

Supporting Information

***Ab Initio* RAFT Emulsion Polymerization of Butyl Acrylate Mediated by Poly(acrylic acid) Trithiocarbonate**

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MALDI-TOF mass spectrometry of macroRAFT PAA-TTC. Samples were prepared by dissolving the polymer in water at a concentration of 10 mg.mL⁻¹. A 10 µL aliquot of this solution was mixed with 10 µL of matrix solution (at 20 mg.mL⁻¹ in THF) and 10 µL of THF. Standards (polystyrene of known structure and molar mass, purchased from Polymer Standards Service) were used to calibrate the mass scale. Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectrometry of poly(acrylic acid) was performed using a Bruker autoflex III smartbeam mass spectrometer, equipped with a laser producing pulses at 337 nm, and using 3-β-indoleacrylic acid as a matrix. Spectra were recorded in linear mode at an accelerating potential of 20 kV.

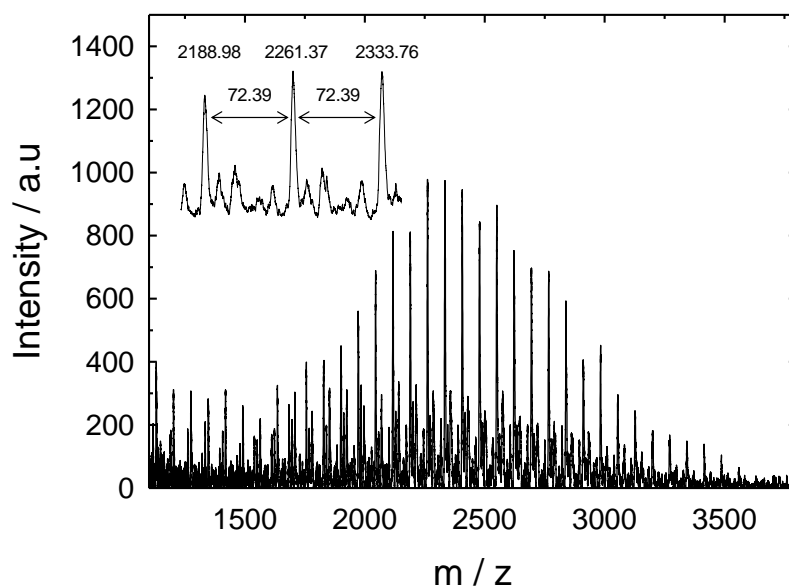


Figure SI-1. MALDI-TOF mass spectrum of PAA-TTC A2-b.

The mass spectrum shown on **Figure SI-1** shows a main distribution which corresponds to the desired poly(acrylic acid) trithiocarbonate macroRAFT agent, PAA-TTC (Na^+ cationized, $n \times 72.06$ (MW of AA) + 364.64 (MW of TTCA) + 22.99 (Na^+); with $n = 26$: calc. mass = 2261.2 vs expt. mass = 2261.4).

Table SI-1. Number-average molar masses of the PAA-TTC A2-b determined by SEC, ^1H NMR and MALDI-TOF analyses.

$M_{n,\text{th}}^{\text{a}}$	$M_{n,\text{exp}}^{\text{b}}$	$M_{n,\text{NMR}}^{\text{c}}$	$M_{n,\text{MALDI}}^{\text{d}}$
($\text{g}\cdot\text{mol}^{-1}$)	($\text{g}\cdot\text{mol}^{-1}$)	($\text{g}\cdot\text{mol}^{-1}$)	($\text{g}\cdot\text{mol}^{-1}$)
2310	2400	2260	2320

^a Theoretical number-average molar mass, M_n , of the macroRAFT at final conversion = $([\text{AA}]_0 \times \text{conversion} \times \text{MW}(\text{AA})) / [\text{TTCA}]_0 + \text{MW}(\text{TTCA})$.

^b Number-average molar mass, M_n , determined by SEC in THF with a PS calibration. Values have been recalculated to designate the non-methylated mass of the polymers = $(\text{MW}(\text{AA})/\text{MW}(\text{AMe})) \times M_n^{\text{PS}}$.

^c M_n calculated from the ^1H NMR spectrum in d^6 -DMSO by the relative integration of the CH from the polymer backbone and the CH_3 from the TTC moiety at 2.2 ppm and 0.8 ppm, respectively.

^d M_n calculated from mass distribution of the MALDI-TOF mass spectrum (Figure SI-1).

Determination of the critical aggregation concentration (CAC) of macroRAFT PAA-TTC A2-b by plotting the intensity of scattered light as a function of PAA-TTC concentration.

