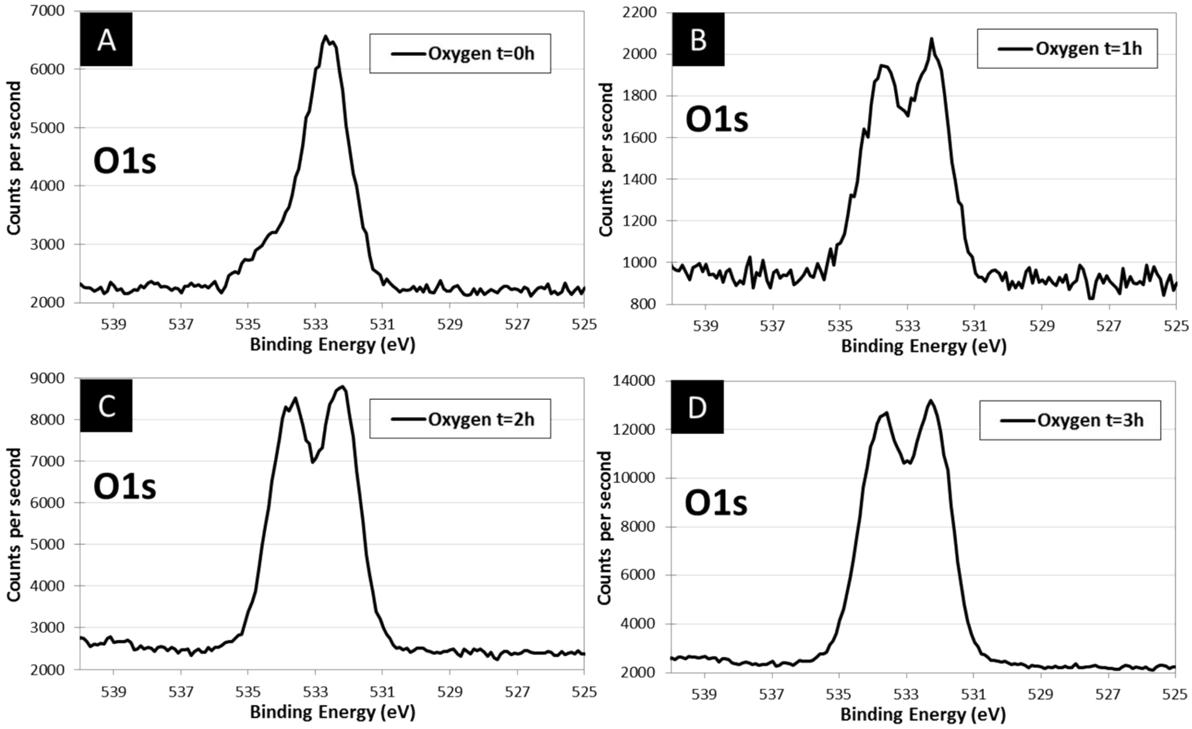

Figure S1: High resolution XPS scans of oxygen (O1s): at t=0h (A), t=1h (B), t=2h (C) and t=3h (D). The atomic percentage of oxygen at the surface of each sample was calculated by integration of the raw peaks, without mathematical treatment. The reference peak for charge compensation is C-C at 284.8 eV. The oxygen spectra for the MMA/S system synthesized by PFEP are displayed.

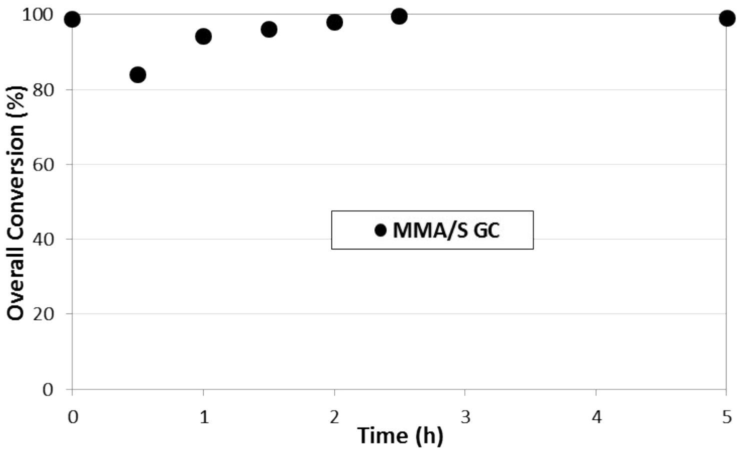

Figure S2: Overall monomer conversion for the PFEP MMA/S system assessed by GC.

