

Supporting information

Synthesis of model polysulfides

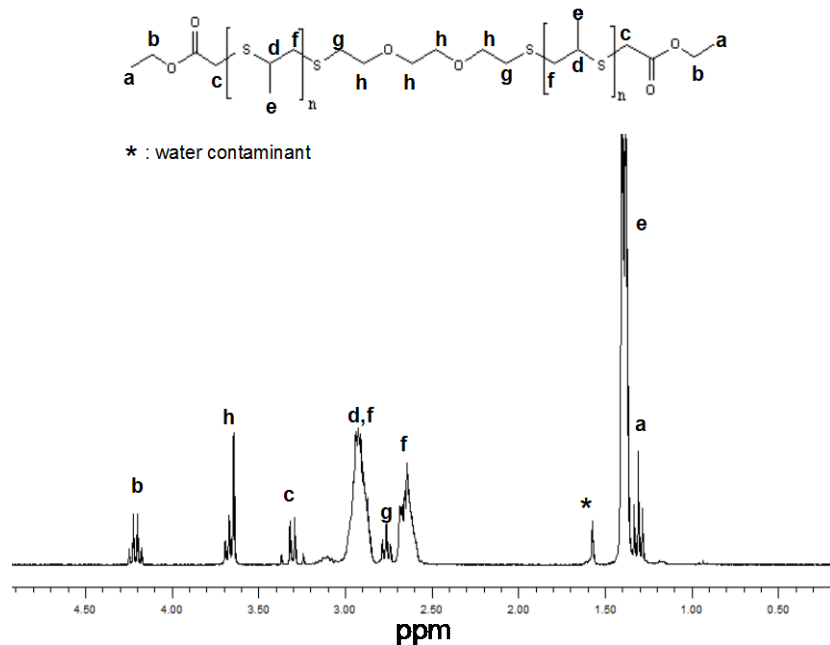


Figure 1SI. ¹H NMR spectrum of PPS with theoretical *overall DP* = 30, end-capped with ethyl 2-bromoacetate.

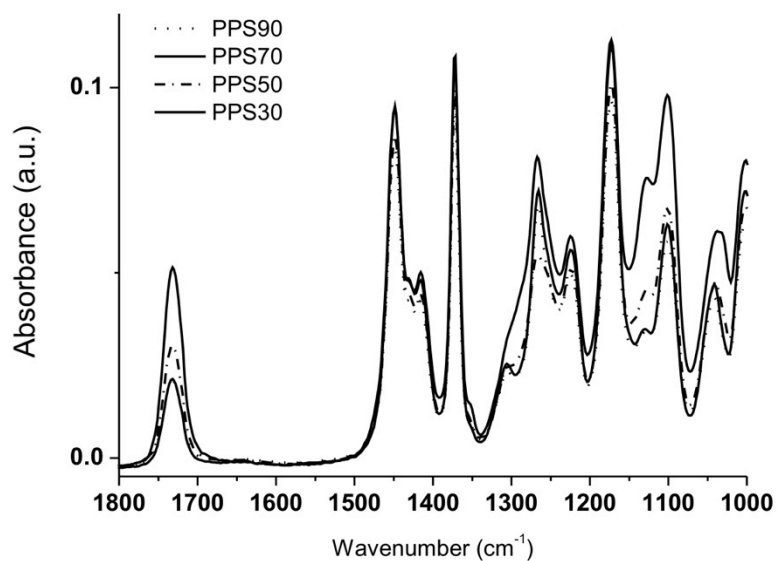


Figure 2SI. FT-IR spectra of PPS with variable DP and end-capped with ethyl 2-bromoacetate. The spectra were normalized against the absorbance of the CH₃ stretching band at 2959 cm⁻¹.

