Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Supplementary Information (ESI)

## Valuable structure-size relationships for tadpole-shaped single-chain nanoparticles with long and short flexible tails unveiled

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## Size data of tadpole-shaped single-chain nanoparticles

**Table S1.** Compilation of the size data from the literature for tadpole-shaped single-chain nanoparticles (TSCNPs) with long tails ($f_1 \geq f_2$).

| Block Copolymer Precursors | | | | | | | TSCNPs | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| # | Inert Block[a] | $N_1$ | $N_2$ | $f_1$ | $R_0^{SEC}$ (nm)[b] | $R_0^{LS}$ (nm)[c] | Intrachain Reaction[d] | $R^{SEC}$ (nm)[b] | $R^{LS}$ (nm)[c] | $R^{CAL}$ (nm)[e] | Ref |
| 1 | PS | 902 | 281 | 0.76 | - | 19.1[f] | Cinnamoyl dimerization | - | 14.2[f] | 16.2 | 1 |
| 2 | PS | 297 | 74 | 0.80 | 5.0 | - | Alkylamino quaternization | 4.4 | - | 4.4 | 2 |
| 3 | | 297 | 74 | | | | | 4.3 | - | 4.4 | |
| 4 | | 151 | 15 | 0.91 | 3.4 | - | | 3.4 | - | 3.2 | |
| 5 | PS | 169 | 30 | 0.85 | 4.0 | - | Alkylamino quaternization | - | 3.5 | 3.6 | 3 |
| 6 | PS / PEO | 2165 | 475 | 0.82 | - | 11.3 | Pyridine quaternization | - | 8.8 | 10.0 | 4 |
| 7 | PEO | 455 | 445 | 0.51 | 8.1 | - | BCB dimerization | 5.1 | - | 5.4 | 5 |
| 8 | | | 342 | 0.57 | 7.2 | - | | 5.9 | - | 5.1 | |
| 9 | | | 338 | 0.57 | | - | | 5.8 | - | 5.1 | |
| 10 | | | 334 | 0.58 | | - | | 4.6 | - | 5.1 | |
| 11 | PMMA | 2250 | 286 | 0.88 | - | 8.0 | Radical coupling | - | 6.0 | 7.4 | 6 |
| 12 | PtBA | 510 | 420 | 0.55 | 11.1 | - | Cinnamoyl dimerization | 8.3 | - | 7.7 | 7 |
| 13 | PNAM | 100 | 100 | 0.50 | - | 3.9 | Boronate ester formation | - | 3.1 | 2.6 | 8 |
| 14 | | 100 | 100 | 0.50 | - | 3.3 | | - | 2.5 | 2.2 | |

[a] PS = Poly(styrene); PEO = Poly(ethylene oxide); PMMA = Poly(methyl methacrylate); PtBA = Poly(*tert*-butyl acrylate); PNAM = poly(4-acryloylmorpholine). [b] For the block copolymer precursors: $R^{SEC}$ (nm) = $1.44\times10^{-2}$ $M_w^{0.561}$ (see ref 9); for the TSCNPs: $R_H^{SEC}$ (nm) = $1.44\times10^{-2}$ $(M_w^{app})^{0.561}$ where $M_w$ is the weight average molecular weight of the precursor and $M_w^{app}$ is the apparent weight average molecular weight of the TSCNPs, as determined by size exclusion chromatography (SEC). [c] Data from dynamic light scattering (DLS) measurements (unless otherwise stated). [d] BCD = Benzocyclobutene. [e] $R^{CAL} = R_0^{\,i} f_1^{3/5}$ ($i$ = SEC or LS) (eq 5 in main text). [f] Data from static light scattering (SLS) measurements.

**Table S2.** Compilation of the size data from the literature for TSCNPs with short tails ($f_1 < f_2$).

| Block Copolymer Precursors | | | | | | | | TSCNPs | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| # | Inert Block[a] | $N_1$ | $N_2$ | $f_1$ | $R_0^{SEC}$ (nm)[b] | $R_0^{LS}$ (nm)[c] | $l$ (nm)[d] | Intrachain Reaction[e] | $x$[f] | $R^{SEC}$ (nm)[b] | $R^{LS}$ (nm)[c] | $R^{CAL}$ (nm)[g] | Ref |
| 1 | PDEA | 78 | 112 | 0.41 | - | 5 | 0.23 | Disulfide exchange | 0.29 | - | 4.0 | 4.0 | 10 |
| 2 | | 52 | 113 | 0.32 | - | 5 | | | 0.28 | - | 4.3 | 3.9 | |
| 3 | | 28 | 109 | 0.20 | - | 4.5 | | | 0.29 | - | 3.5 | 3.3 | |
| 4 | PDMAEMA | 246 | 524 | 0.32 | - | 5.0 | 0.09 | Glaser coupling | 0.36 | - | 3.0 | 3.9 | 11 |
| 5 | PEO | 114 | 726 | 0.14 | 8.8 | - | 0.14 | BCB dimerization | 0.05 | 7.6 | - | 7.1 | 12 |
| 6 | | | 756 | 0.13 | 8.9 | - | | | 0.10 | 6.4 | - | 6.4 | |
| 7 | | | 686 | 0.14 | 8.6 | - | | | 0.20 | 5.2 | - | 5.7 | |
| 8 | PEO | 73 | 184 | 0.28 | 3.6 | - | 0.14 | Diels-Alder reaction | 0.17 | 2.5 | - | 3.1 | 13 |
| 9 | PDMA | 35 | 145 | 0.19 | - | 4.2 | 0.19 | Cinnamoyl dimerization | 0.24 | - | 2.8 | 3.2 | 14 |

