Electronic Supplementary Information for "Molecular Mass Dependence of Adsorbed Amount and Hydrodynamic Thickness of Polyelectrolyte Layers"

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Latex Particles. Surfactant-free sulfate white polystyrene latex particles (SL), surfactant-free amidine polystyrene latex particles (AL) and carboxylate modified polystyrene latex particles (CL) were purchased from International Dynamics Corporation (Portland, USA). Prior to use, negatively charged particle suspensions were purified by ultrafiltration in a stirred cell (Amicon 8010, Millipore, Billerica, USA) with regenerated cellulose membrane filter (PLGC02510, molecular mass cut-off 10 kg/mol). The positively charged particles were purified by dialysis against Milli-Q water using a PVDF membrane (molecular mass cut-off 250 kg/mol) until the conductivity of the surrounding solution was equal to the Milli-Q water used. The properties of the particles with high sphericity are reported in Table S1.

Polyelectrolytes. Poly(styrene sulfonate) sodium salts (PSS) with a wide range of molecular mass were bought from Polymer Standards (Mainz, Germany). Poly(acrylic acid) (PAA) of lower molecular masses were purchased from Polymer Source Inc. (Montreal, Canada) and of highest molecular mass from Sigma-Aldrich (Steinheim, Germany). The polyelectrolytes were used as received without purification, except the high molecular mass PAA which was purified by dialysis with cellulose ester membrane with a molecular mass cut-off of 10 kg/mol. Linear poly(ethylene imines) (LPEI) were obtained from Polysciences (Eppenheim, Germany). High molecular mass LPEI was dissolved at a concentration of about 1 g/L in 0.08 M HCl. The others were dissolved in Milli-Q water. Samples were subsequently dialyzed with a cellulose ester membrane with a molecular mass cut-off adapted to the molecular mass (No. 131270, Spectrum, Breda, The Netherlands). The concentrations of all polyelectrolytes were checked with total carbon and nitrogen analysis (TOCV, Shimadzu). Table S2 reports the characteristics of these polyelectrolytes. All solutions were adjusted with HCl to pH 4.0 and the desired ionic strength with KCl.

Adsorbed Amount. Zetasizer Nano ZS (Malvern Instruments) was used to carry out the electrokinetic measurements. Samples were prepared by mixing about 3-4 mL of water with a variable volume of the appropriate electrolyte solution in order to obtain the desired ionic strength. Subsequently, particles were added by pipeting about 1 mL from the stock solution of roughly 45-50 mg/L. Finally, less than 1 mL of the polymer solution was added to the suspension to obtain the desired dose. The final volume of each sample for measurement was 5.0 mL. The electrophoretic mobilities of the systems SL/LPEI and AL/PAA are shown in Fig. S1. The adsorbed amount at saturation was determined from the onset of the plateau value in the mobility. The resulting values are summarized in Tab. S3 and Fig. S2. They were fitted to the relation $\Gamma = A \times (M / M_0)^b$ and where $M_0 = 1$ g/mol. The respective parameters are given in Tab. S4. The exponent can be summarized as b = –0.06±0.03, which corresponds to the average and standard deviation of all exponents individually obtained for the different polyelectrolyte-particle systems.