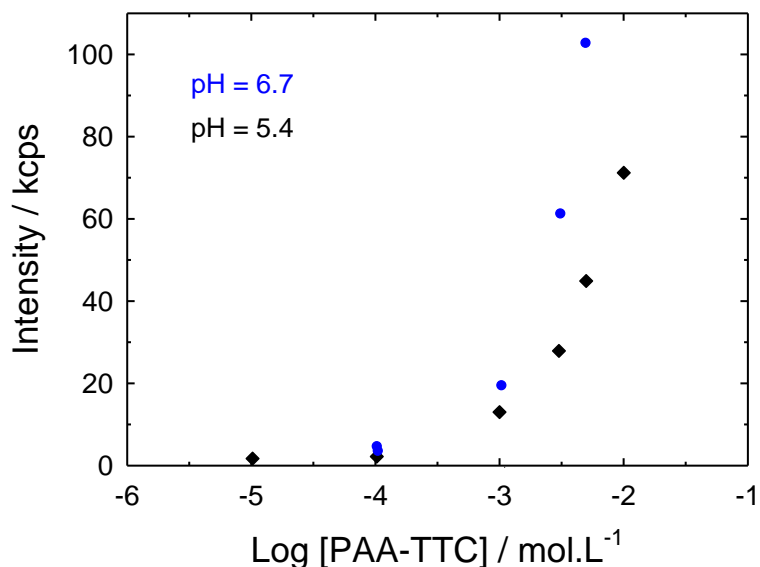


Figure SI-2. Intensity of scattered light vs molar concentration of PAA-TTC A2-b.

The CAC was determined at the intersection of the straight lines (2 mM).

Zeta potential measurements. Zeta-potential measurements were performed on a Malvern ZetaSizer Nano ZS at 20°C. The latex samples were diluted to a solids content of 0.1 wt % with a 8 mM NaCl solution and the pH was adjusted to 5.4 with 0.1 M HCl aqueous solution. The zeta-potential values, calculated from the Smoluchowski relationship, were averaged over 40 runs.

Synthesis of PAA-*b*-PBA diblock copolymers in solution. ACPA (1.2 mg, 4.2×10^{-6} mol), the PAA-TTC macroRAFT agent A3-a (52 mg, 2.1×10^{-5} mol), butyl acrylate (2.00 g, 1.56×10^{-2} mol) and ethanol (2.69 g) were added into a round-bottom septum-sealed flask and purged for 30 min with argon in an ice bath. Then, the polymerization was performed at 65°C to limit ethanol evaporation. The conversion was determined by gravimetric analysis and after methylation, the samples withdrawn during polymerization were analyzed by SEC in THF. The number-average molar mass, M_n , and the dispersity, $\mathcal{D} = M_w/M_n$, were determined using a polystyrene (PS) calibration curve.

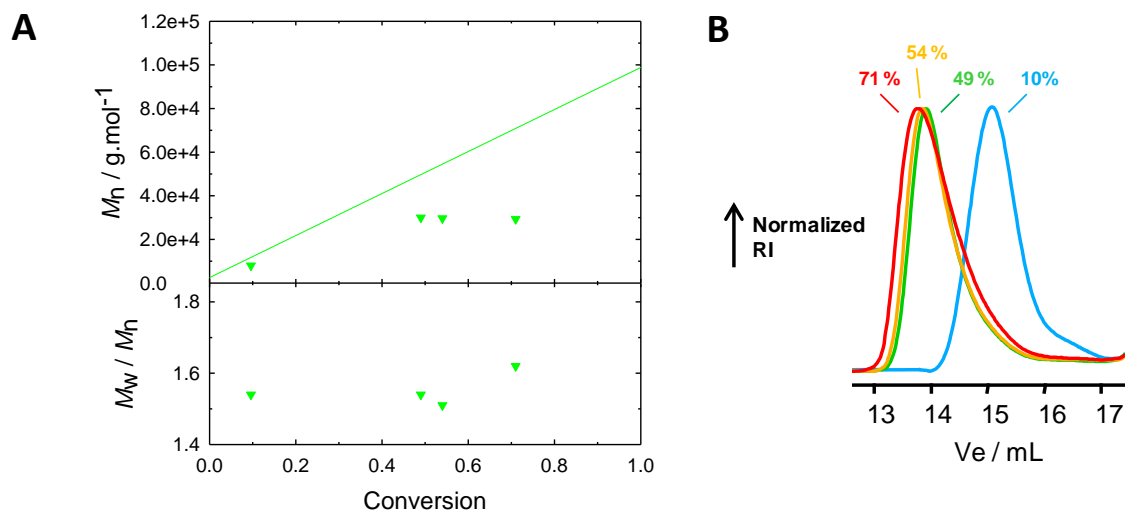


Figure SI-3. Solution polymerization of BA in the presence of PAA-TTC. (A) Number-average molar mass, M_n , and molar mass dispersity, M_w/M_n , versus monomer conversion and (B) evolution of the size exclusion chromatograms (RI traces) with monomer conversion for experiment S1 performed in ethanol at 65°C.