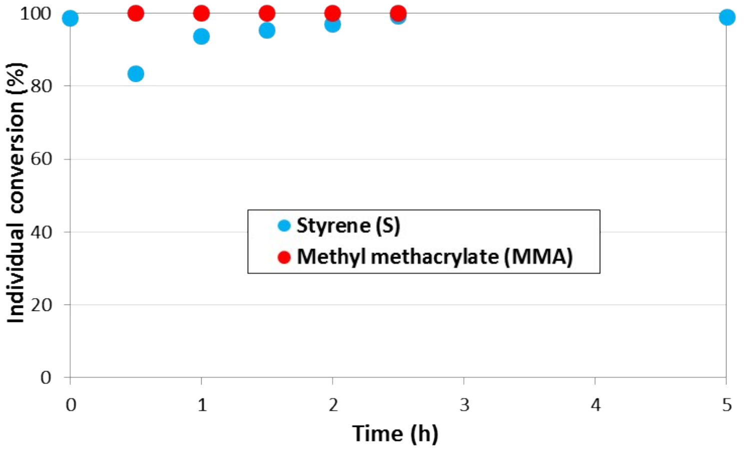

Figure S3: Individual monomer conversions for the PFEP MMA/S system assessed by GC.

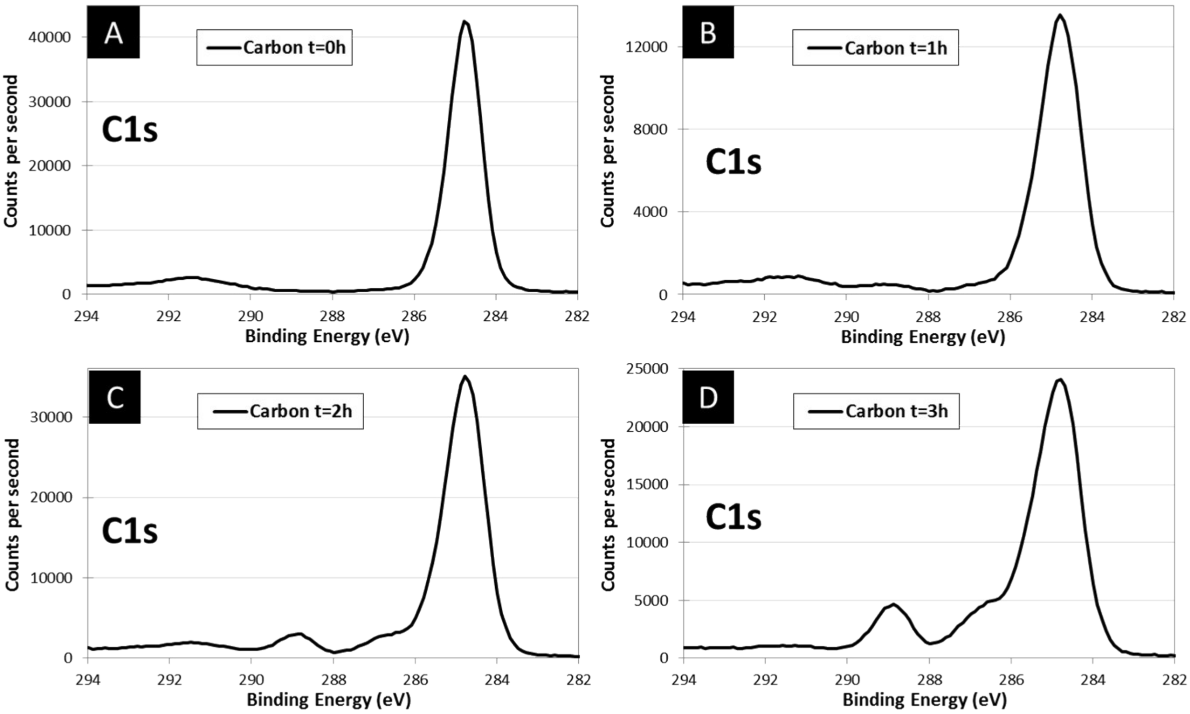

Figure S4: High resolution XPS scans of carbon (C1s): at t=0h (A), t=1h (B), t=2h (C) and t=3h (D). The atomic percentage of carbon at the surface of each sample was calculated by integration of the raw peaks, without mathematical treatment. The reference peak for charge compensation is C-C at 284.8 eV. The carbon spectra for the MMA/S system synthesized by PFEP are displayed.

