SUPPORTING INFORMATIONS

Fluorescent core-shell nanoparticles and nanocapsules using comb-like macromolecular RAFT agents: synthesis and functionalization thereof

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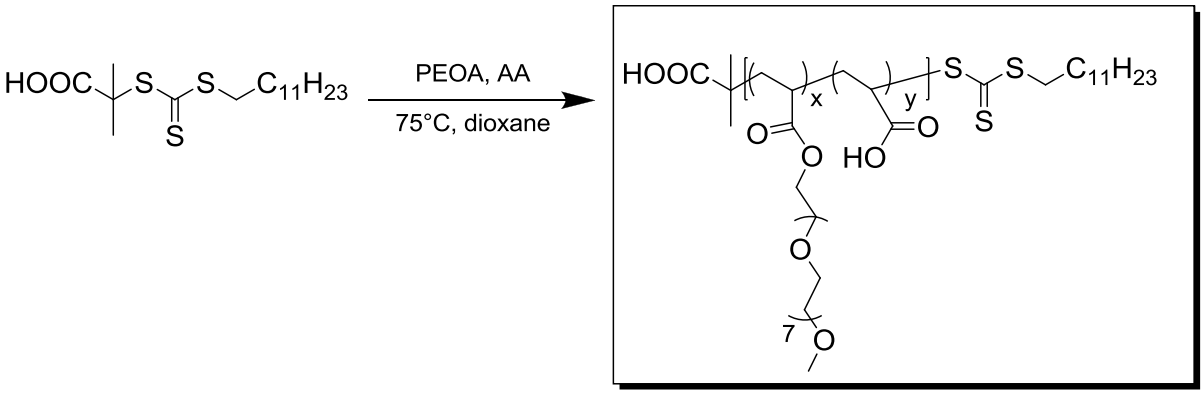
1. Macro-RAFT agents



Scheme SI-1 Synthesis of the macro-RAFT agents

Table SI-1 Experimental results for macro-RAFT agents' synthesis (dioxane, 75°C, $[M]_0$ = 2.1 mol/$L_{dioxane}$, $[RAFT]_0/[ACPA]_0$ = 15).

Macro-RAFT	$[M]_0$/ $[RAFT]_0$	t / min	χ_M[a] / %	n_{APEO}[b]	n_{AA}[b]	$M_{n,th}$ / kg mol^{-1}	$M_{n,SEC}$ / kg mol^{-1}	M_w/M_n
$PPEOA_{11}$	12	140	91	11	-	5.4	5.4	1.17
$P(AA_6$-*co*-$PEOA_6)$	15	110	81	6	6	3.5	3.5	1.21
$P(AA_{11}$-*co*-$PEOA_{11})$	25	140	86	11	11	6.2	6.0	1.16
$P(AA_{16}$-*co*-$PEOA_{17})$	43	140	77	17	16	9.2	8.1	1.20
PAA_3	8	135	39	-	3	0.6	0.6	1.19
PAA_{35}	80	130	46	-	35	2.9	3.4	1.13

[a] Global molar conversion of monomers (M) AA and PEOA determined by ^{1}H NMR in $CDCl_3$. [b] average number of AA and PEOA units per macro-RAFT agent.

