

Electronic supplementary information

Towards a structural characterization of charge-driven polymer micelles

Ilja K. Voets,^{†a} Renko de Vries,[†] Remco Fokkink,[†] Joris Sprakel,[†] Roland P. May,[§] Arie de Keizer,[†] and Martien A. Cohen Stuart[†]*

[†]Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

[§]Institut Max von Laue-Paul Langevin, F-38042 Grenoble Cedex 9, France

*ilja.voets@wur.nl; renko.devries@wur.nl; remco.fokkink@wur.nl; joris.sprakel@wur.nl;
roland.may@ill.fr; arie.dekeizer@wur.nl; martien.cohenstuart@wur.nl

Table S1. Summary of light and neutron scattering results: micellar mass, M_w / kg mol⁻¹, aggregation number given as the number of anionic, P_{agg}^- , and cationic, P_{agg}^+ polymers per micelle, radius of gyration extrapolated to zero angle, R_g^0 / nm, radius of hydration

^a Present address: Adolphe Merkle Institute, University of Fribourg, Route de l'ancienne Papeterie, CH-1723 Marly 1, Switzerland. Phone +41263009190, Fax +41263009624, Email ilja.voets@unifr.ch

extrapolated to zero angle, R_h^0 / nm, radius of gyration (Guinier extrapolation), R_{gu} / nm, average core radius^c (model fitting), $\langle R \rangle$ / nm, average shell radius, R_s / nm, core polydispersity (model fitting), p_{real} , and the ratio of the radii of gyration and hydration, R_g / R_h^0 and R_{gu} / R_h^0 . M_w and R_g^0 (SLS) are averages of Guinier and Zimm extrapolations (difference between extrapolations was ≤ 1 and 8%, respectively). A shortened version including only the most reliable values can be found in the main body of the text (Table 3).

Polymers (M_w)	SLS					SANS				
	P_{agg}^-	P_{agg}^+	R_g^0	R_h^0	R_g/R_h^0	R_{gu}	$\langle R \rangle$	R_s	p_{real}	R_{gu}/R_h^0
PAA ₃₉ - <i>b</i> -PAAm ₉₇ + P2MVP ₄₃ (295)	20.3	18.4	14.8	11.5	1.29	-	8.3	3.2	0.15	-
PAA ₄₄ - <i>b</i> -PAAm ₁₅₀ + P2MVP ₄₃ (580)	29.9	30.6	13.9	15.8	0.88	7.4	11.2	4.6	0.17	0.47
PAA ₃₉ - <i>b</i> -PAAm ₁₉₁ + P2MVP ₄₃ (353)	16.5	14.9	18.0	14.1	1.28	-	10.8	3.3	0.26	-
PAA ₄₄ - <i>b</i> -PAAm ₃₀₀ + P2MVP ₄₃ (653)	21.5	22.0	15.0	19.5	0.77	9.4	12.5	7.0	0.25	0.48
PAA ₃₉ - <i>b</i> -PAAm ₃₈₁ + P2MVP ₄₃ (432)	12.2	11.1	12.2	19.3	0.63	9.3	11.5	7.8	0.27	0.48
PAA ₄₄ - <i>b</i> -PAAm ₆₁₀ + P2MVP ₄₃ (667)	12.6	12.9	14.3	26.1	0.55	12.8	14.5	11.6	0.28	0.49
P2MVP ₄₁ - <i>b</i> -PEO ₉₅ + PAA ₅₁ - <i>b</i> -PEO ₂₅₀ (832)	32.0	39.8	28.6	19.4	1.47	10.4	12.0	7.4	0.17	0.54
P2VMP ₃₈ - <i>b</i> -PEO ₂₁₁ + PAA ₅₁ - <i>b</i> -PEO ₂₅₀ (253)	7.6	10.2	19.2	13.7	1.40	8.1	11.5	2.2	0.24	0.59
P2VMP ₄₂ - <i>b</i> -PEO ₄₄₆ + PAA ₅₁ - <i>b</i> -PEO ₂₅₀ (250)	5.6	6.8	22.1	16.3	1.36	9.9	13.1	3.2	0.27	0.61
P2VMP ₇₁ - <i>b</i> -PEO ₄₅₄ + PAA ₅₁ - <i>b</i> -PEO ₂₅₀ (517)	14.7	10.6	16.3	19.8	0.82	-	-	-	-	-
PAA ₃₉ - <i>b</i> -PAAm ₉₇ + PDMAEMA ₁₅₀ (71)	4.4	1.1	26.9	6.1	4.41	-	-	-	-	-
PAA ₄₄ - <i>b</i> -PAAm ₁₅₀ + PDMAEMA ₁₅₀ (62)	2.9	0.9	28.7	6.2	4.64	-	-	-	-	-
PAA ₃₉ - <i>b</i> -PAAm ₁₉₁ + PDMAEMA ₁₅₀ (124)	5.4	1.4	33.0	9.1	3.62	5.7	-	-	-	0.63
PAA ₄₄ - <i>b</i> -PAAm ₃₀₀ + PDMAEMA ₁₅₀ (73)	2.3	0.7	19.5	8.0	2.44	4.3	-	-	-	0.54