Layer Thickness. Hydrodynamic layer thickness measurements were carried out with time-resolved dynamic light scattering (DLS) on two different instruments. Multi-angle measurements were carried out with an 8-angle goniometer (ALV/CGS-8F, Langen, Germany) equipped with a 532 nm solid-state laser operated at 0.4 W (Verdi V2, Coherent). Second, a compact goniometer system (ALV/CGS-3, Langen, Germany) was used at a fixed scattering angle of 90°. The latter instrument uses a He/Ne laser operating at 633 nm as a light source and an avalanche photodiode as a detector. Borosilicate glass cuvettes (Tube Hemolyse Boro, Fisher Scientific) were cleaned with boiling mixture of concentrated H_2SO_4 and 30% solution of H_2O_2 at volume ratio of 3:1. Afterwards, they were rinsed extensively with Milli-Q water. The washing process with water was repeated 3 times in total. After drying in an oven, the cuvettes were stored in a dust-free environment. Solutions were prepared by mixing 0.1-0.2 mL of particle stock solutions in the range of 1-2 mg/L with different volumes in the range of 0.1-1 mL of the electrolyte stock solutions in order to obtain the desired ionic strength. The volume was completed to 2 mL with filtered water. The final particle concentration was 0.1 mg/L for AL and 0.05 mg/L for SL. The samples were then mixed in a vortex stirrer and inserted into the light scattering instrument. The entire sample preparation was carried out in a laminar flow hood. At such low particle concentrations, any effects of inter-particle forces and of particle aggregation can be excluded. The data acquisition was carried out during 2 hours to obtain a reliable particle radius before polymer adsorption. The correlation function was accumulated during 30 s, and evaluated with second order cumulant analysis. The apparent hydrodynamic radius R_{h} was calculated from the diffusion coefficient D obtained from the first cumulant with the Stokes-Einstein relation

$$D = \frac{kT}{6\pi\eta R_{\mathrm{h}}}$$

where k is Boltzmann's constant, T absolute temperature, and η viscosity of the solvent. Then, 10-20 μL of polyelectrolyte stock solutions were added into the sample in order to reach the desired polymer doses. The same measurement was continued over additional 2 hours to obtain a reliable radius for polyelectrolyte adsorbed state of the particles. The contribution of the free polyelectrolyte is negligible to the scattering intensity and to the viscosity of the solution.

Block averaged values obtained from 40-50 correlation functions are shown in Fig. S3 for SL/LPEI and AL/PAA. The final hydrodynamic radii of the particles before and after polymer addition were obtained as the respective average of these values. The layer thickness was obtained from the differences of the averaged hydrodynamic radii before and after the polymer addition. At given scattering angle, hydrodynamic radius could be measured with a typical accuracy of 0.2 nm. Radii measured at different angles varied typically within 5 nm (Fig. 3a and S3). This systematic variability originates from the fact that scattering intensities depend on the scattering angle and due to the finite sample polydispersity the diffusion coefficients are weighted by the particle form factors differently. The layer thickness was independent of the scattering angle, however, since this number is obtained from the differences of two hydrodynamic radii at the same angle (Fig. S4). The accuracy of the layer thickness measurements is about 0.5 nm for single-angle and 0.2 nm for the multi-angle measurements.

The resulting layer thickness with error bars values for all systems studied together with the experimental conditions are given in Tab. S5, and summarized for SL/LPEI and AL/PAA in Fig. S5.

Table S1. Properties of the latex particles

	TEM Radius[a] (nm)	CV[a,b] (%)	Surface charge density[c] (mC/m^2)	DLS Radius[d] (nm)
SL	135	5.9	−11	142
AL	200	3.3	192	200
CL	153.5	4.2	1489	156

[a] Obtained by transmission electron microscopy (TEM) by the manufacturer.
[b] Particle polydispersity expressed in terms of the coefficient of variation (CV).
[c] By conductomety by the manufacturer.
[d] Measured at a scattering angle of 90° and a particle concentration of 0.1 mg/L in 0.1 mM KCl and pH 4.

Table S2. Properties of the polyelectrolytes used in this study as reported by the manufacturers.

	Molecular Mass[a] M (kg/mol)	Polydispersity[b]
PSS	6.52	<1.2
	63.9	<1.2
	666	<1.2
	5640	<1.35
LPEI	2.5	1.6
	25	1.9
	250	3.4
PAA	20	1.09
	88	1.12
	1250	unknown

[a] Weight averaged molecular mass.
[a] Polydispersity is expressed as ratio of the weight averaged and number averaged molecular mass.

Table S3. Amount of adsorbed polyelectrolyte Γ for the particle/polyelectrolyte systems studied at different ionic strengths.

