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**Polyelectrolyte - Polyelectrolyte Complexes Based on  
Polymer Brushes**

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# 1 Introduction

## 1.1 Polyelectrolyte

### 1.1.1 General Introduction

Polyelectrolytes (PELs) are polymers that carry covalently bound anionic or cationic groups. Due to the strong charging most polyelectrolyte molecules are water soluble. Low-molecular counterions secure the electroneutrality of the system[1-3]. Electrostatic interactions induced by those ions are important in chemistry and biology as well. In biochemistry, for example, interactions between macromolecules often involve charged macromolecules such as proteins and nucleic acids. According to the type of charges, polyelectrolytes can be classified as anionic polyelectrolytes, cationic polyelectrolytes and polyampholytes, a special case of polyelectrolytes carrying both anionic and cationic groups. Figure 1.1 presents examples of these three types of polyelectrolytes.

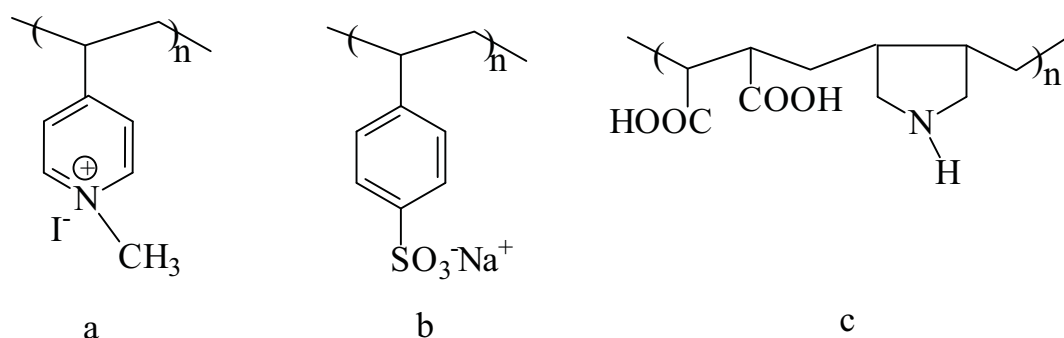


Figure 1.1 Examples of chemical structures of polyelectrolytes (a) cationic PEL poly(4-vinyl-N-methylpyridinium iodide) (MePVP), (b) anionic PEL poly(styrene sulfonate sodium salt) (PSSNa) and (c) amphiphilic poly(maleic acid-co-diallylamine) (PMAcDAA).

Another classification is the separation of PEL into strong and weak polyelectrolytes. Strong polyelectrolytes are completely dissociated in aqueous solutions over the entire pH range from 0 to 14. More precisely, the number and location of charges on the polymer chain is fixed and independent of the medium around the polymer chains. Poly(styrene sulfonate sodium salt) (PSSNa) and poly(4-vinyl-N-methylpyridinium iodide) (MePVP) are strong polyelectrolytes. In weak polyelectrolytes, mostly polyacids or polybases, the position and number of charges along the polymer chain

strongly depend on the environment such as the concentration of added salt, the pH value of the medium, the polymer concentration and so on. The typical behavior of weak polyelectrolytes is similar to weak low molecular electrolytes. Figure 1.2 shows the association/dissociation equilibriums in aqueous solution for weak polyacids and polybases.

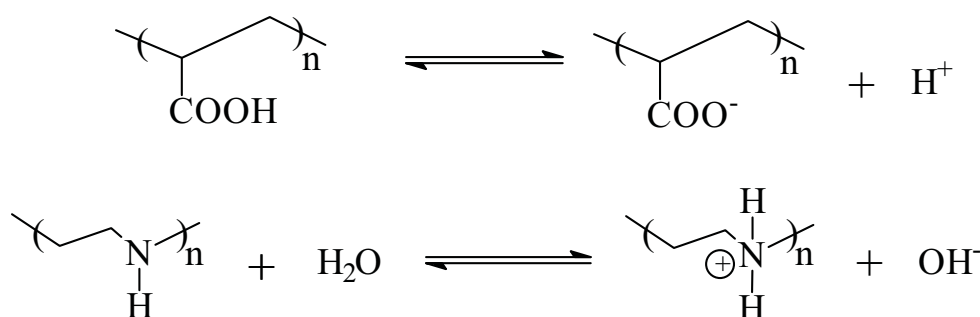


Figure 1.2 Dissociation equilibrium of the weak polyelectrolytes poly(acrylic acid) (PAA) and poly(ethylene imine) (PEI)

In contrast to neutral polymers, where excluded volume effects are the only important interaction, the long range Coulomb interactions in polyelectrolytes play an important role on the physical properties of polyelectrolytes. Therefore, the chemical nature of the solvent strongly affects the behavior of polyelectrolytes in solution. In a non-ionic solvent, the polyelectrolytes behaves similar to uncharged polymers because no dissociation occurs. In aqueous solutions, however, polyelectrolytes are dissociated into the polyions, i.e. one type of charge is located on the polymer chain; the other counterions are distributed around the polyions in the aqueous solution. Thus, the chain conformation of polyelectrolytes in aqueous solutions depends on the concentration of polymers and counterions as well.

