Supporting information

Experimental part

Materials. The monomers (1H,1H,2H,2H-heptadecafluorodecyl acrylate (FDA), methyl methacrylate (MMA) and styrene (Sty) were purchase from Aldrich and deoxygenated for 10 minutes by nitrogen bubbling. BlocBuilder (MAMA) was kindly donated by ARKEMA. CO_2 (N48) was purchase from Air Liquide.

Characterization techniques. Size exclusion chromatography (SEC) was carried out in THF at 45°C at a flow rate of 1 mL/min with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000 using PL gel 5µm (10^5 Å, 10^4 Å, 10^3 Å and 100 Å) columns. Waters gel 5µm (10^5 Å, 10^4 Å, 500 Å and 100 Å) columns were calibrated with PMMA standards. ^{1}H NMR spectra were recorded in CFC113/$CDCl_3$ mixture at 400 MHz in the FT mode with a Brucker AN 400 apparatus at 25°C.

NMP of FDA in $scCO_2$. In a typical experiment, FDA (5ml) was introduced, with the help of a syringe, under CO_2 flux into a 20ml high pressure cell containing 0.6195g of blocbuilder (0.0016mol, expected Mn = 5000 g/mol). The cell was then equilibrated at 100°C and 300 bar for 24h. After polymerization, the cell was cooled down to room temperature and CO_2 was slowly released. The polymer was then dissolved in trifluorotoluene and precipitated in methanol before drying under vacuum at room temperature and characterization by ^{1}H NMR using a 50/50 v/v CFC113/$CDCl_3$ mixture (Figure S1, Table 1 entry 2).

Synthesis of PFDA-b-PnBuA in $scCO_2$. 1g of PFDA-SG1 (Mn = 3800 g/mol) was introduced into a 40ml high pressure cell and 13 ml of nBuA were added under CO_2 flux with the help of a syringe. The cell was then equilibrated at 100°C and 300 bar for 24h. After polymerization, the cell was cooled down to room temperature and CO_2 was slowly released. A small amount of polymer was picked out the cell and characterized by SEC analysis (so, without precipitation avoiding any fractionation of the polymer, Figure S2). After dissolution in THF, the diblock copolymer was precipitated into methanol, dried under vacuum and characterized by ^{1}H NMR using a 25/75 v/v CFC113/$CDCl_3$ mixture. Mn of the PFDA-b-PnBuA diblock copolymer was estimated by comparison of the relative intensity of the peak corresponding the methylene group of the nBuA units (δ = 4.05 ppm, CH_2) and the methylene proton of the FDA units (δ = 4.45 ppm, CH_2).

Dispersion NMP of MMA. In a typical experiment, a 10ml of a styrene/MMA mixture (1.2ml of sty, 13ml of MMA) was introduced, with the help of a syringe, under CO_2 flux into a 40ml high pressure cell containing 0.088g of blocbuilder (0.00015 mol, expected Mn = 57000 g/mol) and 0.45 g of PFDA-SG1 (Mn = 70000 g/mol, 5wt%) The cell was then equilibrated at 70°C and 300 bar for 114h. After polymerization, the cell was cooled down to room temperature and CO_2 was slowly released. PMMA was then collected as a white powder that was redissolved in THF for SEC characterization.

Effect of the styrene loading. The effect of the styrene loading on the polymerization control was also investigated. Indeed, Charleux demonstrated that the NMP of MMA using blocbuilder was controlled due to the presence of a styryl-SG1 moiety at the ω chain end. A same experiment was then repeated at 70°C and 300 bar using 5w% of PFDA-SG1 (Mn = 70000 g/mol) as precursor of the surfactant but the styrene loading was decreased from 8.8 mol% to 0 mol%. From the results shown in Table 4, the dispersion NMP MMA was controlled when it is conducted in the presence of 8.8 or 4.4 mol% of styrene (Table 4, entries 1 and 2). For lower styrene/MMA molar ratio (Table 4, entries 3 and 4), the polymerization control is lost as evidenced by a broadening of the molecular weight distribution and an experimental molecular weight value largely different from the theoretical one.