System	M (kg/mol)	Ionic Strength (M)			
		10^{-4}	10^{-3}	10^{-2}	10^{-1}
		Adsorbed Amount Γ (mg/m^2)			
AL/PSS	6.52	0.57 ± 0.07	0.65 ± 0.07	0.71 ± 0.06	1.04 ± 0.05
	63.9	0.53 ± 0.11	0.59 ± 0.05	0.66 ± 0.01	0.92 ± 0.01
	666	0.47 ± 0.01	0.49 ± 0.04	0.63 ± 0.02	0.89 ± 0.01
	5640	0.37 ± 0.02	0.45 ± 0.01	0.59 ± 0.03	0.79 ± 0.01
SL/LPEI	2.5	0.08 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.16 ± 0.01
	25	0.07 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.14 ± 0.001
	250	0.04 ± 0.01	0.08 ± 0.02	0.09 ± 0.03	0.11 ± 0.02
CL/LPEI	2.5	0.46 ± 0.05	0.48 ± 0.03	0.55 ± 0.01	0.80 ± 0.01
	25	0.44 ± 0.02	0.48 ± 0.01	0.54 ± 0.03	0.79 ± 0.01
	250	0.39 ± 0.02	0.47 ± 0.01	0.53 ± 0.01	0.66 ± 0.02
AL/PAA	5.7	0.79 ± 0.04	0.96 ± 0.03	1.16 ± 0.05	1.21 ± 0.05
	20	0.74 ± 0.04	0.88 ± 0.07	1.10 ± 0.03	1.14 ± 0.04
	88	0.59 ± 0.03	0.73 ± 0.01	1.05 ± 0.01	1.08 ± 0.02

Table S4. Non-linear fitting parameters for different particle/polyelectrolyte systems at different ionic strengths to the equation $\Gamma = A \times (M / M_0)^b$

System	Ionic Strength (M)	A (mg/m^2)	b
AL/PSS	10^{-4}	0.98 ± 0.14	0.06 ± 0.01
	10^{-3}	1.06 ± 0.07	-0.06 ± 0.01
	10^{-2}	1.33 ± 0.16	-0.06 ± 0.01
	10^{-1}	1.42 ± 0.09	-0.04 ± 0.01
SL/LPEI	10^{-4}	0.20 ± 0.06	-0.11 ± 0.03
	10^{-3}	0.21 ± 0.01	-0.08 ± 0.01
	10^{-2}	0.22 ± 0.01	-0.07 ± 0.01
	10^{-1}	0.32 ± 0.02	-0.09 ± 0.01
CL/LPEI	10^{-4}	0.59 ± 0.04	-0.03 ± 0.01
	10^{-3}	0.63 ± 0.01	-0.03 ± 0.02
	10^{-2}	0.71 ± 0.02	-0.03 ± 0.01
	10^{-1}	1.12 ± 0.25	-0.04 ± 0.02
AL/PAA	10^{-4}	1.90 ± 0.55	-0.10 ± 0.03
	10^{-3}	2.25 ± 0.50	-0.09 ± 0.02
	10^{-2}	1.60 ± 0.04	-0.04 ± 0.02
	10^{-1}	1.75 ± 0.04	-0.04 ± 0.02

Table S5. Hydrodynamic layer thickness *L* of adsorbed polyelectrolytes at different ionic strengths for the particle/polyelectrolyte systems studied. The left column also indicates the polymer dose used.

System	*M* (kg/mol)	Ionic Strength (M)			
		10^{-4}	10^{-3}	10^{-2}	10^{-1}
		Layer Thickness *L* (nm)			
AL/PSS 20 mg/g	6.52	2.56 ± 0.34	2.48 ± 0.28	2.45 ± 0.31	3.70 ± 0.33
	63.9	2.55 ± 0.31	2.59 ± 0.31	2.67 ± 0.28	5.75 ± 0.38
	666	2.42 ± 0.41	2.46 ± 0.32	3.27 ± 0.33	6.78 ± 0.41
	5640	2.43 ± 0.42	2.39 ± 0.27	3.26 ± 0.54	8.01 ± 0.41
SL/LPEI 50 mg/g	2.5	1.86 ± 0.37	1.91 ± 0.38	1.66 ± 0.45	3.52 ± 0.28
	25	1.62 ± 0.33	1.93 ± 0.43	1.86 ± 0.36	4.85 ± 0.33
	250	2.00 ± 0.34	1.90 ± 0.18	1.74 ± 0.28	6.50 ± 0.28
AL/PAA 600 mg/g	20	2.44 ± 0.36	2.40 ± 0.28	2.55 ± 0.42	4.87 ± 0.38
	88	2.66 ± 0.27	2.48 ± 0.34	2.75 ± 0.41	5.86 ± 0.48
	1250	3.24 ± 0.37	3.10 ± 0.39	2.94 ± 0.48	7.58 ± 0.53

