

Internal Structure & Charge Compensation of Polyelectrolyte Multilayers

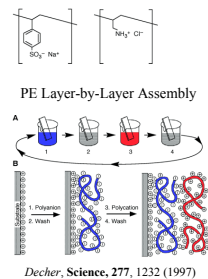
Qiang (David) Wang

Department of Chemical and Biological Engineering, Colorado State University



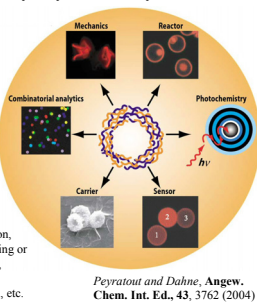
1. Introduction

Polyelectrolytes (PE) are charged polymers



Why Layer-by-Layer Assembly?

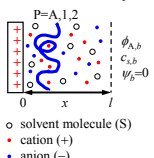
- Simple, fast, cheap
- Self-healing
- Versatile
- Synthetic PE: conducting & light-emitting polymers, reactive polymers, polymeric complexes, polymeric dyes, ...
- Natural PE: DNA, RNA, proteins, viruses, ...
- Charged nano-particles and platelets, ...
- Potential Applications: surface modification, enzyme immobilization, gene transfection, separation membranes, conducting or light-emitting devices, batteries, optical data storage, controlled particle and catalyst preparation, etc.



Peyratout and Dahne, Angew. Chem. Int. Ed., 43, 3762 (2004)

2. Theoretical Formalism

Model System for PE Adsorption



- Monovalent, 1D system
- Ions from salt = counterions from PE and substrate
- Ions have no volume
- Polymer segments have the same density ρ_A as solvent molecules
- All polymer segments have the same statistical segment length a

Parameters in the model:

- σ_{SF} substrate charge density;
- v_p charge valency of PE;
- p_p degree of ionization of PE;
- χ_{PP} Flory-Huggins parameter between polymer segments;
- χ_{PS} Flory-Huggins parameter between polymers and solvent;
- $\phi_{A,B}$ bulk polymer concentration;
- $c_{b,b}$ bulk salt concentration;
- $\epsilon=80$ dielectric constant.

Quantities to be solved:

- $\psi(x)$ electrostatic potential (in units of $k_B T / e$);
- $\phi_p(x)$ polymer segmental density.

Sequential Layer-by-Layer (LbL) Assembly

Adsorption of A from its bulk solution, in the presence of 1 & 2 of which the density profiles are fixed; A=1 for odd layer i and 2 for even i . A washing step follows each deposition and slightly modifies $\phi_{A,i}(x)$ to $\phi_{A,i}^0(x)$. $\phi_1(x)$ and $\phi_2(x)$ to be used in the $(i+1)^{th}$ deposition are then accumulated from $\phi_{A,i}^0(x)$ for all $i \leq i$.

$$\text{PB Eq. } \frac{\epsilon}{N} \frac{d^2 \psi}{dx^2} = \sum \phi_i(x) \frac{d g_i(x)}{d \psi(x)} + v_p \rho_p \phi_{p,i} e^{v_p \psi(x)} + 2c_{b,b} \sinh \psi(x)$$

$$\text{GSDA } \Rightarrow \frac{d^2 \sqrt{\phi_p}}{dx^2} = [\omega_p(x) - N g_p(x) - \omega_p] \sqrt{\phi_p(x)}$$

$$\omega_p(x) = N \left[\sum (\chi_{pA} - \chi_{pS}) \phi_A(x) + \chi_{pS} \left[1 - \sum \phi_A(x) \right] \right] - \ln \left[1 - \sum \phi_A(x) \right]$$

$$\omega_p = \omega_p(x=l)$$

$$\text{@ } x=0: \frac{d \sqrt{\phi_p}}{dx} = 0, \frac{d \psi}{dx} = -\frac{\sqrt{N}}{\epsilon} \sigma_{SF}; \text{ @ } x=l: \frac{d \sqrt{\phi_p}}{dx} = 0, \frac{d \psi}{dx} = 0.$$

All lengths are normalized by $\sqrt{N}/6a$.

