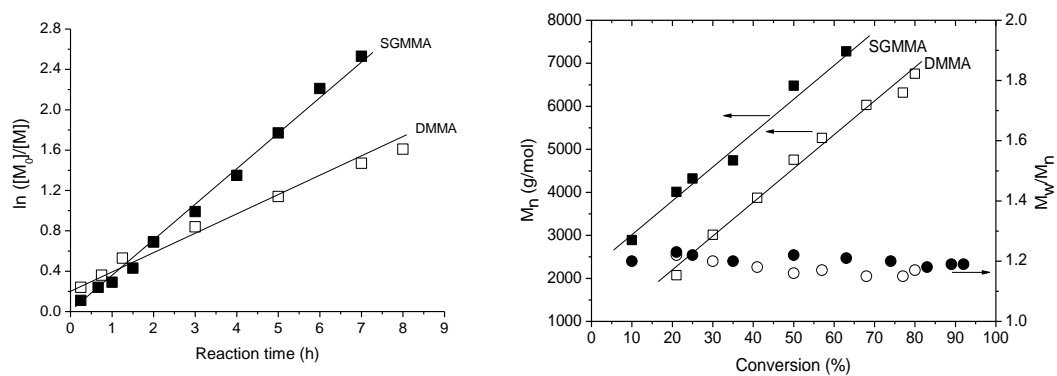


## Supporting information

### Homopolymerization of DMMA and SGMMA



**Figure 1SI.** Evolution of monomer conversion as a function of time (*left*) and of  $\overline{M}_n$  and polydispersity as a function of monomer conversion (*right*) for the ATRP of DMMA (open symbols) and SGMMA (closed symbols) initiated by ethyl 2-bromoisobutyrate. Polymerization conditions: [initiator]:[CuCl]:[HMTETA] :[monomer] = 1:1:1:30, reaction carried out at 45 °C in THF (33 wt.%) for DMMA and at 70 °C in dioxane (50 wt.%) for SGMMA.

**Table 1SI.** Summary of the deprotection conditions and results for Sil-DMMA3 and Sil-SGMMA3 (reaction time: 8 hours, but negligible differences were recorded after 48 hours). With Sil-DMMA3 two fractions were generally obtained, a water-soluble and a water-insoluble one. The two parameters, PDMS/PGMMA and residual protecting group, respectively provide information about the integrity of the macromolecular structure and the efficiency of deprotection.

Sample	Physical state	Aqueous acid <sup>a</sup>	<sup>1</sup> H NMR	
			PDMS/PGMMA (mol/mol) <sup>b</sup>	Residual protecting groups (mol %) <sup>c</sup>
Sil-DMMA3	=	=	1.1	100
	dispersion	10X, 3.7% HCl	0.7 (water sol.) 1.1 (water ins.)	57 (water sol.) 92 (water ins.)
	10% THF sol.	0.4X, 3.7 % HCl	0.7 (water sol.) 1.5 (water ins.)	39 (water sol.) 46 (water ins.)
	dispersion	10X, 44% HCOOH	1.2 (water sol.)	11 (water sol.)
	10% THF sol.	0.4X, 44% HCOOH	= 1.1 (water ins.)	= 90 (water ins.)
	dispersion	10X, 66% HCOOH	0 (water sol.) 10.6 (water ins.)	0 (water sol.) 0 (water ins.)
	10 % THF sol.	0.4X, 66% HCOOH	= 1.1 (water ins.)	= 91 (water ins.)
	Sil-SGMMA3	=	=	1.3
10 % THF sol.		1X H <sub>2</sub> O + 1X AcOH	1.2	2
10 % THF sol.		1X H <sub>2</sub> O + 2X AcOH	1.4	4
10 % THF sol.		1X H <sub>2</sub> O + 3X AcOH	1.4	0
10 % THF sol.		1X H <sub>2</sub> O + 4X AcOH	1.4	1
10 % THF sol.		1X H <sub>2</sub> O + 5X AcOH	1.1	2

<sup>a</sup> expressed in relation to the weight of polymer; for example, if 100 mg of polymer, 10X means 1 g of aqueous acidic phase.

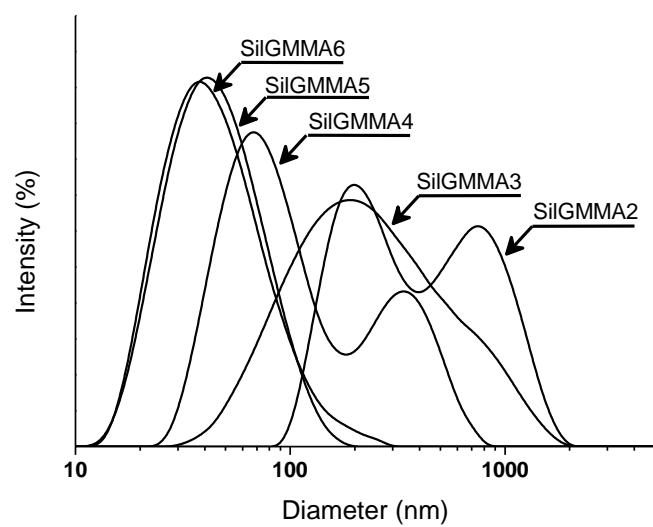
<sup>b</sup> ratio between the integrals of the peak at 0 ppm (Si-CH<sub>3</sub>) and that of the peak at 0.8-1.2 ppm (polymer chain CH<sub>3</sub>). ±0.1

<sup>c</sup> ratio between the integrals of the peak at 1.3 ppm (C(CH<sub>3</sub>)<sub>2</sub>) or of that at 0.05-0.13 ppm (Si-CH<sub>3</sub>) and that of the peak at 0.8-1.2 ppm (polymer chain CH<sub>3</sub>).