2. Fluorescent monomer

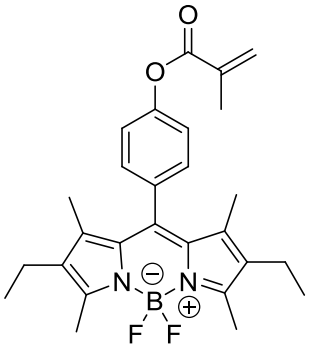
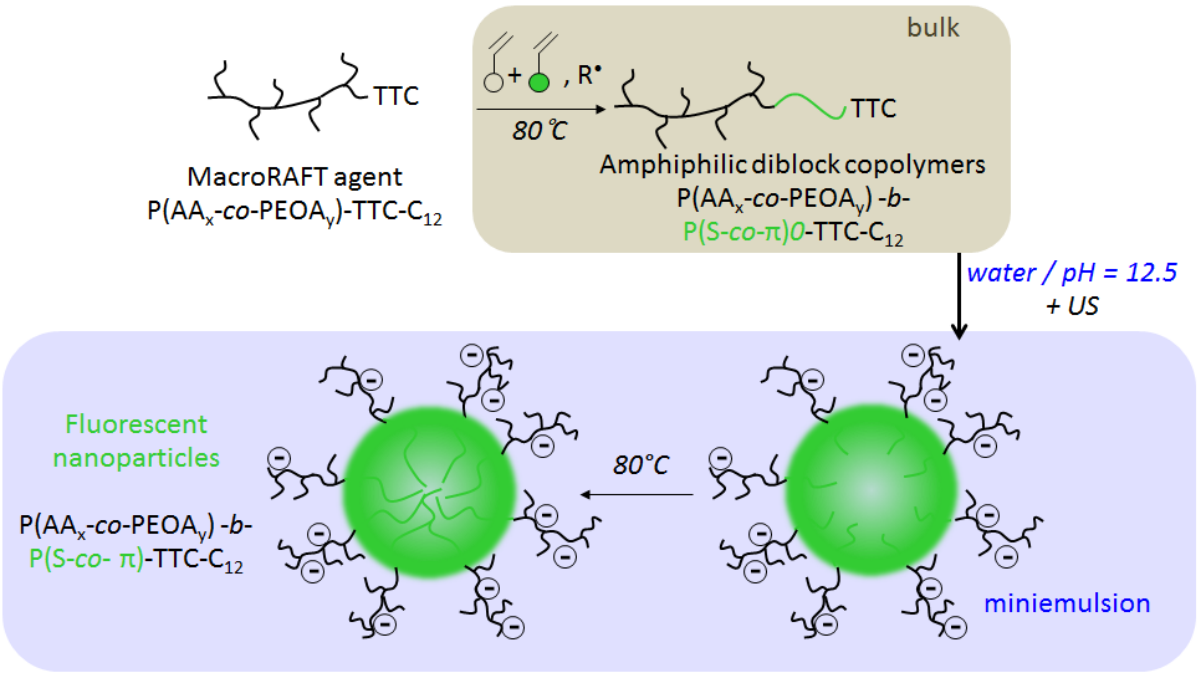


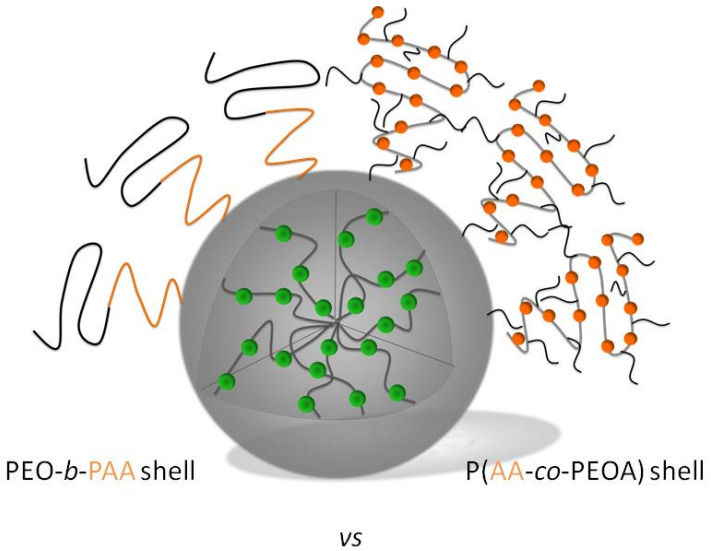
Figure SI-1 Fluorescent monomer: BODIPY phenyl methacrylate (π)

3. Miniemulsion polymerization process



Scheme SI-2 Synthetic pathway towards fluorescent nanoparticles using a one-pot phase inversion process (π = BODIPY monomer).

4. Nanoparticles' structure



Scheme SI-3 Schematic representation of both types of nanoparticles' shells described in the article: *linear* PEO-*b*-PAA *vs comb-like* P(AA-*co*-PEOA).