Equilibrium Adsorption of PE Mixtures (1+2/S)

Adsorption of PE mixtures (1 & 2) from a bulk solution.

$$\frac{\epsilon}{N} \frac{d^2 \psi}{dx^2} = \sum \left[\phi_i(x) \frac{d g_i(x)}{d \psi(x)} + v_p \rho_p \phi_{p,i} e^{v_p \psi(x)} \right] + 2c_{b,b} \sinh \psi(x)$$

$$\frac{d^2 \sqrt{\phi_p}}{dx^2} = [\omega_p(x) - N g_p(x) - \omega_p] \sqrt{\phi_p(x)}$$

$$\frac{d^2 \sqrt{\phi_2}}{dx^2} = [\omega_2(x) - N g_2(x) - \omega_2] \sqrt{\phi_2(x)}$$

$$\omega_p(x) = N \left[\sum (\chi_{p1} - \chi_{pS}) \phi_1(x) + \chi_{pS} \left[1 - \sum \phi_i(x) \right] \right] - \ln \left[1 - \sum \phi_i(x) \right]$$

$$\omega_2(x) = N \left[\sum (\chi_{21} - \chi_{2S}) \phi_1(x) + \chi_{2S} \left[1 - \sum \phi_i(x) \right] \right] - \ln \left[1 - \sum \phi_i(x) \right]$$

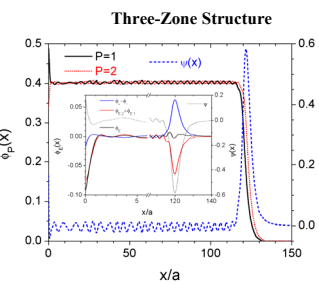
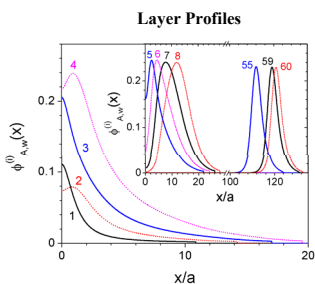
$$\text{@ } x=0: \frac{d \sqrt{\phi_p}}{dx} = 0, \frac{d \psi}{dx} = -\frac{\sqrt{N}}{\epsilon} \sigma_{SF}; \text{ @ } x=l: \frac{d \sqrt{\phi_p}}{dx} = 0, \frac{d \psi}{dx} = 0.$$

$g_i(x) = \begin{cases} -v_p \rho_p \psi(x) & \text{for smeared charge distribution (strongly dissociating PE)} \\ \ln \left[1 - p_i + p_i e^{-v_p \psi(x)} \right] & \text{for annealed charge distribution (weakly dissociating PE)} \end{cases}$

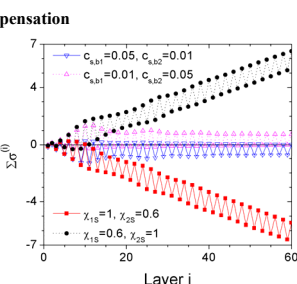
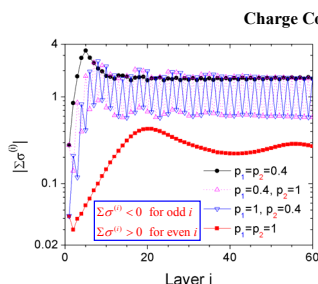
3. Multilayers of Strongly Dissociating PE

Default values: $\sigma_{SF}=0.1$ (2.61 mC/m²), $v_1=-1, v_2=1, p_p=0.5, \chi_{12}=0, \chi_{1S}=0.05$ (0.667 M), $\phi_{A,B}=7.5 \times 10^{-4}$ (10 mM); numbers in parentheses are based on $a=0.5$ nm, $\rho_0=a^{-3}$, and $T=300$ K.

