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Polyelectrolytes with Defined Molecular Architecture II

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Polyelectrolytes with Defined Molecular Architecture II

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Preface

Back in 1996 the German Science Foundation (Deutsche Forschungsgemeinschaft) has launched a nationwide research center on "Polyelectrolytes with defined molecular architecture—synthesis, function and theoretical description" (DFG-Schwerpunkt-Programm 1009: Polyelektrolyte mit definierter Molekülarchitektur—Synthese, Funktion und theoretische Beschreibung). On average 25 research groups from all over Germany and one French group were funded for a total of six years in order to attack and solve long standing problems in the field, to explore new ideas and to create new challenges.

The scientific achievements of this center of research are summarized in the present volumes of Advances in Polymer Science, volume 165 and 166. Financially supported by a "Coordination Funds" the interdisciplinary cooperation between the very many participating research groups was greatly enhanced and has consequently led to contributions involving an unusually large number of authors.

We hope that the center has brought German Polyelectrolyte Research into an international leading position and that it will constitute the nucleus for future activities in this field.

On behalf of all of my colleagues I wish to thank the "Deutsche Forschungsgemeinschaft" for financial and in particular Dr. K.-H. Schmidt and Dr. F.-D. Kuchta for administrative support and to the voluntary reviewers of the proposals, Prof. Blumen, Univ. Freiburg, Prof. Fuhrmann, Univ. Clausthal, Prof. Heitz, Univ. Marburg, Prof. Maret, Univ. Konstanz, Prof. Möller, Univ. Ulm, Dr. Winkler, BASF Ludwigshafen, Prof. Wulf, Univ. Düsseldorf, for their invaluable judgment and advice.

Mainz, February 2003 Manfred Schmidt

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Polyelectrolytes with Defined Molecular Architecture I

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Stiff-Chain Polyelectrolytes

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Abstract Rod-like polyelectrolytes represent ideal model systems for a comprehensive comparison of theory and experiment because their conformation is independent of the ionic strength in the system. Hence, the correlation of the counterions to the highly charged macroion can be studied without the interference of conformational effects. In this chapter the synthesis and the solution behavior of rigid, rod-like cationic polyelectrolytes having poly(*p*-phenylene) (PPP) backbones is reviewed. These polymers can be characterized precisely and possess degrees of polymerization of up to $P_n \approx 70$. The analysis of the uncharged precursor polymer demonstrated that the PPP backbone has a high persistence length (ca. 22 nm) and hence may be regarded in an excellent approximation as rod-like macromolecules. The solution properties of the PPP-polyelectrolytes were analyzed using electric birefringence, small-angle X-ray scattering (SAXS) and osmometry. Measurements of the electric birefringence demonstrate that these systems form molecularly disperse systems in aqueous solution. The dependence of electric birefringence on the concentration of added salt indicates that an increase of ionic strength leads to stronger binding of counterions to the polyion. Data obtained from osmometry and small-angle X-ray scattering can directly be compared to the prediction of the Poisson-Boltzmann theory and simulations of the restricted primitive model. Semi-quantitative agreement is achieved.

Keywords Rod-like polyelectrolytes · Poisson-Boltzmann theory · Osmotic coefficient · Electric birefringence · SAXS

Abbreviations and Symbols

Latin characters:

a	radius of macroion
f	scattering factor (SAXS)
f'	real part of scattering factor *f*
f''	imaginary part of scattering factor *f*
I(q)	scattering intensity of solution
I_0(q)	scattering intensity of isolated molecule
L	length of rod-like molecule
n(r)	radial distribution of counterions around rod
q	magnitude of scattering vector
R_M	Manning radius (Eq. (5))
R_0	cell radius
RPM	restricted primitive model
S(q)	structure factor describing interaction between solute molecules

Greek characters:

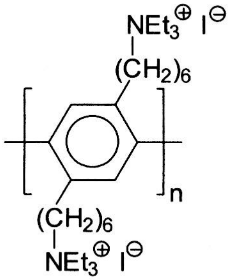
α	cosin of angle between long axis of rod-like molecule and scattering vector q
β	integration constant of cell model (Eq. (4))
ϕ	osmotic coefficient
ϕ_∞	osmotic coefficient in Manning limit
κ	screening constant
λ_B	Bjerrum length (Eq. (2))
Π	osmotic pressure
ξ	charge parameter (Eq. (1))

