Electronic Supplementary Material (ESI) for Soft Matter

Support Information

Protein Immobilization and Separation by Anionic/Cationic Spherical Polyelectrolyte Brushes Based on Charge Anisotropy

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Dissociaton Behavior of SPB

Potentiometric titrations were used to determine dissociation degree α (Figure SI-1) and apparent dissociation constant pK_a (Figure SI-2) as a function of pH. Dissociation degree α was deduced from the blank-corrected titration of SPB_{PAA} samples with 0.1 M HCl using the procedure for poly(acrylic acid) to give the relationship between α and pH shown in Figure SI-1. The dissociation of SPB_{PAA} was increased with increasing pH. SPB_{PAA} reached full dissociation at pH 9. While for blank-corrected titration of SPB_{PAEMH} samples with 0.1 M NaOH using the procedure for poly(2-aminoethyl methacrylate hydrochloride) to give the relationship between α and pH shown in Figure SI-3. The dissociation of SPB_{PAEMH} was increased with decreasing pH. SPB_{PAEMH} reached full dissociation at pH 4.

pK_a can be deduced from

$$\mathrm{p}K_a = \mathrm{pH} + \log\frac{1-\alpha}{\alpha}$$

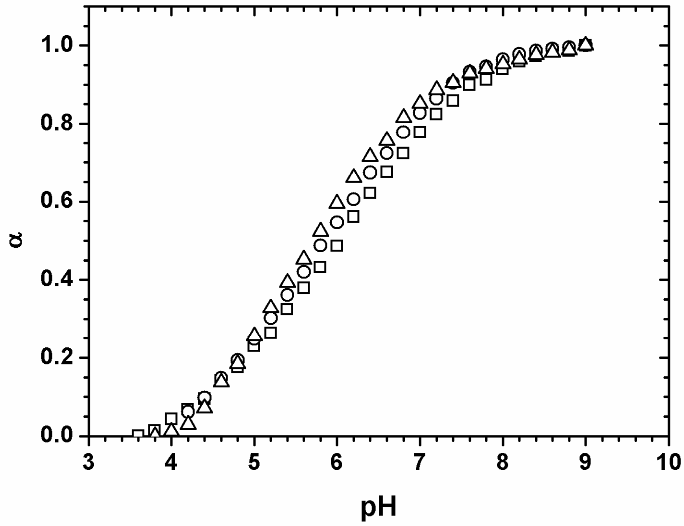

Figure SI-1. Dissociation degree α versus pH curves for SPB_{PAA} at various ionic strengths by potentiometric titrations. Symbols denote: (**Δ**) 100 mM, (○) 50 mM, and (□) 10 mM.

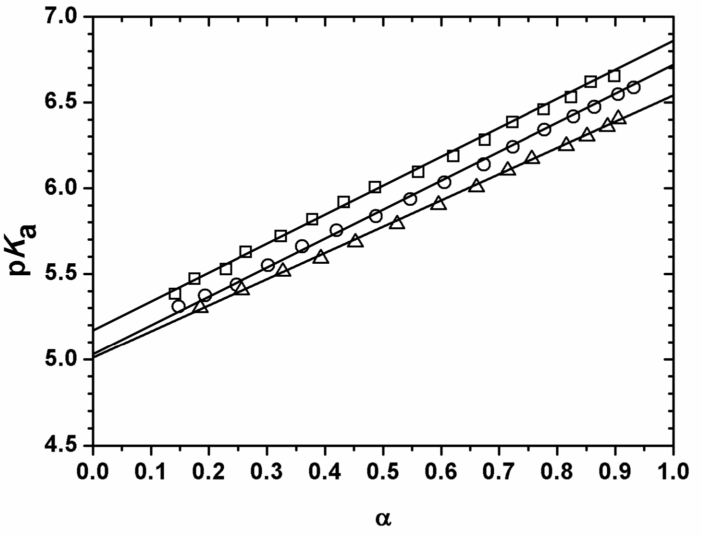

Figure SI-2. Apparent dissociation constant pK_a versus dissociation degree α curves for SPB_{PAA} at various ionic strengths by potentiometric titrations. Symbols denote: (**Δ**) 100 mM, (○) 50 mM, and (□) 10 mM.

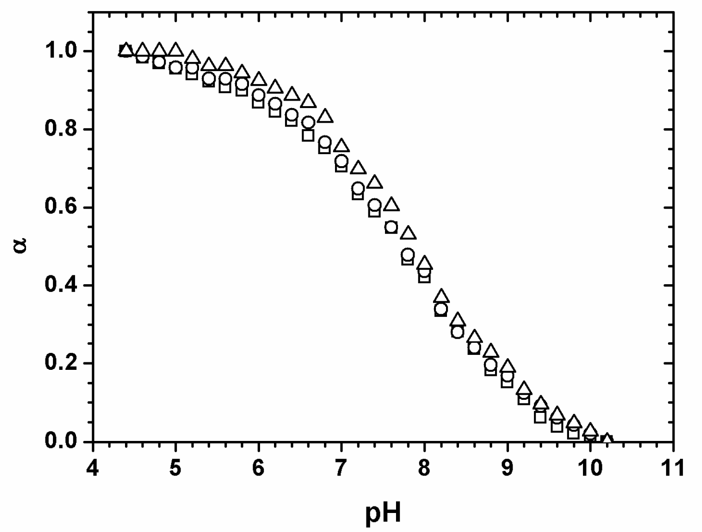

Figure SI-3. Dissociation degree α versus pH curves for SPB_{PAEMH} at various ionic strengths by potentiometric titrations. Symbols denote: (**Δ**) 100 mM, (○) 50 mM, and (□) 10 mM.