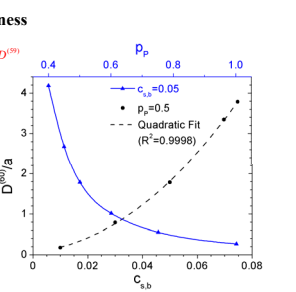
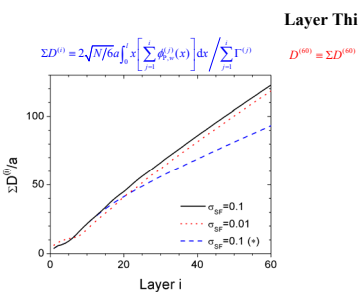
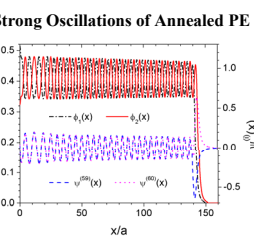
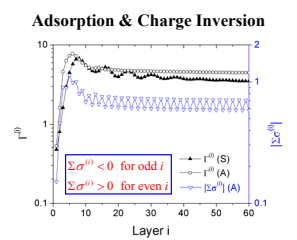
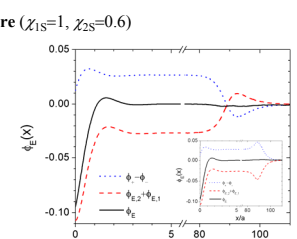
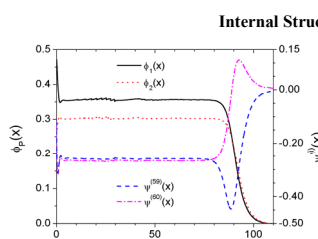
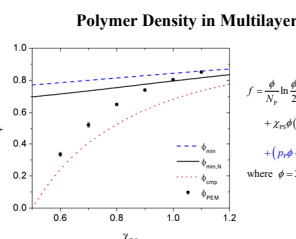
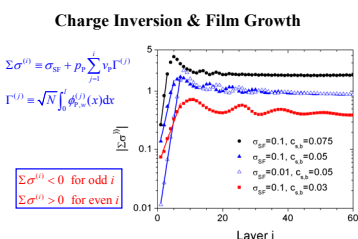
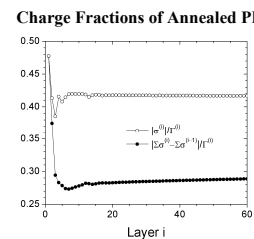
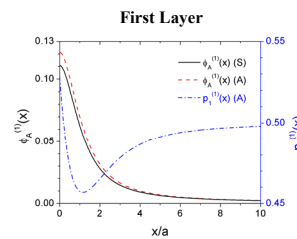
3.1. Symmetric PE



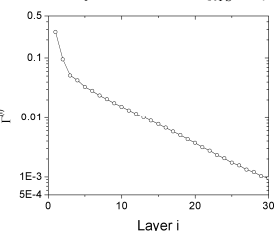
3.2. Asymmetric PE



4. Multilayers of Weakly Dissociating PE



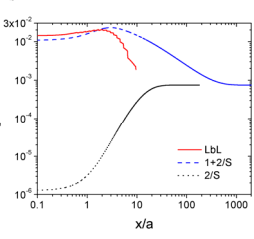
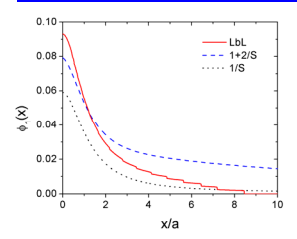
No Multilayer in θ -Solvent ($\chi_{PS}=0.5$)



6. Summary

- Using a continuum self-consistent field theory, we have modeled the sequential LbL assembly of flexible PE on flat substrates as a series of kinetically trapped states. Up to 60 depositions of oppositely charged PE (1 & 2) are performed, each followed by a washing step.
- We have investigated in detail the effects of degree of ionization and charge distribution of PE, bulk salt concentrations, solvent qualities for 1 and 2, and their incompatibility on the internal structure and charge compensation of multilayer.
- Our modeling captures many qualitative features of LbL assembly observed in experiments. Further work to refine the modeling and to compare with experimental results is undergoing.

5. Non-Equilibrium Effects ($\chi_{PS}=0.5$)



• Q. Wang, J. Phys. Chem. B, 110, 5825 (2006)
 • Q. Wang, Macromolecules, 38, 8911 (2005).
 • Q. Wang, T. Yaniguchi, and G. H. Fredrickson, J. Phys. Chem. B, 108, 6733 (2004); 109, 9855 (2005).