Nanoparticle freeze drying

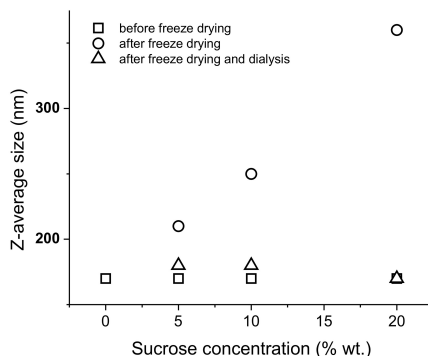


Figure 3SI. Z-average size of PA₄ nanoparticles obtained with a 0.02 Pluronic/PS weight ratio after synthesis and purification (solid squares), after freeze drying of dispersions containing different amounts of sucrose (open circles) and after the removal of sucrose via dialysis (through membranes with 3,500 Da MWCO, open triangles), which provided nanoparticles virtually indistinguishable from the starting ones.

Nanoparticle oxidation

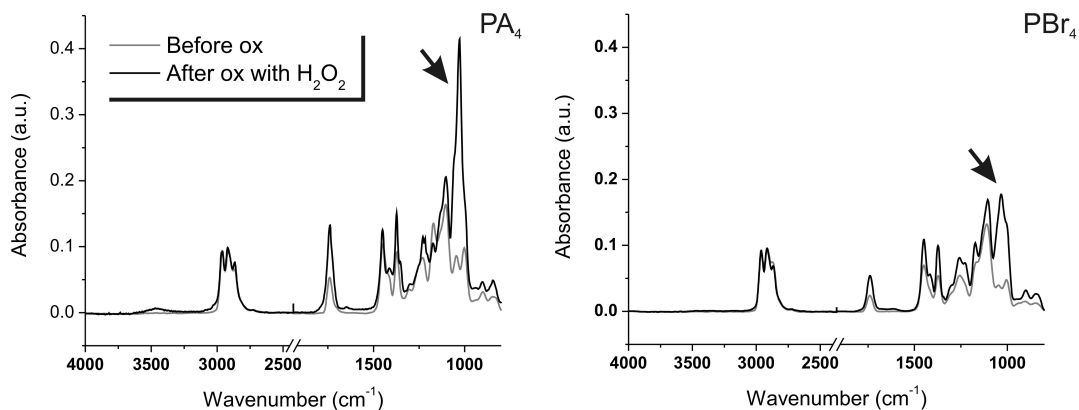


Figure 4SI. Comparison of FT-IR spectra of PPS nanoparticles (Z-average size: 160 nm) before and after 4 h oxidation with H₂O₂ (15% wt.). The spectra were normalized against the CH₃ stretching band at 2958 cm⁻¹. With both the PA₄ (left) and the PBr₄ (right) cross-linkers, the main spectral difference is the appearance of an S=O stretching band (arrow). The carbonyl band shows an increase in strength, which may be due to hydrolytic processes (the stretching of a carboxylate can be stronger than that of an ester and can be localized in the same spectral area) although the higher polarity of the environment may play a role too. However, the increase is very moderate if other bands are used for normalization.

