Electronic Supplementary Information for

Copper bromide complexed by fluorinated macro-ligands: towards microspheres by ATRP of vinyl monomers in scCO2.

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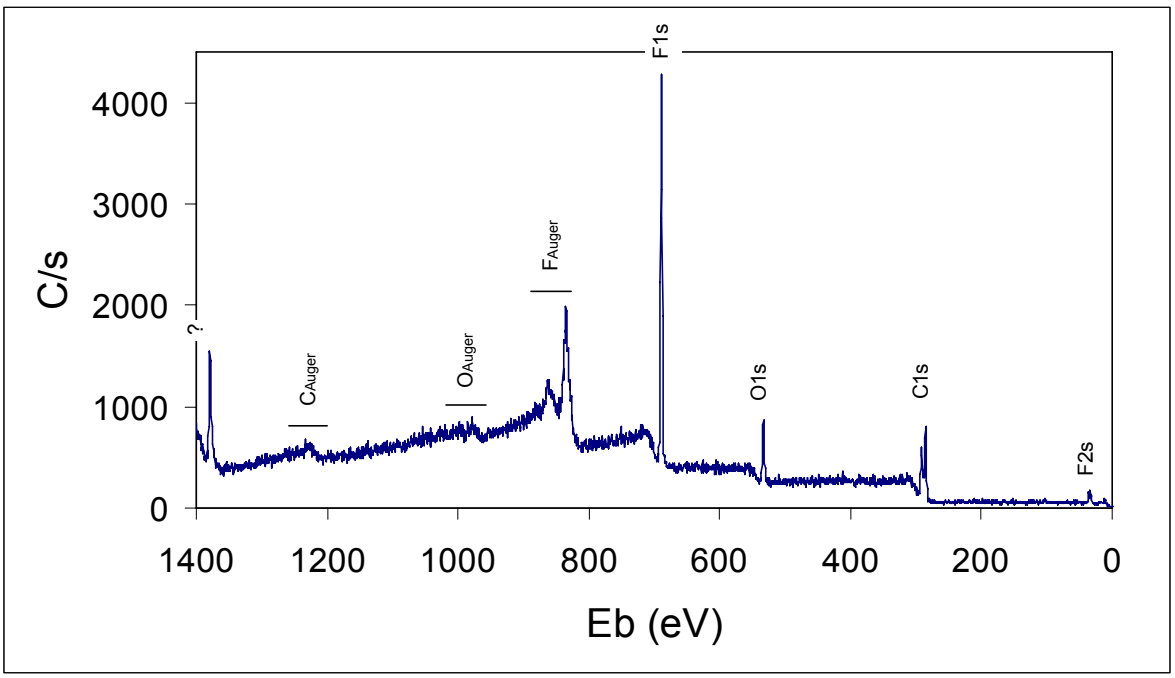
Experimental Section

CuBr (Aldrich, 98%) was purified by dispersion within glacial acetic acid under stirring for a few hours, filtered, washed with ethanol, dried under reduced pressure at 80°C and stored under nitrogen. Methyl methacrylate (MMA, Aldrich 99%) was distilled under reduced pressure in order to remove the inhibitor. α-bromophenylacetate (Aldrich,), N,N,N',N'-tetraethyldiethylenetriamine (TEDETA, Aldrich, 90%) and 2,2'-azo-bis(2-methylpropionitrile) (AIBN, Fluka) were used as received. Size exclusion chromatography (SEC) was performed in THF at 45°C with a flow rate of 1ml/min using a SDF S5200 autosampler liquid chromatograph equipped with SDF refractometer index detector 2000. Columns (HP PL gel 5µm; 10^5 Å, 10^4 Å, 10^3 Å, 100Å) were calibrated with poly(methyl methacrylate) standards. The fluorinated macroligand was synthesized as reported elsewhere.[1]

Cloud points measurements. A 130 ml high pressure view cell equipped with two sapphire windows aligned at 180 ° is used to perform cloud points measurements. The cloud points at the liquid + liquid ↔ fluid phase transition were observed visually by slowly decreasing the pressure in the vessel through the release valve. The cloud point was defined as the pressure at which the binary mixture lost transparency and became cloudy.

ATRP of MMA in scCO$_2$. In a typical experiment, the macroligand (15000 g/mol, 2.7L/chain, 1.56 g, 1.04 10^{-4} mol) and copper bromide (0.0402 g, 2.8 10^{-4} mol) were introduced in a 35 ml pre-heated high pressure cell at 70°C and deoxygenated by CO_2 purge. Methyl-α-bromophenylacetate (0.1286 g, 5.61 10^{-4} mol) and MMA (12ml, 0.112 mol) were introduced in a glass tube and deoxygenated by nitrogen purge before being injected under CO_2 flux in the high pressure cell with the aid of a glass syringe. Pressure was finally equilibrated to 320 bars using an ISCO syringe pump and the reaction medium magnetically stirred at 1000 rpm. After 16h, the reactor was cooled and pressure was rapidly removed. The resulting polymer was dried under vacuo before being analyzed by SEC using THF as eluent.

XPS spectrum of the PMMA particles produced by dispersion ATRP. Spectrum recorded after supercritical fluid extraction of the polymeric complex.



[1] Grignard B., Calberg C., Jerome C., Jerome R., Detrembleur C., accepted in Eur. Polym. J.