

Supporting information:

Grafting of GPM onto silica. Silica (Cab-O-Sil, specific area = 380 m²/g, 4.5 silanol groups/nm², 20 g) was dried in vacuo at 150°C for 24h, before being dispersed in 1L of dry toluene. 3-glycidoxypropyltrimethoxysilane (150 ml, 0.68 mol) was added to the reaction medium, and the temperature was raised to 100°C. After 24h, silica was purified by 3 cycles of centrifugation (5000 rpm, 20 min)/redispersion in toluene followed by 2 cycles of centrifugation (5000 rpm, 20 min)/redispersion in methanol before drying in vacuo overnight. Finally, a post-thermal treatment was carried out at 100°C until the weight loss determined by TGA was constant.

Macroligand synthesis. The macroligand was prepared according to the procedure reported in reference 18

Immobilization of the macroligand by the “grafting onto” approach. In a typical experiment, epoxy-modified silica (3 g, 2.08 10⁻³ mol of epoxide) and a macroligand (5000 g/mol, 2 TEDETA/chain, 1.08 g, 2.16 10⁻⁴ mol) were introduced in a 40 ml glass tube in the presence of 25 ml of dry TFT. After 5 days at room temperature, silica was purified by 5 cycles of centrifugation (5000 rpm, 20 min)/redispersion in TFT, before drying in vacuo overnight.

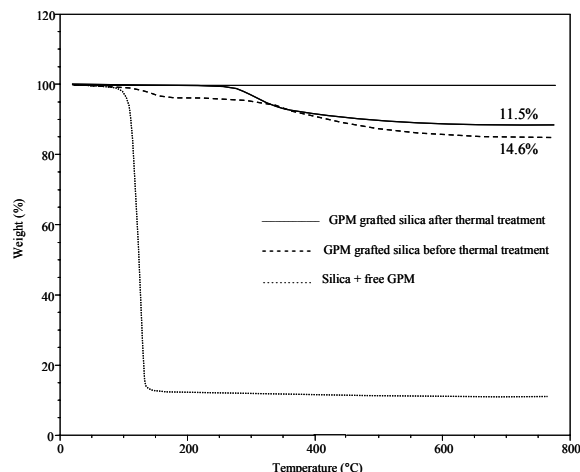
Homogenous ATRP of FMA. In a typical example, the catalyst (CuBr, 0.0254 g, 1.77 10⁻⁴ mol) and the macroligand (M_n = 5000 g/mol, 2 TEDETA/chain, 0.8845 g, 1.77 10⁻⁴ mol) were introduced in a 35 ml high pressure reactor equipped with a stirring bar and oxygen was removed by CO₂ venting for 15 minutes. Temperature was then increased with an oil bath pre-heated at 70°C. FMA (12 ml, 8.43 10⁻² mol) was introduced in a glass tube and mixed with methyl α-bromophenylacetate (0.0811 g, 3.54 10⁻⁴ mol) before being deoxygenated by a nitrogen purge (5 minutes). The mixture was then injected in the pre-heated high pressure reactor under CO₂ flow with a glass syringe before adjusting the pressure at 320 bar.

Supported ATRP of FMA. In a typical experiment, the catalyst (CuBr, 0.0254 g, 1.77 10⁻⁴ mol) and the supported macroligand (M_n = 5000 g/mol, 2 TEDETA/chain, weight loss = 20%, 2.214 g, 1.77 10⁻⁴ mol of amino groups) were introduced in a 35 ml high pressure reactor equipped with a stirring bar. Oxygen was removed by CO₂ venting for 15 min. The temperature was increased up to 70°C with a pre-heated oil bath. FMA (12 ml, 8.43 10⁻² mol) was introduced in a glass tube and mixed with methyl α-bromophenylacetate (0.0811 g, 3.54 10⁻⁴ mol) before being deoxygenated by nitrogen purge (5 minutes). The mixture was then injected in the pre-heated high pressure cell, under CO₂ flow with a glass syringe before adjusting the pressure at 320 bar.

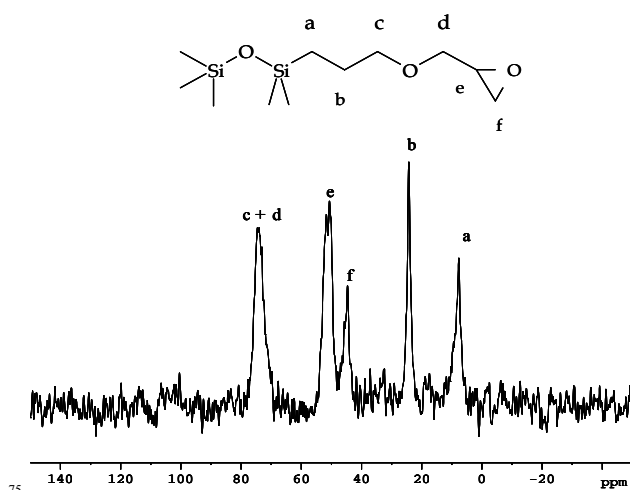
Macroligand characteristics		Silica characteristics	
M _n (g/mol)	Nr TEDETA/chain	macroligand grafting	
		Weight loss (%)	Nr macroligand/nm ²
5000	2	20	0.060
15000	4	40	0.041

Table S1: Grafting of macroligands onto Cab-O-Sil EH5 by the “grafting onto” approach

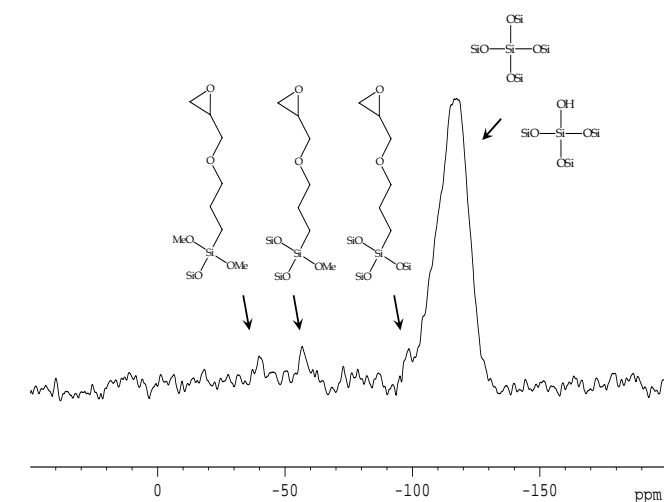
Additional schemes



Scheme 1: Thermogravimetric curves of silica bearing physically adsorbed GPM and the GPM grafted silica after and before thermal treatment at 100°C



Scheme 2: ¹³C solid state NMR spectrum of silica grafted by GPM



Scheme 3: CP-MAS ²⁹Si solid state NMR spectrum of silica grafted by GPM