Differential scanning calorimetry for the triblock copolymer PAA-*b*-PBA-*b*-PS, L10.

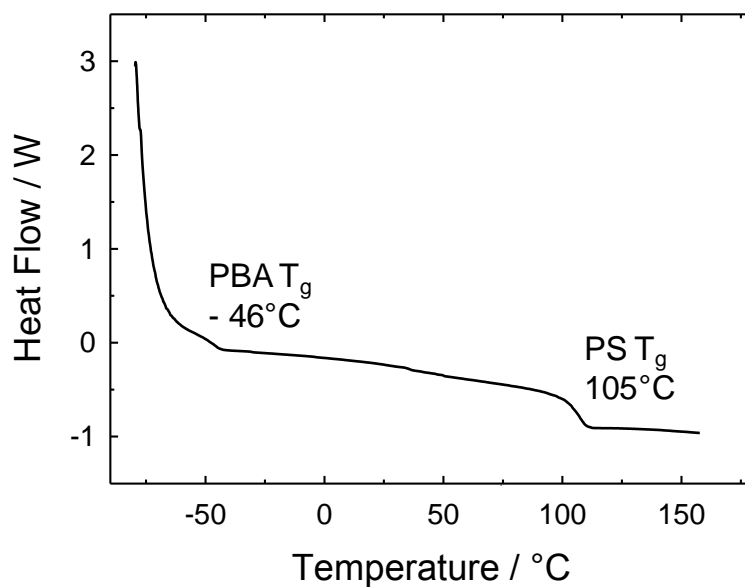


Figure SI-4. Heat flow vs temperature for latex PAA-*b*-PBA-*b*-PS (expt L10).

Calculations. The size data for experiment L2 is converted to the number of particles per unit volume of the water phase, N_p , using:

$$N_p = \frac{6 \tau}{\pi D_{n,TEM}^3 d_p} \quad \text{equation 1}$$

where τ is the experimental solids content (mass of polymer per L of water), $D_{n,TEM}$ the particle diameter measured from cryo-TEM (60×10^{-7} cm), and d_p the PBA density ($d_p = 1.026$ g.cm⁻³ at 50°C)¹.

Dividing the number of macroRAFT agent PAA-TTC by the number of particles leads to $N_{macroRAFT}$, the number of macroRAFT agents per particle:

$$N_{macroRAFT} = \frac{[macroRAFT]_0 N_a}{N_p} \quad \text{equation 2}$$

The average area per macroRAFT agent chain at the core particle surface can be calculated as follows:

$$A_{macroRAFT} = \frac{\pi D_{n,TEM}^2}{N_{macroRAFT}} \quad \text{equation 3}$$

Estimation of the PBA block dimension. The relation between chain and particle dimensions was investigated. According to the results obtained by SEC, PAA-*b*-PBA diblock copolymers were obtained, i.e. the large majority of chains was supposed to derive from the initial PAA-TTC macroRAFT agent. These diblock copolymers self-assemble during polymerization into particles that are self-stabilized by PAA chains present at the particle surfaces. In order to corroborate this idea, the dimension of the PBA chains inside the particles was estimated. The PBA chain can be considered to be tethered at one end to a surface (the particle surface). As an approximation, the Alexander theory², which applies to the calculation of the length of a polymer brush attached to a flat surface, was used to calculate the PBA chain length L . A is the calculated average area occupied by a PAA-TTC calculated above, N is the number of C-C bonds ($DP_n \times 2$) and a the C-C bond length (0.154 nm):

$$L = \frac{Na^{5/3}}{A^{1/3}} \quad \text{equation 4}$$

With $A = 14.6 \text{ nm}^2$ and $DP_n = 728$, a PBA length of 26.4 nm was calculated. Considering that the chains are attached on a curved surface, the length given by the Alexander theory must be underestimated. The result was considered consistent with the particles diameter observed in cryo-TEM (60 nm).

Table SI-2. Solution polymerization of *n*-butyl acrylate with PAA-TTC macroRAFT agent in ethanol performed at 65°C.

Exp.	PAA-TTC	$M_{n,PAA}^a$ (kg.mol ⁻¹)	[BA] ₀ (mol.L ⁻¹)	[PAA-TTC] ₀ (mol.L ⁻¹)	[ACPA] ₀ (mol.L ⁻¹)	[BA] ₀ / [PAA-TTC] ₀	Time (min)	Conv. ^b %	$M_{n,th}^c$ (kg.mol ⁻¹)	$M_{n,exp}^d$ (kg.mol ⁻¹)	M_w/M_n^d
S1	A3-a	2.5	2.8	3.7×10^{-3}	7.5×10^{-4}	757	400	71	71	29	1.62

^a Experimental M_n of the PAA-TTC macroRAFT agent determined by SEC in THF with a PS calibration.