[a] PDA = Poly(2-(diethylamino)ethyl methacrylate); PDMAEMA = Poly(2-(dimethylamino)ethyl methacrylate); PEO = Poly(ethylene oxide); PDMA = poly(*N,N*′-dimethylacrylamide). [b] For the block copolymer precursors: $R^{SEC}$ (nm) = $1.44\times10^{-2}\ M_w^{0.561}$ (see ref 9); for the TSCNPs: $R^{SEC}$ (nm) = $1.44\times10^{-2}\ (M_w^{app})^{0.561}$ where $M_w$ is the weight average molecular weight of the precursor and $M_w^{app}$ is the apparent weight average molecular weight of the TSCNPs, both determined by size exclusion chromatography (SEC). [c] Data from dynamic light scattering (DLS) measurements. [d] $l \simeq R_0/(N_1+N_2)^{3/5}$ where $R_0$ is the size of the TSCNP precursor in good solvent for both blocks at high dilution. [e] BCB = Benzocyclobutene. [f] $x$ is the TSCNP intrachain cross-linking degree. [g] Calculated from eq. 6 in the main text: $R^{CAL} \simeq R_0^i\left[f_1+f_2\left(KR_{2\theta}^2\right)^{-1/3}\right]^{3/5}$ ($i$ = SEC or LS) where $f_2 = 1-f_1$, $K = Ax \simeq 5x$ and $R_{2\theta}^2 \equiv l^2 N_2$.

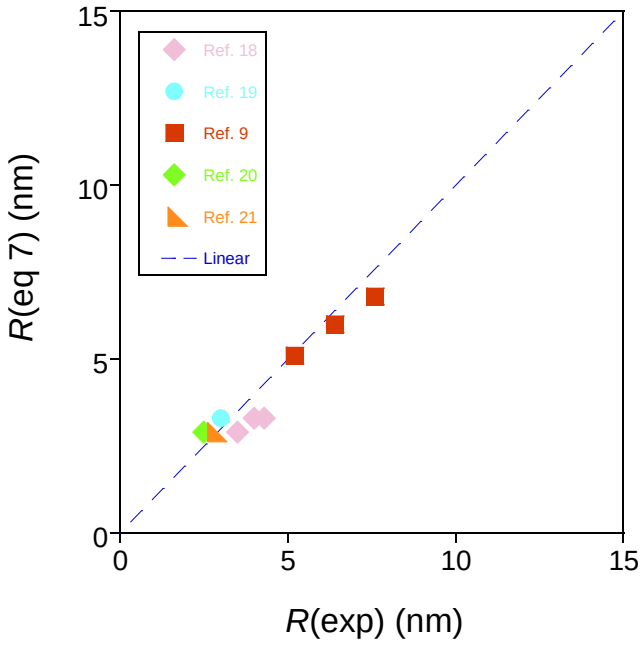


**Figure S1.** Comparison of the experimental size data, $R$(exp), for TSCNPs with short flexible tails ($f_1 < f_2$) with predicted size data (solid symbols) obtained from eq 7: $R \simeq R_0\left(5xl^2N_2\right)^{-1/5}$ (see main text).

**Table S3.** Validation test of the predictive capabilities of eq 5 (TSCNPs with long tails, $f_1 \geq f_2$) for hybrid TSCNPs with silica-like heads and long PEO tethers.[15]

| Block Copolymer Precursor | | | | | | TSCNPs | | | |
|---|---|---|---|---|---|---|---|---|---|
| # | Inert Block[a] | $N_1$ | $N_2$ | $f_1$ | $R_0^{SEC}$ (nm)[b] | Intrachain Reaction[d] | $R^{SEC}$ (nm)[b] | $R^{CAL}$ (nm)[c] | $\varepsilon$ (%)[d] |
| 1 | PEO | 114 | 87 | 0.57 | 3.6 | Hydrolysis / Polycondensation | 3.1 | 2.6 | 16.1 |