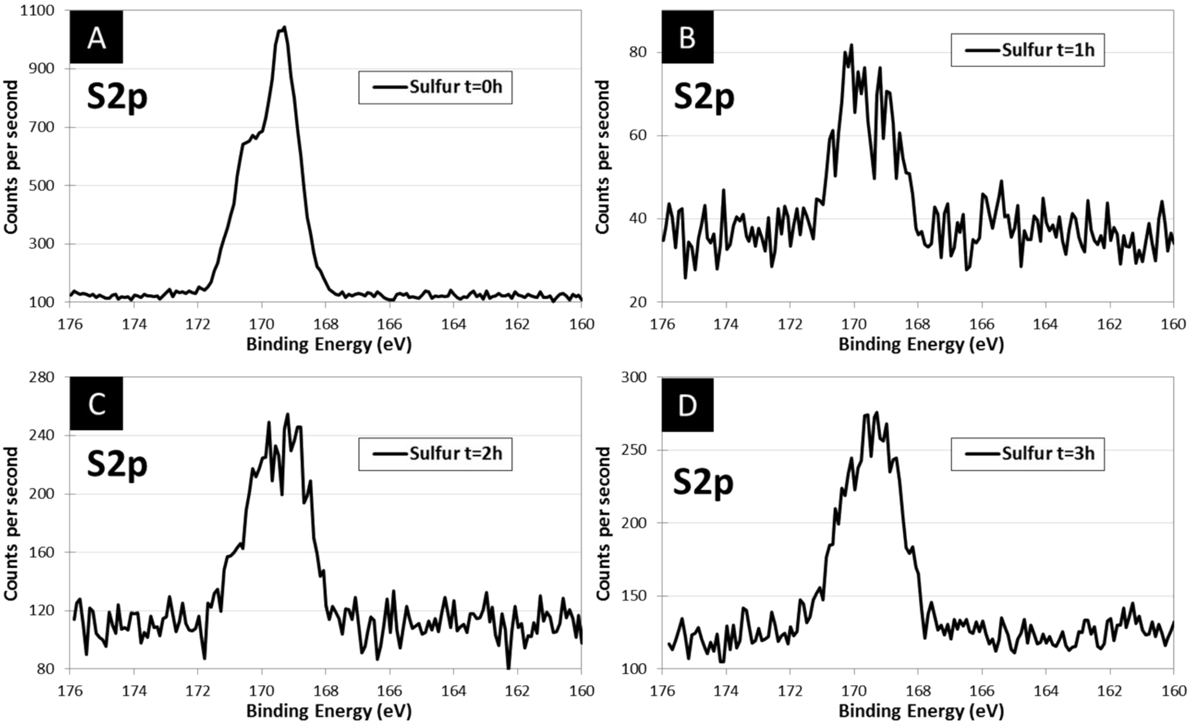

Figure S5: High resolution XPS scans of sulfur (S2p): at t=0h (A), t=1h (B), t=2h (C) and t=3h (D). The atomic percentage of oxygen at the surface of each sample was calculated by integration of the raw peaks, without mathematical treatment. The reference peak for charge compensation is C-C at 284.8 eV. The sulfur spectra for the MMA/S system synthesized by PFEP are displayed.