5. Core-shell polystyrene nanoparticles (NP)

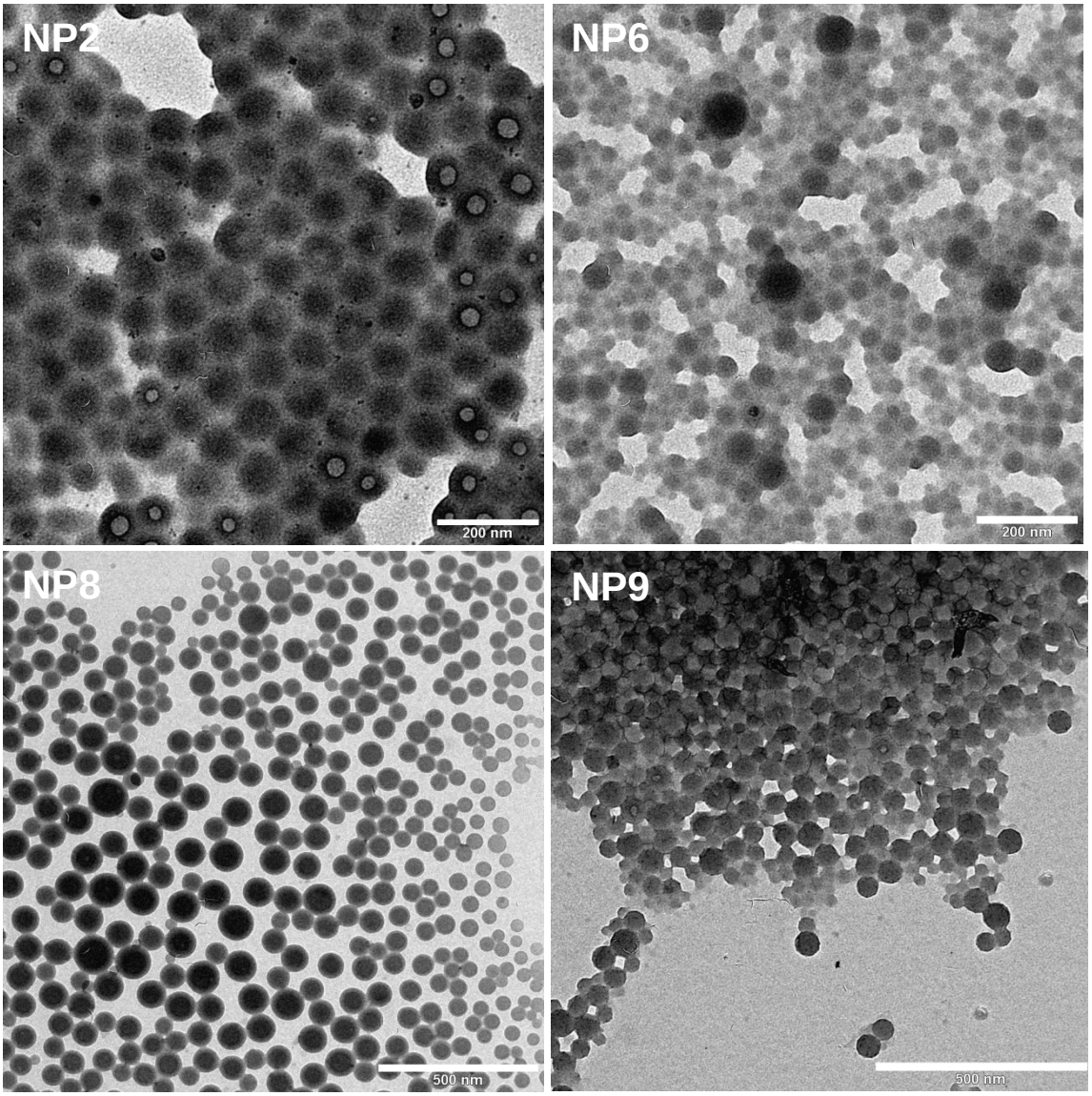


Figure SI-2 Transmission electron microscopy images of the PS nanoparticles possessing a P(AA_x-*co*-$PEOA_y$) shell. Scale bar: **NP2**, **NP6**: 200 nm, **NP8**, **NP9**: 500 nm.