[a] PEO = Poly(ethylene oxide). [b] For the block copolymer precursors: $R^{SEC}$ (nm) = $1.44\times10^{-2}$ $M_w^{0.561}$ (see ref 9); for the TSCNPs: $R^{SEC}$ (nm) = $1.44\times10^{-2}$ $(M_w^{app})^{0.561}$ where $M_w$ is the weight average molecular weight of the precursor and $M_w^{app}$ is the apparent weight average molecular weight of the TSCNPs, as determined by size exclusion chromatography (SEC). [c] $R^{CAL} = R_0^{SEC} f_1^{3/5}$ (eq 5 in main text). [d] $\varepsilon(\%) = (|R^{CAL} - R^{SEC}| / R^{SEC}) \times 100$.

**Table S4.** Validation test of the predictive capabilities of eq 7 (TSCNPs with short tails, $f_1 < f_2$) for hybrid TSCNPs with silica-like heads and short PEO tethers.[15]

| Block Copolymer Precursors | | | | | | | TSCNPs | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| # | Inert Block[a] | $N_1$ | $N_2$ | $f_1$ | $R_0^{SEC}$ (nm)[b] | $l$ (nm) | Intrachain Reaction | $x$ | $R^{SEC}$ (nm)[b] | $R^{CAL}$ (nm)[c] | $\varepsilon$ (%)[d] |
| 1 | PEO | 114 | 470 | 0.20 | 6.8 | 0.14 | Hydrolysis / Polycondensation | 0.1 | 5.4 | 5.0 | 7.4 |
| 2 | | | 388 | 0.23 | 6.5 | | | 0.17 | 4.5 | 4.5 | 0.0 |
| 3 | | | 382 | 0.23 | 6.7 | | | 0.24 | 4.5 | 4.3 | 4.4 |
| 4 | | | 365 | 0.24 | 6.8 | | | 0.31 | 4.8 | 4.2 | 12.5 |
| 5 | | | 151 | 0.43 | 4.4 | | | 0.30 | 3.5 | 3.3 | 5.7 |
| 6 | | | 298 | 0.28 | 6.1 | | | 0.29 | 4.4 | 4.0 | 9.1 |
| 7 | | | 401 | 0.22 | 7.0 | | | 0.28 | 4.4 | 4.3 | 2.3 |
| 8 | | | 505 | 0.18 | 7.8 | | | 0.25 | 5.8 | 4.7 | 19.0 |

[a] PEO = Poly(ethylene oxide). [b] For the block copolymer precursors: $R^{SEC}$ (nm) = $1.44\times10^{-2}$ $M_w^{0.561}$ (see ref 9); for the TSCNPs: $R^{SEC}$ (nm) = $1.44\times10^{-2}$ $(M_w^{app})^{0.561}$ where $M_w$ is the weight average molecular weight of the precursor and $M_w^{app}$ is the apparent weight average molecular weight of the TSCNPs, as determined by size exclusion chromatography (SEC). [c] $R^{CAL} \simeq R_0^{SEC}\left(5xl^2N_2\right)^{-1/5}$ (eq 7 in main text). [d] $\varepsilon(\%) = (|R^{CAL} - R^{SEC}| / R^{SEC}) \times 100$.

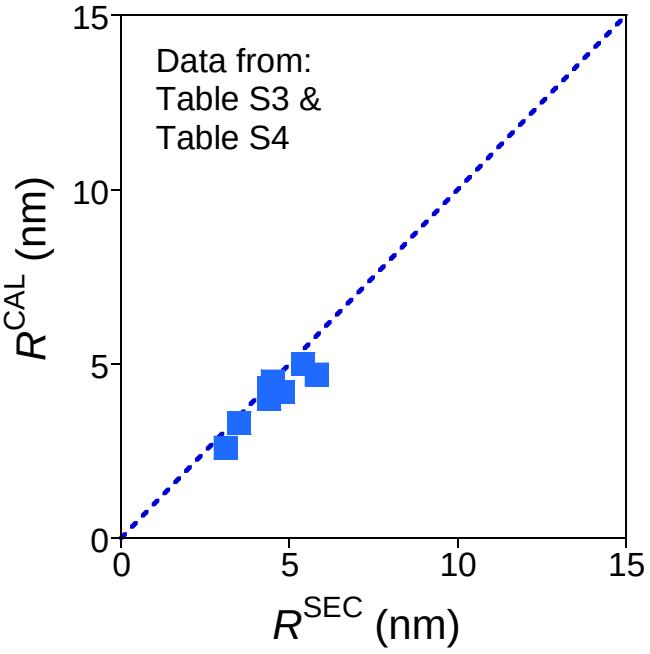


**Figure S2.** Visual comparison of validation test results.

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