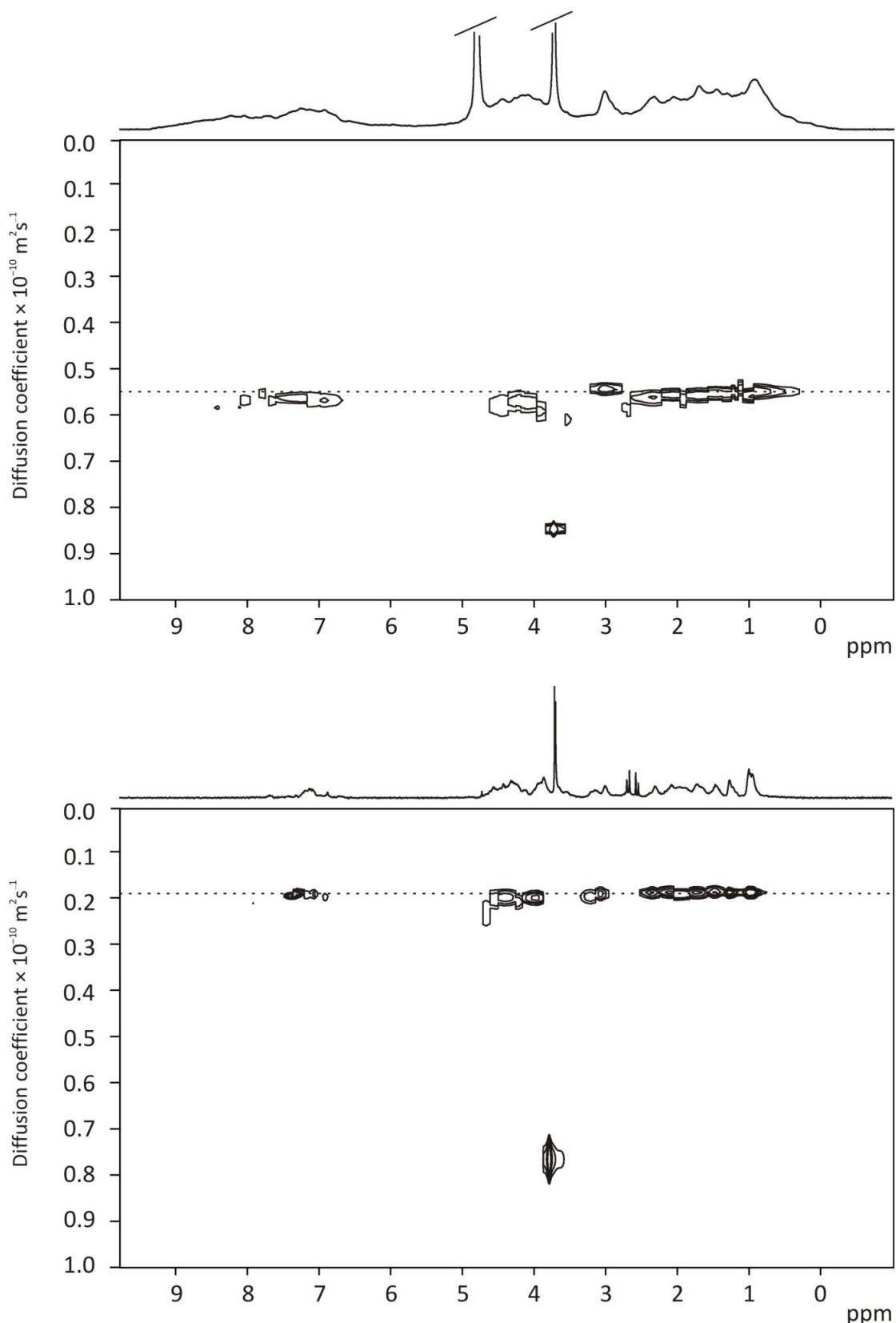
**Table 2SI.** Degree of polymerization of the methacrylic chain for the different Sil-SGMMA copolymers before and after deprotection with a 1:5 polymer/AcOH weight ratio.

Sample	$\overline{DP}_n^a$	
	protected	deprotected
SII-(S)GMMA1	22	13
SII-(S)GMMA2	29	20
SII-(S)GMMA3	44	40
SII-(S)GMMA4	53	55
SII-(S)GMMA5	78	76
SII-(S)GMMA6	102	122

<sup>a</sup> Calculated from the ratio of the <sup>1</sup>H NMR resonance of P(S)GMMA chain group (CH<sub>3</sub> at 0.7-1.2 ppm) and the resonance of PDMS chain (CH<sub>3</sub> at 0.07 ppm in CDCl<sub>3</sub> for the polymers before deprotection and at -0.06 ppm in DMSO-d<sub>6</sub> for the deprotected polymers)



**Figure 2SI.** Size distributions of 1 mg/ml suspensions of SiI-GMMA triblock copolymers in PBS 10% D<sub>2</sub>O prepared by dilution of a DMSO solution measured by DLS.



**Figure 3SI.** DOSY plots for BSA (*top*) and BPF (*bottom*) in PBS 10%D<sub>2</sub>O. For both proteins the commercially available samples contained small amounts of methanol, which is responsible of the sharp peak at 3.5 ppm; it is easy to see that the methanol peak is associated with a higher diffusion coefficient. Resonances of ethylene glycol are also visible in the BPF monodimensional spectrum, but do not appear in the full DOSY spectrum due to their low intensity. Solvent suppression was used in the case of BPF to remove the intense water signal.