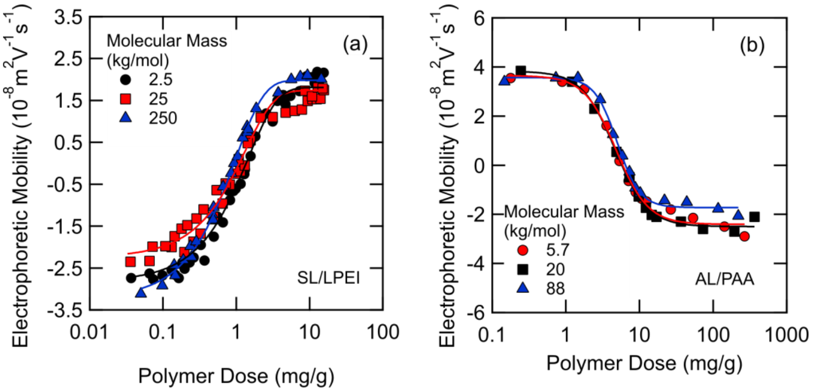

Figure S1. Electrophoretic mobility of particle/polyelectrolyte systems as a function of the polyelectrolyte dose for different molecular masses. (a) SL/LPEI at an ionic strength of 0.01 M, (b) AL/PAA at an ionic strength of 10^{-4} M.

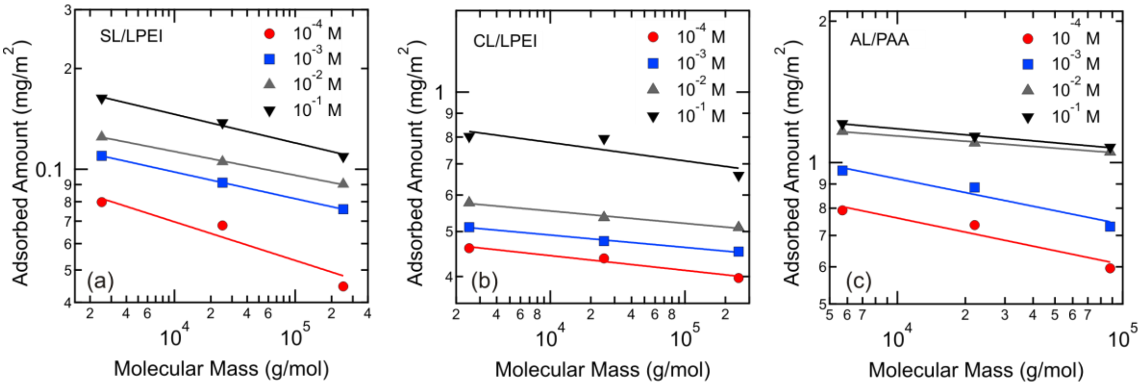

Figure S2. Amount of adsorbed polyelectrolyte as a function of molecular mass in the systems at different ionic strengths. (a) SL/LPEI, (b) CL/LPEI, (c) AL/PAA. The best fits are shown as solid lines and resulting parameters are given in Table S4.