Entry	Styrene loading (%)	Conv (%)[a]	Mn theo (g/mol)[b]	Mn exp (g/mol)[c]	PDI
1	8.8	94	53000	55000	1.23
2	4.4	95	52000	56000	1.26
3	2.2	85	47000	25000	1.55
4	0	91	50000	29000	1.44

Table S1: Dispersion NMP of MMA in $scCO_2$ at 70°C and 300 bar in the presence of 5wt% PFDA-SG1 (Mn = 70000 g/mol), [MMA]/[BlocBuilder]= 550
a gravimetrically determined
b estimated from the relation Mn = ((w MMA + w styrene)/n alkoxyamines) x conv.
c estimated using a PMMA standard calibration

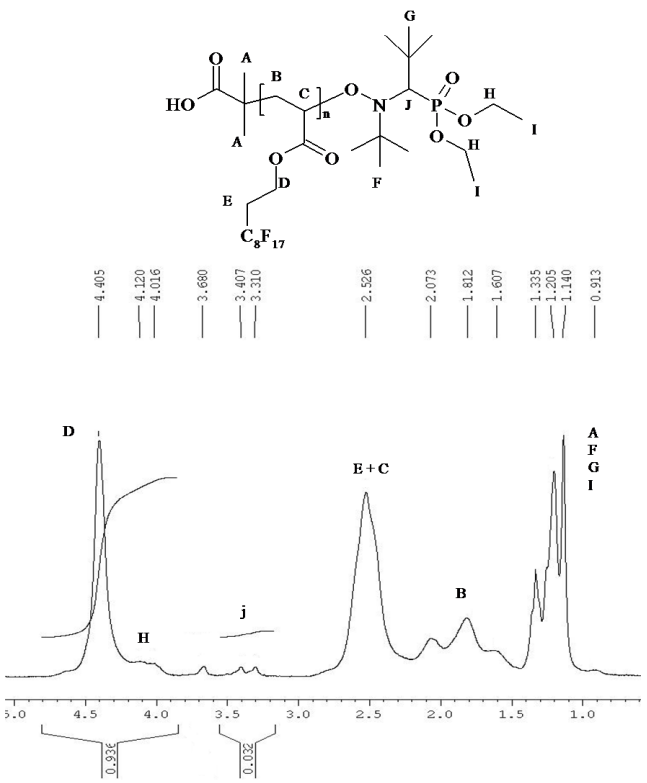

Figure S1: Structure and ^{1}H NMR characterization of PFDA prepared by homogeneous NMP in $scCO_2$ (Mn exp = 7000 g/mol, table 1, entry 2)

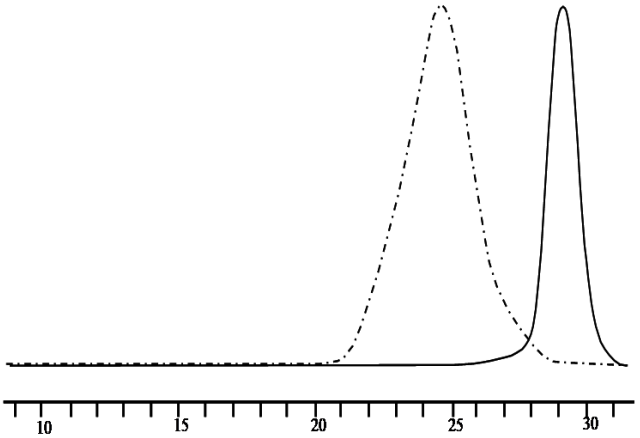

Figure S2: SEC traces of PFDA-SG1 of Mn = 3800 g/mol (….) and PFDA-b-PnBuA diblock copolymer (3800-b-45000,—)

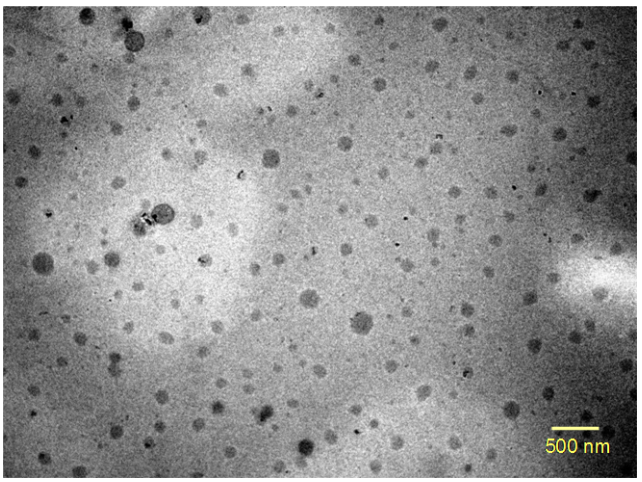

Figure S3: TEM picture of PFDA-b-PMMA micelles present in the PMMA matrix of Mn = 57000 g/mol (image obtained by deposition of few drops of a PMMA solution of concentration equal to 5.25 10^{-4} mol/l, followed by the slow evaporation of the solvent)