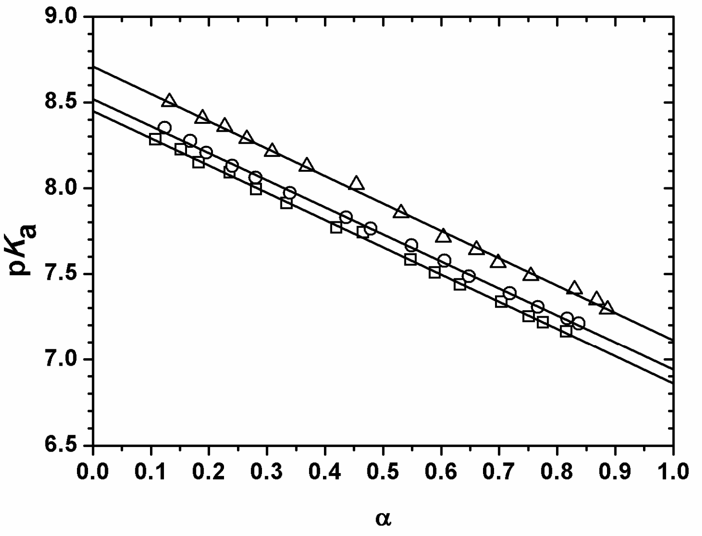

Figure SI-4. Apparent dissociation constant pK_a versus dissociation degree α curves for SPB_{PAEMH} at various ionic strengths by potentiometric titrations. Symbols denote: (**Δ**) 100 mM, (○) 50 mM, and (□) 10 mM.

Determination and Calculation of SPB Grafting Density

With the molecular weight M_n obtained by GPC and the amount of PAA/PAEMH on the surface being know, the number of chains per particle and hence the grafting density σ may be calculated (as follow). Selecting SPB_{PAA} as the model particles, we hypothesize the diameter of PS core as D (nm), molecular weight of PAA determined by GPC as M_{PAA} (g/mol), the total weight of PS core as m_{PS} (g), and the total weight of PAA as m_{PAA} (g).

The contour length L_c is calculated by

$$L_c = 0.2516 \times \frac{M_n}{M_{AA}} \text{ (nm)}$$

Where M_n is the molecular weight of PAA determined by GPC, M_{AA} is the molecular weight of AA (72 g/mol), the length of AA monomer is estimated to 0.2516 nm.

The volume V'_{PS} of a single PS core can be calculated by

$$V'_{PS} = \frac{4\pi}{3} \cdot \left(\frac{D}{2}\right)^3 \ (m^3)$$

The superficial area S'_{PS} of a single PS core can be calculated by

$$S'_{PS} = 4\pi \cdot \left(\frac{D}{2}\right)^2$$

The weight m'_{PS} of a single PS core can be calculated by

$$m'_{PS} = \rho \cdot V'_{PS} = 1.05 \times 10^3 \times V'_{PS}$$

Where ρ is density of PS.

The total amount N_{PS} of PS core can be calculated by

$$N_{PS} = \frac{m_{PS}}{m'_{PS}} = \frac{m_{PS}}{1.05 \times 10^6 \times V'_{PS}}$$

The total amount N_{PAA} of PAA chains can be calculated by

$$N_{PAA} = N_A \cdot \frac{m_{PAA}}{M_{PAA}} = 6.02 \times 10^{23} \times \frac{m_{PAA}}{M_{PAA}}$$

Where N_A is Avogadro's constant.

The amount N'_{PAA} of PAA chains grafted on a single PS core can be calculated by

$$N'_{PAA} = \frac{N_{PAA}}{N_{PS}} = \frac{1.05 \times 10^{29} \cdot m_{PAA} \cdot \pi \cdot D^3}{M_{PAA} \cdot m_{PS}} = \sigma \cdot S'_{PS}$$

The grafting density σ of chains can be deduced from

$$\sigma = \frac{1}{S'_{PAA}} = \frac{N'_{PAA}}{S'_{PS}} = \frac{1.05 \times 10^{29} \cdot m_{PAA} \cdot D}{M_{PAA} \cdot m_{PS}} (m^{-2})$$

For SPB_{PAA} system:

$$\sigma = \frac{1.0535 \times 10^{29} \cdot m_{PAA} \cdot D}{M_{PAA} \cdot m_{PS}} = \frac{1.05 \times 10^{29} \cdot 0.1 \cdot 80}{15600 \cdot 1} = 0.054 \ \approx 0.05 (nm^{-2})$$

$$N'_{PAA} = \sigma \cdot S'_{PS} = \sigma \cdot \pi \cdot D^2 = 0.054 \cdot 3.14 \cdot 80^2 = 1085 \approx 1100$$

For SPB_{PAEMH} system:

$$\sigma = \frac{1.05 \times 10^{29} \cdot m_{PAEMH} \cdot D}{M_{PAEMH} \cdot m_{PS}} = \frac{1.05 \times 10^{29} \cdot 0.098 \cdot 78}{15500 \cdot 1} = 0.052 \ \approx 0.05 (nm^{-2})$$

$$N'_{PAEMH} = \sigma \cdot S'_{PS} = \sigma \cdot \pi \cdot D^2 = 0.052 \cdot 3.14 \cdot 78^2 = 993 \approx 1000$$