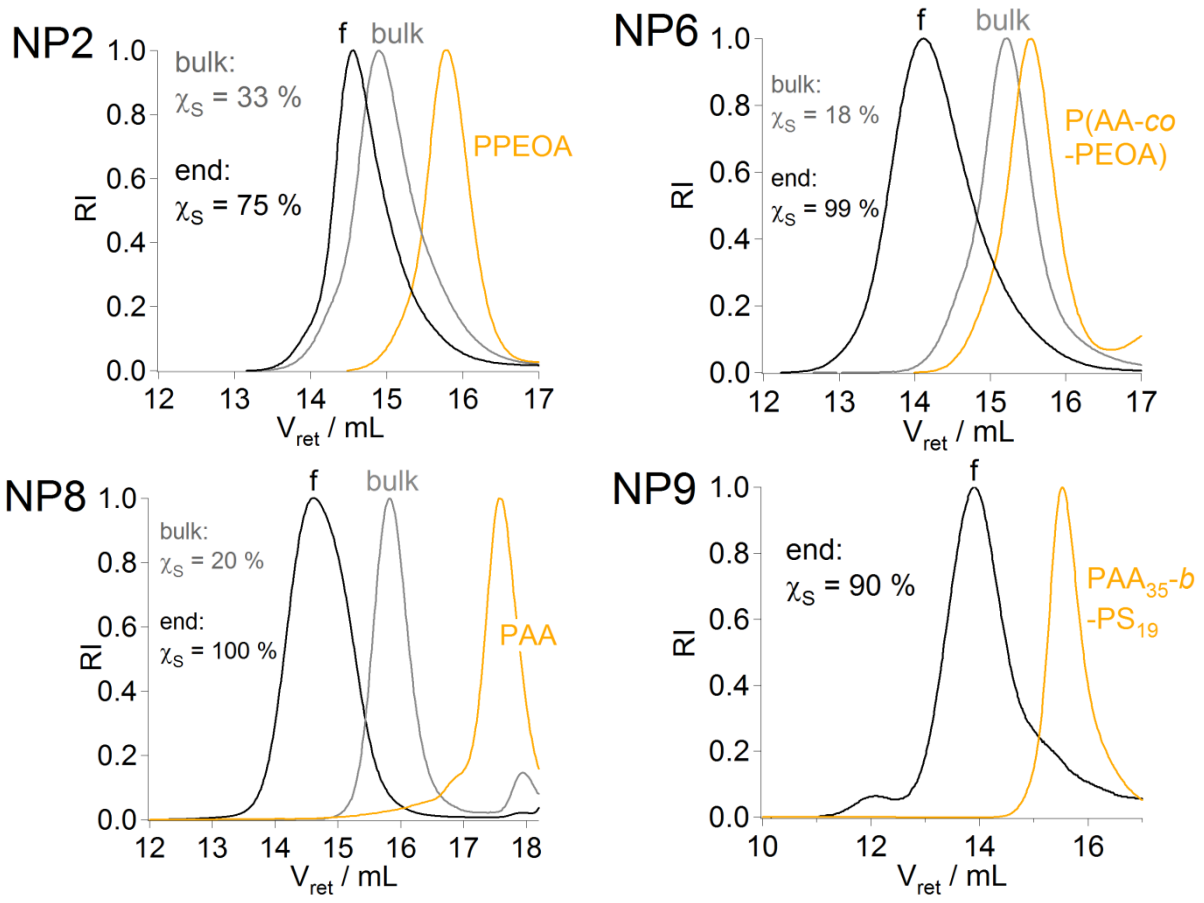


Figure SI-3 Size exclusion chromatograms in THF (RI detection) for polymeric chains of **NP2**, **NP6, NP8** and **NP9** at the beginning of the polymerization (corresponding to the isolated macro-RAFT agent) (— yellow), end of mass polymerization (— grey) and end of miniemulsion polymerization (— black).