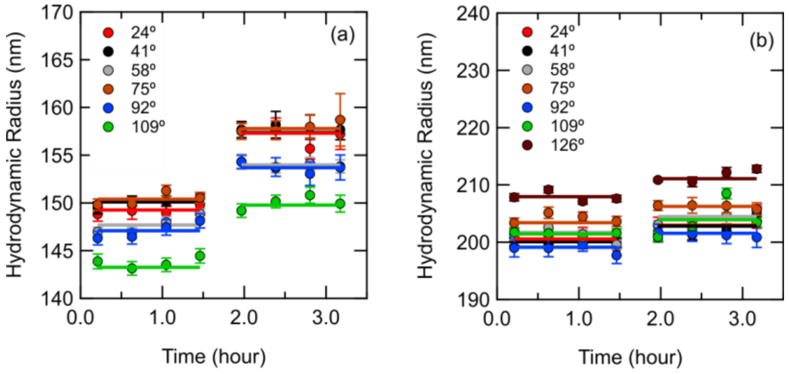

Figure S3. Time-dependence of the apparent hydrodynamic radius of the particle suspension before and after addition of the polyelectrolyte measured by time-resolved multi-angle DLS. (a) SL/LPEI of 250 kg/mol at an ionic strength of 0.1 M and (b) AL/PAA of 20 kg/mol at an ionic strength of 10^{-4} M.

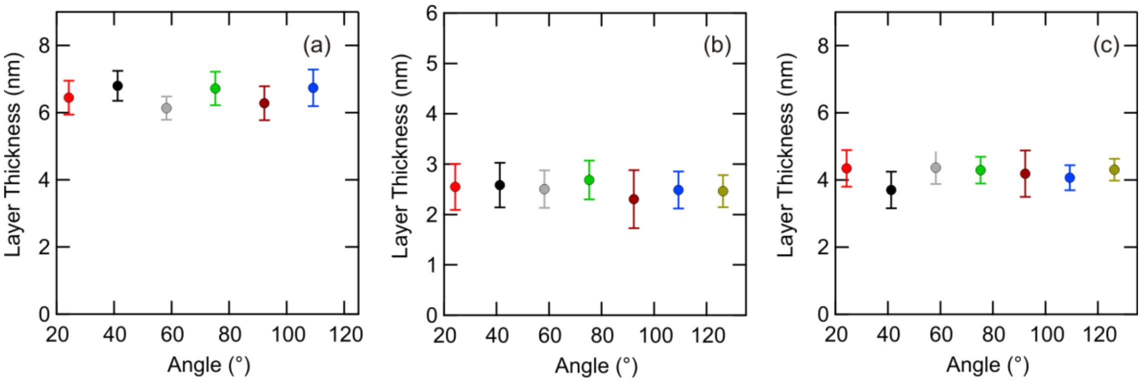

Figure S4. Measured layer thickness with multi-angle DLS at different scattering angles. The average of these numbers gives an accurate estimate of the layer thickness. (a) SL/LPEI of 250 kg/mol at an ionic strength of 0.1 M, (b) AL/PAA of 20 kg/mol at 10^{-4} M, and (c) AL/PSS of 6520 kg/mol at 0.3M.

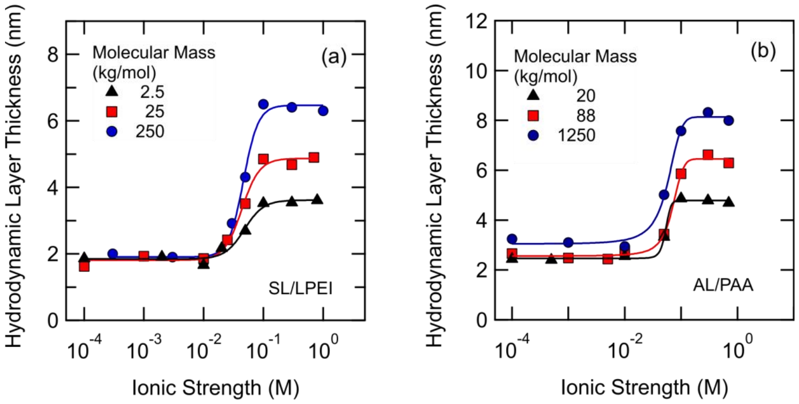

Figure S5. Hydrodynamic layer thickness of adsorbed polyelectrolytes as a function of ionic strength for different molecular masses. (a) SL/LPEI and (b) AL/PAA.