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Core–shell–corona macromolecular architectures *via* electrostatic co-assembly

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Experimental Section

Materials: A sample of the polyisobutylene-*block*-poly(*tert*-butyl methacrylate) (PIB-*b*-P*t*BMA) diblock copolymer was synthesized via a combination of living cationic and anionic polymerizations as described elsewhere [S1,S2]. The values of number-average molecular mass M_n for the PIB and P*t*BMA blocks determined by means of size exclusion chromatography with the use of the PIB and P*t*BMA standards were found to be 1 100 g/mol ($DP_n^{PIB} \cong 20$) and 14 500 g/mol ($DP_n^{PtBMA} \cong 100$), respectively; the estimated polydispersity index of the PIB-*b*-P*t*BMA diblock copolymer was 1.16. To prepare the polyisobutylene-*block*-poly(methacrylic acid) (PIB-*b*-PMAA) diblock copolymer, the *tert*-butyl methacrylate groups of the PIB-*b*-P*t*BMA precursor were hydrolyzed with hydrochloric acid in dioxane at 80 °C [S2]. A sample of the poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (P2VP-*b*-PEO) diblock copolymer was synthesized via sequential anionic polymerization as described elsewhere [S3]. The values of number-average molecular mass M_n for the P2VP and PEO blocks measured by means of a combination of matrix-assisted laser desorption ionization time-of-flight mass spectrometry and ^{1}H-NMR were found to be 7 350 g/mol ($DP_n^{P2VP} \cong 70$) and 20 000 g/mol ($DP_n^{PEO} \cong 455$), respectively; the estimated polydispersity index of the P2VP-*b*-PEO diblock copolymer was 1.03 as determined by means of size exclusion chromatography. To prepare the exhaustively quaternized poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (qP2VP-*b*-PEO) diblock copolymer, the 2-vinylpyridine groups of the P2VP-*b*-PEO precursor were quaternized with a 10-fold excess of dimethylsulfate in dioxane at room temperature for about a week [S4], followed by diluting with a small amount of twice-distilled water, adjusting pH to pH 7 with 1 M NaOH, and performing a long-time dialysis (MWCO = 3500) against twice-distilled water to rid of low-molecular-weight impurities. Tris(hydroxymethyl)aminomethane (TRIS) and its hydrochloride (TRIS-HCl) were obtained from Fluka (Germany). Sodium chloride (NaCl) was purchased from ICN (USA). All other chemicals were of analytical grade and utilized without further purification. Twice-distilled water was used as a solvent for preparation of all solutions.

Preparation of Sample Solutions: The PIB-*b*-PMAA diblock copolymer was dissolved in 0.1 M NaOH at 50−60 °C under continuous stirring. The P2VP-*b*-PEO was dissolved in twice-distilled water. These stock solutions of the diblock copolymers were further diluted with 0.1 M NaCl in 0.01 M TRIS/TRIS-HCl of pH 7 and their pH was precisely adjusted to pH 7 with 0.5 M HCl or NaOH. The sample solutions of IPECs were prepared at 0.1 M NaCl and pH 7 by slow (dropwise) addition of an aqueous solution of the P2VP-*b*-PEO diblock copolymer to an aqueous solution of the PIB-*b*-PMAA micelles under continuous vigorous stirring. After preparation, they were kept under the stirring for at least 24 h before performing any experiments.

Turbidimetric Titration: Turbidimetric titrations of an aqueous solution of the PIB-*b*-PMAA micelles with an aqueous solution of qP2VP-*b*-PEO (or qP2VP) was carried out in quartz cuvettes (1 cm × 1 cm) on a Perkin Elmer Lambda EZ 201 double-beam spectrophotometer at a wavelength of 500 nm in the isoionic mode at pH 7. As these polymers do not absorb light at this wavelength, the observed increase in absorbance of their aqueous mixtures was caused exclusively by light scattering. The turbidimetric titrations were run under continuous vigorous stirring; the time interval between subsequent additions of the titrant was equal to 1 min.

Analytical Ultracentrifugation (AUC): AUC experiments were performed in the scan mode with a Beckman Spinco Model E (USA) analytical ultracentrifuge equipped with an UV−vis absorption optical detector. The sedimentation profiles were recorded at a wavelength of 280 nm, and the speed of rotor rotation was 20 000 rpm.