^b Monomer conversion determined by gravimetric analysis.

^c Theoretical M_n of the polymer at final conversion = $([BA]_0 \times \text{conversion} \times \text{MW (BA)}) / [PAA-TTC]_0 + M_n (\text{PAA-TTC})$.

^d Number-average molar mass and molar mass dispersity determined by SEC in THF with a PS Calibration. The M_n value designates the methylated mass of the polymers.

Table SI-3. Emulsion polymerization of *n*-butyl acrylate performed at 70°C with PAA-TTC macroRAFT agent.

Expt.	PAA-TTC	$M_{n,PAA}^a$ (kg.mol ⁻¹)	τ_{BA}^b (wt %)	% wt PAA ^c	[BA] ₀ (mol.L _{H₂O} ⁻¹)	[PAA-TTC] ₀ (mol.L _{H₂O} ⁻¹) ^d	[ACPA] ₀ (mol.L _{H₂O} ⁻¹) ^e	[BA] ₀ / [PAA-TTC] ₀	Time (min)	Conv. ^f %	$M_{n,th}^g$ (kg.mol ⁻¹)	$M_{n,exp}^h$ (kg.mol ⁻¹)	M_w/M_n^h	D_z^i (nm)	σ^i	Coag. (wt %)
L9	A2-a	2.4	15.3	2.5	1.4	1.9×10^{-3}	3.8×10^{-4}	737	95	81	80	122	1.58	70	0.08	0

^a Experimental M_n of the PAA-TTC macroRAFT agent determined by SEC in THF with a PS calibration.

^b Solids in wt % based on the overall weight of latex = $m(\text{BA}) / m(\text{latex})$.

^c Poly(acrylic acid) content = $m_0(\text{PAA})/m_0(\text{BA})$.

^d mol.L_{H₂O}⁻¹ is the apparent concentration calculated on the basis of the overall amount of water.

^e ACPA (4,4'-azobis-4-cyanopentanoic acid) was neutralized by NH₄OH (30 wt % in water).

^f Monomer conversion determined by gravimetric analysis.

^g Theoretical M_n of the latex at final conversion = $([BA]_0 \times \text{conversion} \times \text{MW (BA)}) / [PAA-TTC]_0 + M_n (\text{PAA-TTC})$.

^h Number-average molar mass and molar mass dispersity determined by SEC in THF with a PS Calibration. The M_n value designs the methylated mass of the polymers.

ⁱ D_z is the Z-average particle diameter and σ the dispersity factor σ derived from dynamic light scattering.

Table SI-4. Emulsion Polymerization of styrene performed at 70°C with PAA-*b*-PBA latex L9.

Exp.	PAA- <i>b</i> -PBA	$M_{n,PAA-b-PBA}$ ^a (kg.mol ⁻¹)	τ_{Sty} ^b (wt %)	$[S]_0$ (mol.L _{H2O} ⁻¹) ^c	$[PAA-b-PBA]_0$ L9 (mol.L _{H2O} ⁻¹)	$[AIBN]_0$ (mol.L _{H2O} ⁻¹)	$[S]_0/[PAA-b-PBA]_0$	Time (min)	Conv. ^d %	$M_{n,th}$ ^e (kg.mol ⁻¹)	$M_{n,exp}$ ^f (kg.mol ⁻¹)	M_w/M_n ^f	D_z ^g (nm)	σ ^g
L10	L9	122	34.0	2.7	8.2×10^{-3}	1.8×10^{-3}	329	440	92	154	223	2.30	96	0.08

^a Experimental methylated M_n of the PAA-*b*-PBA L9 determined by SEC in THF with a PS calibration.

^b Solids in wt % based on the overall weight of latex = (m(S) + m(BA)) / mtot .

^c mol.L_{H2O}⁻¹ is the apparent concentration calculated on the basis of the overall amount of water.

^d Styrene conversion determined by gravimetric analysis.

^e Theoretical M_n of the latex at final conversion = ($[S]_0 \times \text{conversion} \times MW(S)$) / $[PAA-b-PBA]_0 + M_n(PAA-b-PBA)$.

^f Number-average molar mass and molar mass dispersity determined by SEC in THF with a PS Calibration. The M_n value designs the methylated polymer.

^g D_z is the Z-average particle diameter and σ the dispersity factor derived from dynamic light scattering.

References

1. C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such and B. S. Hawkett, *Macromolecules*, 2005, **38**, 2191-2204.
2. S. Alexander, *J. Phys. France*, 1977, **38**, 983.