Support Information

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

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**Dissociation Behavior of SPB**

Potentiometric titrations were used to determine dissociation degree $\alpha$ (Figure SI-1) and apparent dissociation constant $pK_a$ (Figure SI-2) as a function of pH. Dissociation degree $\alpha$ 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 $\alpha$ 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 $\alpha$ 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

$$pK_a = \text{pH} + \log \frac{1-\alpha}{\alpha}$$

**Figure SI-1.** Dissociation degree $\alpha$ versus pH curves for SPB$_{PAA}$ at various ionic strengths by potentiometric titrations. Symbols denote: (△) 100 mM, (○) 50 mM, and (□) 10 mM.
**Figure SI-2.** Apparent dissociation constant $pK_a$ versus dissociation degree $\alpha$ 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 $\alpha$ 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 $\alpha$ curves for SPB$_{PAEMH}$ at various ionic strengths by potentiometric titrations. Symbols denote: (△) 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 known, the number of chains per particle and hence the grafting density $\sigma$ 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
$$V'_{PS} = \frac{4\pi}{3} \cdot \left(\frac{D}{2}\right)^3 \text{ (m}^3\text{)}$$

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 $\rho$ 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 $\sigma$ of chains can be deduced from

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

For SPB$_{PAA}$ system:

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

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

For SPB$_{PAEMH}$ system:

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

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