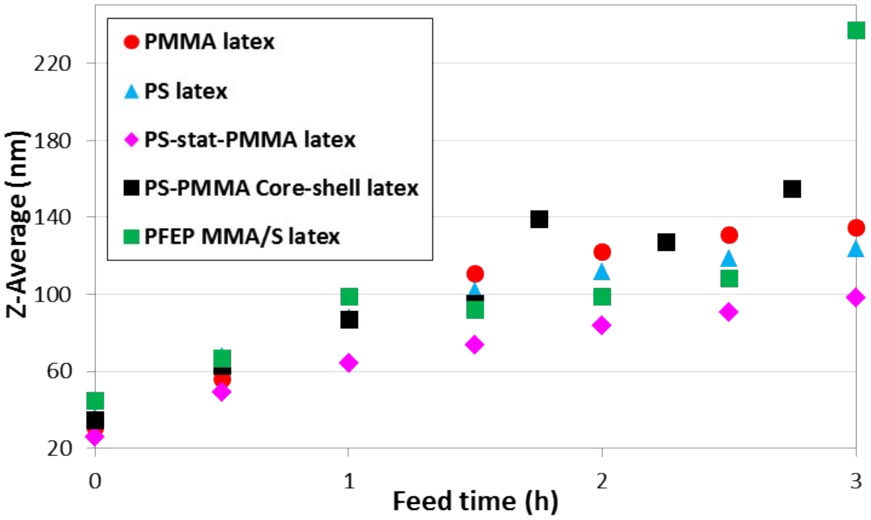

Figure S6: Evolution of the nanoparticle diameter during feed time for different systems: PMMA latex (red dots), PS latex (blue dots), PS-stat-PMMA latex (purple dots), PS-PMMA core-shell latex (black dots) and PFEP MMA/S latex (green dots).

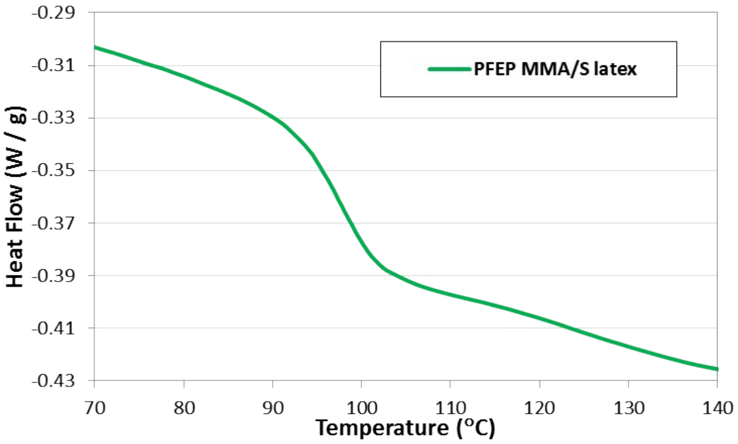

Figure S7: DSC thermogram of the PFEP MMA/S final latex. The second heating scan is displayed.

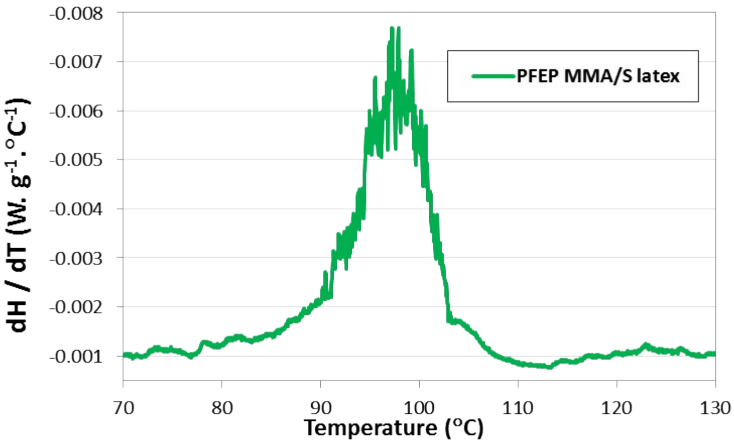

Figure S8: DSC differentiated thermogram of the PFEP MMA/S final latex. The second heading scan is displayed.

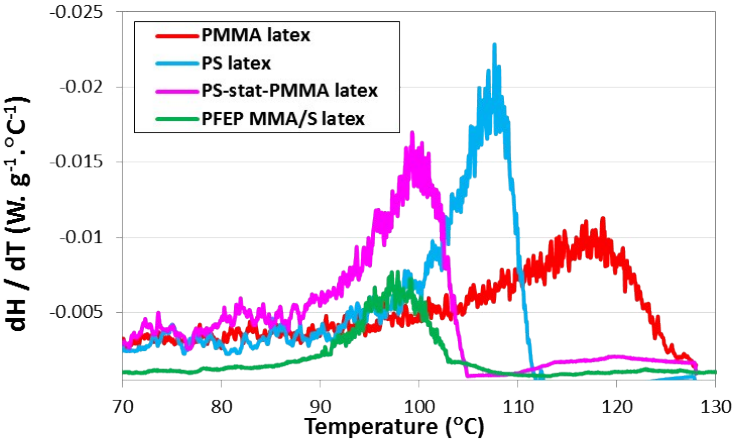

Figure S9: DSC differentiated thermograms of different systems: PMMA latex (red line), PS latex (blue line), PS-stat-PMMA latex (purple line) and PFEP MMA/S latex (green line). The second heating scans are displayed.