PAA ₃₉ - <i>b</i> -PAAm ₃₈₁ + PDMAEMA ₁₅₀ (122)	3.3	0.9	26.4	10.5	2.51	6.5	-	-	-	0.62
PAA ₄₄ - <i>b</i> -PAAm ₆₁₀ + PDMAEMA ₁₅₀ (121)	2.2	0.6	22.6	12.1	1.87	7.3	-	-	-	0.60

Small angle neutron scattering

As the q -range for the experiments on S-C3Ms of PAA-*b*-PAAm and PDMAEMA₁₅₀ was too limited to obtain reliable values from model fitting, no model fitting results are given for this system. The small angle scattering curves are shown in Figure S1.

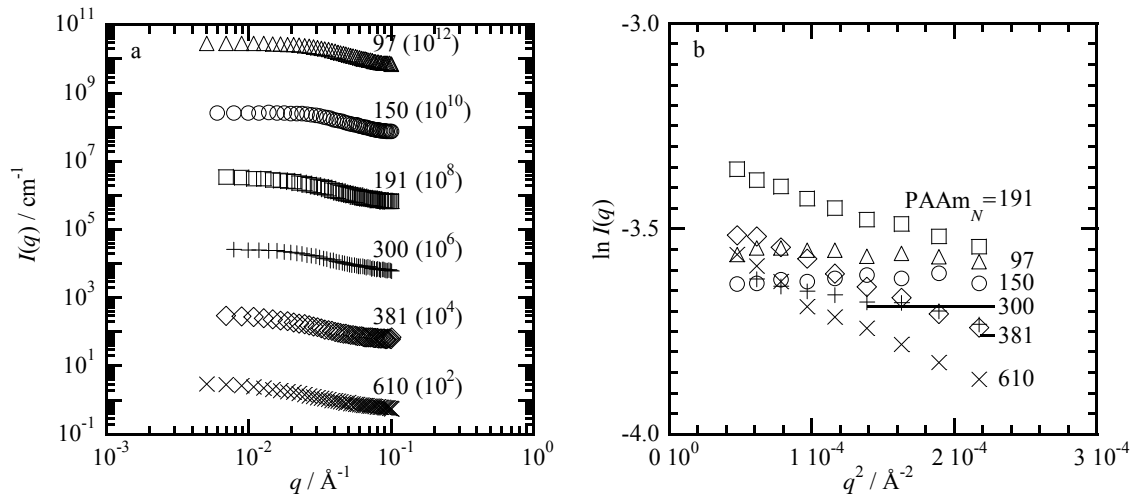


Figure S1. (a) Scattering curves, $I(q) / \text{cm}^{-1}$ versus $q / \text{\AA}^{-1}$ and (b) Guinier representations (used q -range is $0.007 < q < 0.15 \text{\AA}^{-1}$), $\ln I(q)$ versus $q^2 / \text{\AA}^{-2}$ for C3Ms of PDMAEMA₁₅₀ and (Δ) PAA₃₉-*b*-PAAm₉₇, (\circ) PAA₄₄-*b*-PAAm₁₅₀, (\square) PAA₃₉-*b*-PAAm₁₉₁, ($+$) PAA₄₄-*b*-PAAm₃₀₀, (\diamond) PAA₃₉-*b*-PAAm₃₈₁, (\times) PAA₄₄-*b*-PAAm₆₁₀ ($f_+ = 0.50$, $C = 5.1\text{-}5.3 \text{ g l}^{-1}$, $T = 25^\circ\text{C}$). The scattering curves include incoherent scattering due to solvent and hydrogenated polymer segments. Data points $\leq 0.007 \text{\AA}^{-1}$ were discarded due to lack statistics and/or

upturns resulting from a small fraction of aggregates.