However, the exact conformation of the polyelectrolyte chains in solution is not yet clear. For example, it is well-known that in semidilute salt-free (or very low salt concentration) systems polyelectrolyte solutions show an anomalous behavior that the reduced viscosity abruptly increases with decreasing polyelectrolyte concentration [1]. Based on rigid-rod chain model [4-5], it was interpreted that in dilute solutions the counterions escape from the polymer chains so that the polyelectrolyte chains are

extended and accordingly the viscosity of the solution increases. At higher polyelectrolyte concentration the self-screening effect of the polyelectrolytes results in a decrease of the repulsive force between the charges along the chain. Therefore, the polymer chains start to collapse and the size of the polymer chains become smaller and accordingly the viscosity of the solution increases. However Schmidt et al [6-9] argued that in this regime electrostatically interacting clusters between the macroions may be formed using worm-like chain model based on their light scattering experiments. If large amount of small electrolytes (i.e. salt) are added to the polyelectrolyte solution, the concentration of the counterions increases. This enhances the screening effect and thus a further decrease of the repulsive force between the charges along the chain is observed. Thus the polymer chain shrinks. At a certain salt concentration, the conformation and the properties of polyelectrolyte in aqueous solution are similar to that of neutral polymers because of the strong screening effect.

Besides the ionic strength and the concentration of the polyelectrolyte, the pH value of the medium strongly affects the conformation and the properties of weak polyelectrolytes in aqueous solutions, because the pH determines the degree of dissociation of weak ionic groups and thus the charge density of the polyelectrolytes.

### 1.1.2 Theoretical Description of Polyelectrolytes

Compared to the well-established theories describing neutral polymers in solution, the understanding of the conformation and properties of polyelectrolyte in solution is still rather poor. In this part, some theoretical background of polyelectrolytes in solution will be briefly introduced. Before that, a few basic parameters for the description of polyelectrolytes are introduced:

1. The Kuhn length  $l$  [10], which characterizes the stiffness of a given polymer chain, is defined as:

$$l = \langle R^2 \rangle / R_{\max} \quad (1-1)$$

where  $R_{\max} = N_0 a_0 = N_K l$  is the contour length or maximum length of the end-to-end vector,  $N_0$  is the number of monomer units per chain,  $a_0$  is monomer bond length and  $N_K$  is the number of sequences which have the length  $l$ ;

$$\langle \mathbf{R}^2 \rangle = \sigma N_0 a_0^2 = N_K l^2 \quad (1-2)$$

is the mean square displacement where  $\sigma$  is a parameter related to the hindrance in the internal motion of the chain segments. Stiffer chains have larger value of  $l$ , and for a perfectly stretched chain one obtains  $l = \mathbf{R}_{max}$ .

2. The persistence length  $q$  [11] is a characteristic length along the chain after which the directional correlation between the segments disappears. For very flexible chains,  $q$  is close to  $l$ , whereas for stiff chains  $q$  approaches infinity. For polyelectrolyte solutions,  $q$  becomes a function of the salt concentration. At high salt concentration, it is small and thus the chain is more flexible.
3. The Debye length  $\kappa^{-1}$  [12], which is a characteristic distance of screening, is defined as:

$$\kappa^{-1} = (\epsilon_0 \epsilon kT / 2e^2 I)^{1/2} \quad (1-3)$$

where  $\epsilon_0$  is the bulk dielectric constant,  $\epsilon$  is the dielectric function,  $kT$  is the thermal energy,  $e$  is the elementary charge and  $I$  is the ionic strength defined by

$$I = 1/2 \sum z_i^2 n_i, \quad (1-4)$$

$z_i$  is the valence of the  $i$ -th species and  $n_i$  is the concentration of the  $i$ -th species.

4. The Bjerrum length  $l_b$  [1] is the distance at which the Coulomb interaction between two unscreened elementary charges is equal to the thermal energy,

$$l_b = e^2 / (4\pi \epsilon_0 \epsilon kT) \quad (1-5).$$

### 1.1.2.1 Poisson-Boltzmann Equation and Debye-Hückel Theory

When a charged object is immersed into an electrolyte solution, it will attract counterions and repel co-ions. To describe the distribution of counterions in such a system, a usual approach is to apply the Poisson-Boltzmann (PB) equation [1],

$$\nabla^2 \langle \psi(r) \rangle = -\frac{e}{\epsilon_0 \epsilon} \sum_i z_i n_i \exp\left[-\frac{z_i e \langle \psi(r) \rangle}{kT}\right] \quad (1-6)$$

where  $\nabla^2$  is the Laplace operator and  $\psi(r)$  is the local electrostatic potential at the distance  $r$  from the charge center. This equation, which is based on a mean field potential, is of importance for the theoretical study of small electrolytes, and was later found valid for polyelectrolytes as well.