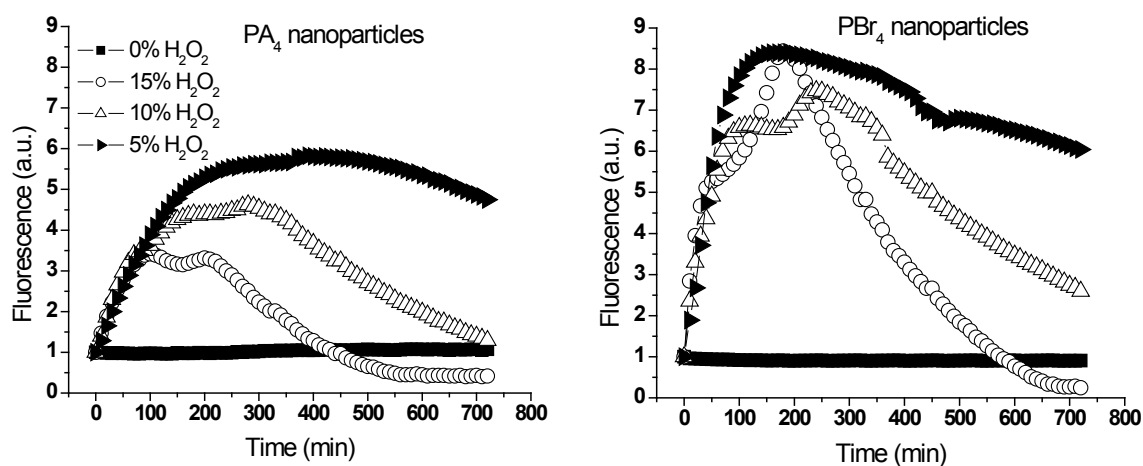


Figure 5SI. Fluorescence emission intensity of Nile Red-loaded PA₄ (left) and PBr₄ (right) nanoparticles vs. H₂O₂ concentration and time (excitation at 540 nm, emission at 620 nm; 1:25000 Nile Red/thioether molar ratio). Although a higher fluorescence intensity can be detected for the second kind of particles, the kinetic behavior is substantially identical.

Table 1SI. T₂ relaxivity measurements of PA₄ nanoparticles (50 nm in Z-average size). The relaxivity of the protons associated to the methyl group on the PPS chain and the relaxivity of the protons associated to the CH₂ of PEG and CH₃ of PPG of the surfactant, Pluronic F127, were measured on untreated nanoparticles and on PPS nanoparticles, 3 h after being treated with 5% H₂O₂.

	<i>Polysulfide</i>		<i>Pluronic</i>	
	CH ₃ (1.5/1.6 ppm)		CH ₂ (3.7 ppm, PEG)	CH ₃ (PPG)
untreated	43 ms		111 ms	89 ms
5% H ₂ O ₂	934 ms		333 ms	266 ms

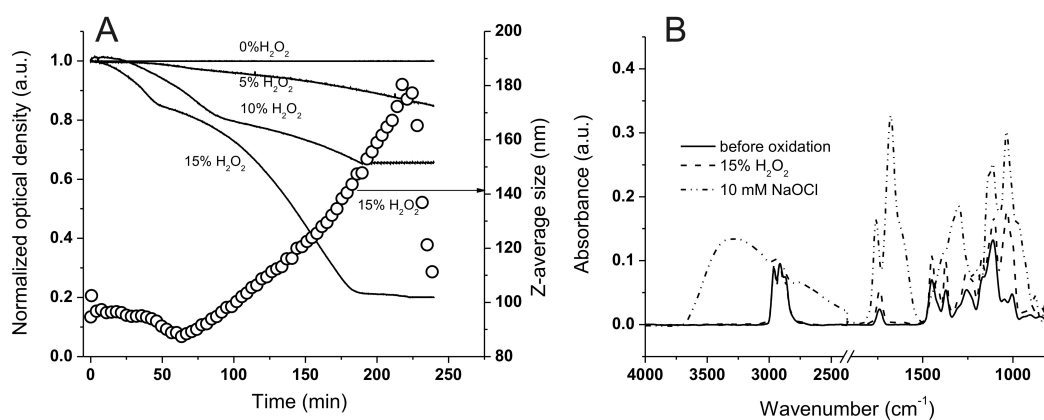


Figure 6SI. Oxidation of PBr₄ nanoparticles in deionized water (0.32 mg/mL) at 37 °C and pH = 7.4. **A.** Optical density at 600 nm (solid lines) and Z-average size (open circles) of nanoparticle dispersion vs. H₂O₂ concentration and time. As expected on the basis of the higher hydrolytical lability of the PBr₄ esters, signs of solubilization (drop both in size and in scattered intensity) were recorded after 220 minutes exposure to 15% wt. H₂O₂; however, FT-IR analysis did not show appreciable presence of carboxylate groups (flat baseline below 1700 cm⁻¹) either after 220 minutes with 15% or after 24 h with 10% wt. H₂O₂, suggesting that the “solubilization” process is likely to initially produces branched polymer structures (= a few cleaved esters would be necessary for solubilization). **B.** Comparison of FT-IR spectra of the nanoparticles before and after 4 h oxidation with H₂O₂ (15% wt.) or OCl⁻ (10 mM). The spectra were normalized against the CH₃ stretching band at 2958 cm⁻¹.