

# **Adsorbed Triblock Copolymers Deliver Reactive Iron Nanoparticles to the Oil/water Interface**

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## Supporting Information

### **Polymer synthesis**

*Synthesis of poly(tert-BMA).* 612 mg tosyl chloride and 0.33 ml Pentamethyldiethylenetriamine (PMDETA)[(N-[2-(Dimethylamino)ethyl]N,N',N'-trimethyl-1,2-ethanediamine)] were dissolved in 3 ml deoxygenated acetone, 3 ml deoxygenated anisole, and 39 ml deoxygenated t-butyl methacrylate). 159.3 mg CuCl was then added under nitrogen, and the reaction proceeded for 5 hours at 60 °C. The reaction mixture was diluted with tetrahydrofuran (THF), passed through neutral alumina, the solvent and monomer was evaporated and the polymer was dried until reaching a constant weight. The polymer was analyzed by Gel Permeation Chromatography (GPC), using PMMA standards ( $M_n$  5800 and 6790, DP 42 and 48, polydispersity 1.38 and 1.26 for the first block of the PSS-462 triblock and PSS-650 triblock, respectively).

*Synthesis of poly((tert-BMA)-(MMA)).* 4g poly(t-butyl methacrylate) (DP 42) 22.9 mg CuBr<sub>2</sub>, 252.1 mg 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) were dissolved in 5.5 ml deoxygenated methyl methacrylate, and 10 ml deoxygenated anisole. 72.5 mg CuBr was then added under nitrogen. The reaction was carried out at 30 °C for 2.5 hours. The reaction mixture was diluted with THF, passed through neutral alumina, the solvent was evaporated and the polymer was dried until reaching a constant weight. The polymer was analyzed by GPC using PMMA standards ( $M_n$  8400 and 8490, TBMA<sub>42</sub>MMA<sub>26</sub> and TBMA<sub>48</sub>MMA<sub>17</sub>, polydispersity 1.32 and 1.23 for the first two blocks of the PSS-462 triblock and PSS-650 triblock, respectively).

*Synthesis of poly((tert-BMA)-(MMA)-(St)).* 2g poly(t-butyl methacrylate)-block-poly(methyl methacrylate) and 33 µl PMDETA were dissolved in 15.4 ml deoxygenated styrene and 2 ml deoxygenated anisole. 27.5 mg CuBr was then added under nitrogen. The reaction was carried out at 80 °C for 2 days. The reaction mixture was diluted with THF, passed through neutral alumina, the solvent was evaporated and the polymer was dried until reaching a constant weight. The polymer was analyzed by GPC using polystyrene standards ( $M_n$  56100 and 75600, TBMA<sub>42</sub>MMA<sub>26</sub>St<sub>462</sub> and TBMA<sub>48</sub>MMA<sub>17</sub>St<sub>650</sub>, polydispersity 1.24 and 1.62 for the PSS-462 triblock and PSS-650 triblock, respectively).

*Preparation of acetyl sulfate.* 40 ml chloroform and 28 ml acetic anhydride were mixed and cooled to 0 °C. 10.4 ml sulfuric acid was then added slowly. The reaction was allowed to stir for 10 minutes.

*Preparation of poly((MAA)-(MMA)-(PSS)).* 5g poly((tert-BMA)-(MMA)-(St)) were dissolved in 200 ml CHCl<sub>3</sub>. 78 ml acetyl sulfate was then added and the reaction mixture was stirred overnight at 60°C. 50 ml of methanol was added to terminate the reaction and an appropriate amount of NaHCO<sub>3</sub> was introduced until the pH was neutral. 50 ml of water was then added, and the organic solvents were evaporated. The polymer was purified by dialysis versus distilled water.

The evolution of the molecular weight distribution during block extension of the PMAA<sub>42</sub>-PMMA<sub>26</sub>-PSS<sub>462</sub> is shown in Figure S1. A clear shift is observed after each step, demonstrating the high efficiency of block extension.

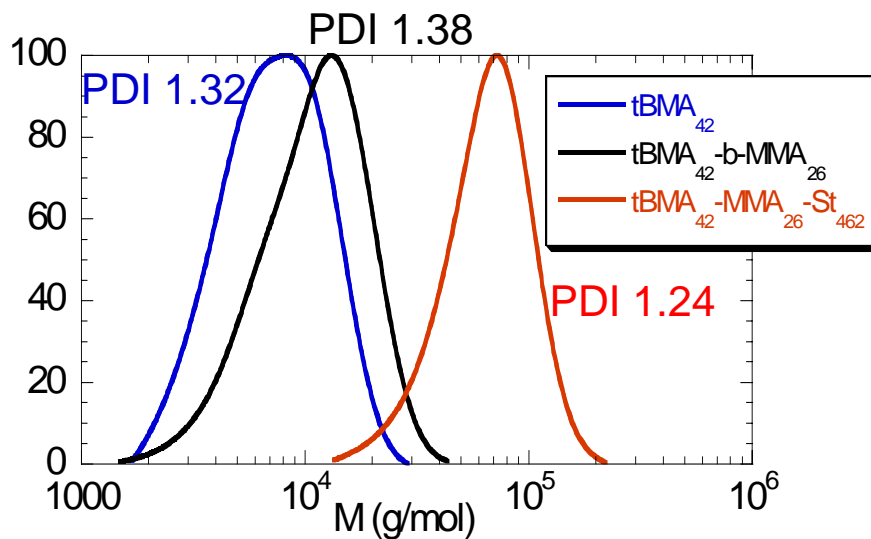


Figure S1. GPC traces of the (co)-polymer after each step

Table S1. Emulsion preparation and characteristics for nanoiron using different modifiers

Modifier	Particle:Polymer	No. of Phases	Stability
PMAA <sub>42</sub> -PMMA <sub>26</sub> -PSS <sub>462</sub>	3g/L : 2.00 g/L	2 (emulsion + H <sub>2</sub> O)	> 6 months
PMAA <sub>48</sub> -PMMA <sub>17</sub> -PSS <sub>650</sub>	3g/L : 2.00 g/L	2 (emulsion + H <sub>2</sub> O)	> 6 months
PBMA <sub>43</sub> -PSS <sub>811</sub>	3g/L : 2.00 g/L	2 (no emulsion)	N/A
PSS-340 (unwashed)	3g/L : 1.28 g/L	2 (no emulsion)	N/A
PSS-970 (unwashed)	3g/L : 3.66 g/L	2 (no emulsion)	N/A
PSS-340 (washed)	3g/L : 1.28 g/L	2 (no emulsion)	N/A
PSS-970 (washed)	3g/L : 3.66 g/L	2 (no emulsion)	N/A
PSS-340 (Supernatant)	3g/L : 1.28 g/L	3 (very large droplets)	< 1 day
PSS-970 (Supernatant)	3g/L : 3.66 g/L	3 (~0.2 ml emulsion phase)	> 1 week