6. Fluorescent nanoparticles (FNP)

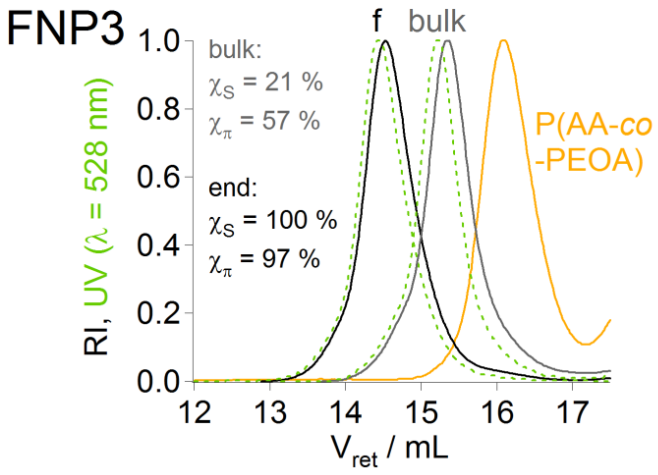


Figure SI-4 Size exclusion chromatograms in THF (plain lines: RI detection, broken — green lines: UV-vis. detection at λ = 528 nm) for polymer chains of **FNP3** at the beginning of the polymerization (corresponding to the isolated macro-RAFT agent) (— yellow), end of mass polymerization (— grey) and end of miniemulsion polymerization (— black).

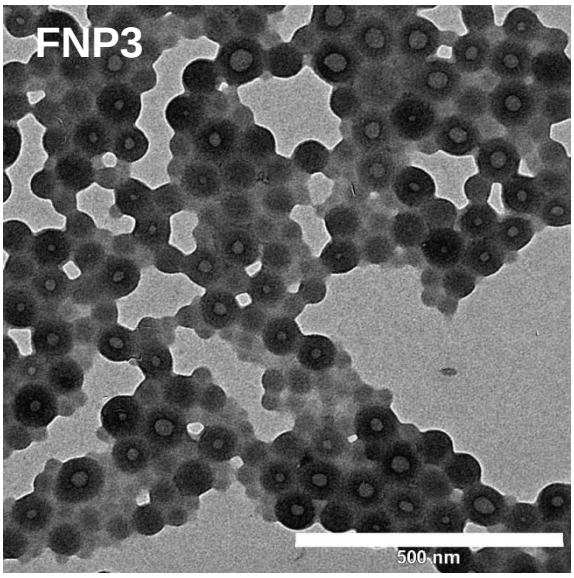


Figure SI-5 Transmission electron microscopy images of the fluorescent nanoparticles **FNP3** possessing a P(AA_6-*co*-$PEOA_6$) shell. Scale bar: 500 nm.

7. Equations

The aggregation number N_{agg} was calculated using the following equation:

$$N_{agg} = \frac{N_{chain}}{N_{FNP}} = \frac{V_{FNP}}{V_{PS}} \times N_{chain} = \frac{\frac{4}{3}\pi r^3}{m_S \rho_{PS}} \times N_{chain} \qquad \textbf{Equation SI-1}$$

where N_{chain} is the total number of growing chains (which is equal to the number of macro-RAFT agent assuming they are all incorporated in the nanoparticles), N_{FNP} is the number of fluorescent nanoparticles, V_S the total volume of polystyrene in the synthesis, V_{NP} is the volume of one fluorescent nanoparticle, m_S the converted mass of styrene in the synthesis, r_{PS} the polystyrene density and r the core radius of the nanoparticles determined by TEM microscopy.

The number of BODIPY units per polymer chain was calculated using the equation:

$$\eta_\pi = \frac{n_\pi}{n_{RAFT}} \qquad \textbf{Equation SI-2}$$

where n_π and n_{RAFT} are respectively the number of moles of BODIPY and macro-RAFT agent used in the nanoparticles synthesis.

The number of BODIPY monomers per NP was calculated using the equation:

$$N_\pi = N_{agg} \times \eta_\pi \qquad \textbf{Equation SI-3}$$

The density of polymer chains on the surface of the nanoparticles (d) was estimated by:

$$d = \frac{N_{agg}}{4\pi \left(\frac{D_{TEM}}{2}\right)^2} \qquad \textbf{Equation SI-4}$$

where N_{agg} is the aggregation number (Equation SI-1) and D_{TEM} is the diameter of the core of the nanoparticles determined with the TEM images.