Dynamic Light Scattering (DLS): DLS measurements were carried out in sealed cylindrical glass cells with a diameter of 10 mm at a scattering angle of 90° with the use of equipment consisting of a PhotoCor laser goniometer (PhotoCor Corp., USA), a PhotoCor-SP correlator (PhotoCor Corp., USA) with 288 channels (logarithmic time scale from 2.5×10^{-8} up to 6 800 s), and a He–Ne laser (632.8 nm, 15 mW) as a light source. Before experiments, the prepared sample solutions were thoroughly filtered by being passed at least three times through 13-HV nylon filters (Millipore, Germany) with a pore size of 0.45 μm. The autocorrelation functions were measured for at least 3-5 min and analyzed using the CONTIN program.

Static Light Scattering (SLS): SLS experiments were performed using a Sofica laser scattered light photometer (Sofica, Germany). The prepared sample solutions were thoroughly filtered by being passed at least three times through 13-HV nylon filters (Millipore, Germany) with a pore size of 0.45 μm and then dialyzed against 0.1 M NaCl in 0.01 M TRIS/TRIS-HCl with pH 7 at least for 3 days. Afterwards, their refractive index increments dn/dc were measured on a Chromatix KMX-16 differential refractometer (ALV, Germany) with a He–Ne laser (630 nm, 2 mW) as a light source. The obtained static light scattering data were processed by plotting a Zimm diagram.

References

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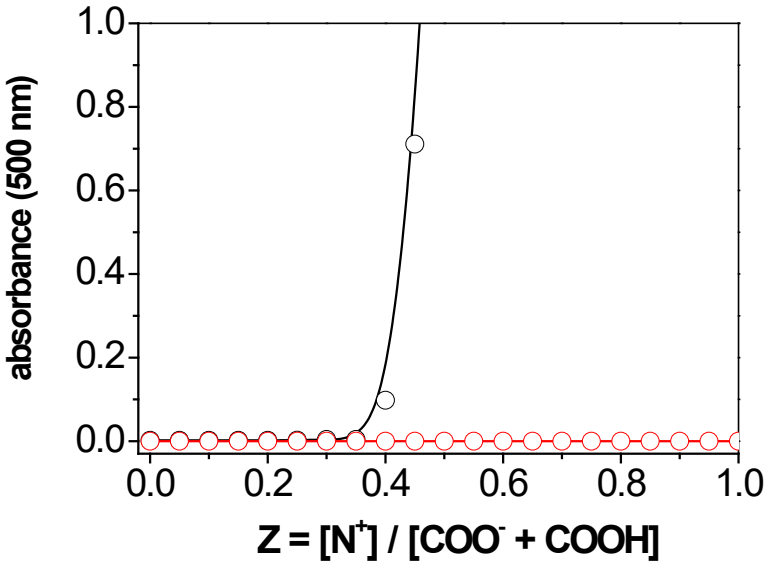

Figure S1. Turbidimetric titration curves obtained at 500 nm for the solution of the PIB-*b*-PMAA micelles titrated with the solution of qP2VP-*b*-PEO (open red circles) and qP2VP with DP_n of 36 [S5] (open black circles). Conditions: 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS·HCl), 25 °C.

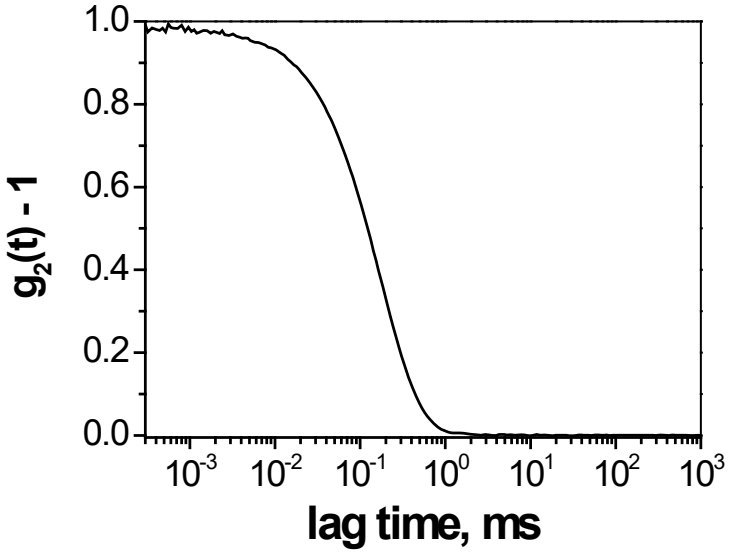

Figure S2. The normalized intensity autocorrelation function for the aqueous mixture of the PIB-*b*-PMAA micelles and qP2VP-*b*-PEO at Z = 1 measured at a scattering angle of 90°. Conditions: 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS·HCl), 25 °C.