Scaling properties

In the main body of the text, we have listed (plotted) only the most reliable data in Table 3 (Figure 5). For the sake of completeness, we provide all experimentally obtained values in Table S1 and Figure S2.

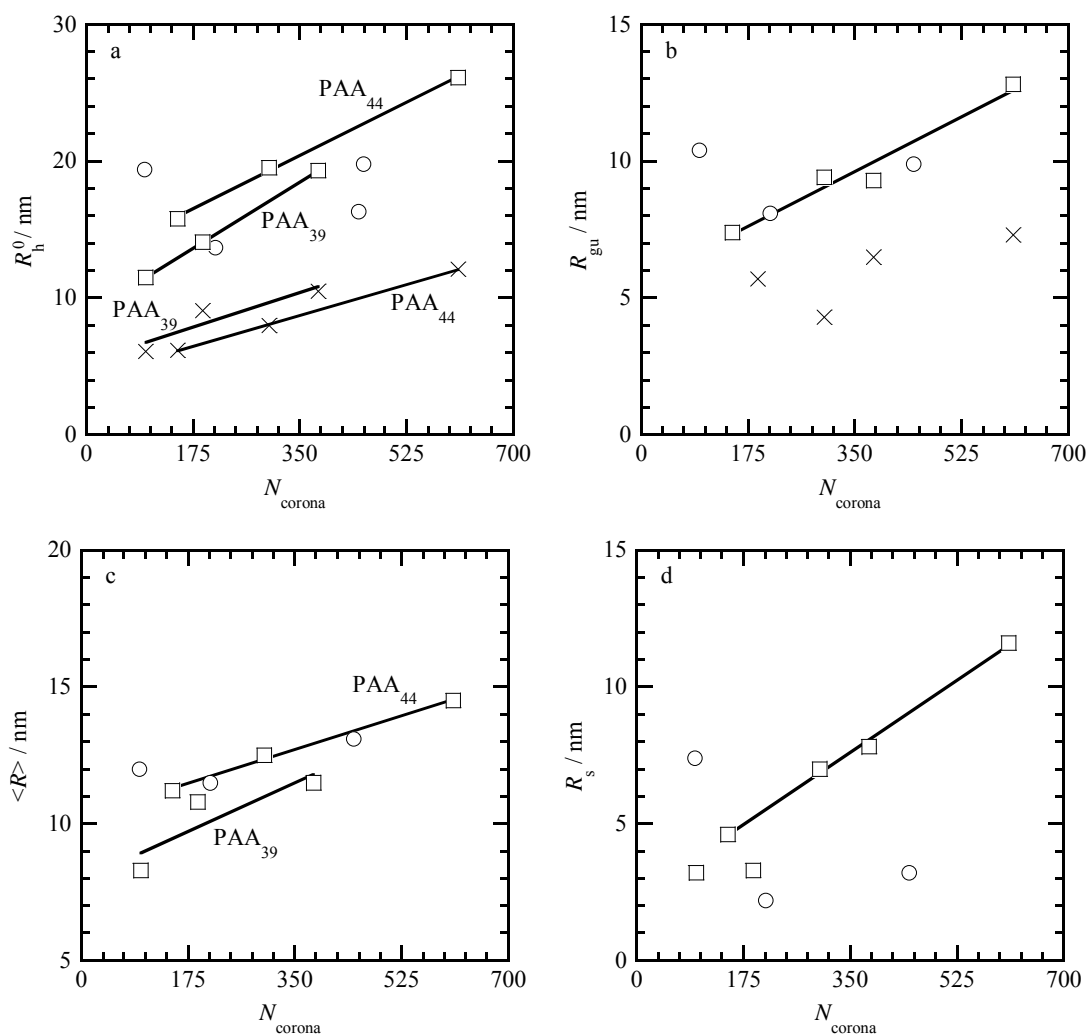


Figure S2. (a) R_h^0 , (b) R_{gu} , (c) $\langle R \rangle$, and (d) R_s as a function of N_{corona} for C3Ms of (○)

PAA₅₁-*b*-PEO₂₅₀ and P2MVP-*b*-PEO, (\square) P2MVP₄₃ and PAA-*b*-PAAm, and (\times) PDMAEMA₁₅₀ and PAA-*b*-PAAm. Lines represent linear scaling consistent with the experimental data.