1
Introduction

The understanding of flexible polyelectrolytes in dilute solutions of low ionic strength still presents a considerable challenge in macromolecular science despite of many decades of research [1–5]. This is due to the long-range nature of the Coulombic forces between the charged macromolecules. In the case of flexible polyelectrolytes, a decrease of the ionic strength may lead to an expansion of the coils due to strong intramolecular forces as well as to stronger intermolecular electrostatic interactions. Conformationally rigid, rod-like polyelectrolytes, on the other hand, remain in their extended chain conformation regardless of the ionic strength of the system. Because conformative effects are ruled out here, only the Coulombic interactions determine the solution properties of these polymers.

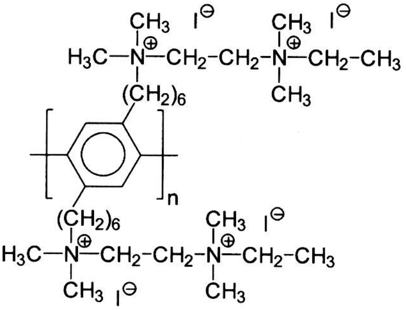
Based on these considerations, a number of studies have been performed using naturally occurring rod-like helical polyelectrolyte systems such as DNA or xanthane [6, 7]. However, at very low ionic strengths and at elevated temperatures, the helical conformation and thus the rod-like shape is lost. Moreover, systematic variation of the charge density, i.e., the number of ionic groups per unit length, is not possible using these biopolymers. Therefore, the development of well-defined synthetic rod-like polyelectrolytes is necessary to analyze quantitatively intermolecular interactions, the correlation of the counterions with the macroion, and structure formation in solution depending on ionic strength, temperature, and polyelectrolyte concentration.

The first syntheses of rod-like polyelectrolytes were published in the early eighties [8, 9]. They were based on poly(1,4-phenylenebenzobisoxazoles) and poly(1,4-phenylenebenzobisthiazoles). In the recent decade, we [10–14] and others [15,16] developed various efficient precursor routes to synthetic rod-like poly(*p*-phenylene) (PPP) polyelectrolytes which take advantage of both the concept of solubilizing side chains [17,18] and the efficient Pd-catalyzed aryl-aryl coupling reaction [19–21]. This progress was rendered possible mainly by (*i*) the high tolerance of the Pd-catalyzed polycondensation reactions toward functional groups in the starting materials and (*ii*) the outstanding thermal and chemical stability of the PPP backbone which allows transformation of the uncharged precursor PPPs into polyelectrolytes by a variety of organic reactions. By these precursor routes, high-molecular-weight carboxylated and sulfonated PPP polyelectrolytes with homogeneous constitution and known degrees of polymerization (P_n) have been prepared first. The polymers thus available combine exceptional hydrolytic, thermal and chemical stability with a high charge density of up to four ionic groups per *p*-phenylene repeating unit. Hence, these systems present nearly ideal model polyelectrolytes to be studied in solution.



Scheme 1 Chemical structure of polyelectrolyte **PPP-1**

Recently, the stiff-chain polyelectrolytes termed **PPP-1** (Scheme1) and **PPP-2** (Scheme2) have been the subject of a number of investigations that are reviewed in this chapter. The central question to be discussed here is the correlation of the counterions with the highly charged macroion. These correlations can be detected directly by experiments that probe the activity of the counterions and their spatial distribution around the macroion. Due to the cylindrical symmetry and the well-defined conformation these polyelectrolytes present the most simple system for which the correlation of the counterions to the macroion can be treated by analytical approaches. As a consequence, a comparison of theoretical predictions with experimental results obtained in solution will provide a stringent test of our current model of polyelectrolytes. Moreover, the results obtained on **PPP-1** and **PPP-2** allow a refined discussion of the concept of "counterion condensation" introduced more than thirty years ago by Manning and Oosawa [22, 23]. In particular, we can compare the predictions of the Poisson-Boltzmann mean-field theory applied to the cylindrical cell model and the results of Molecular dynamics (MD) simulations of the cell model obtained within the restricted primitive model (RPM) of electrolytes very accurately with experimental data. This allows an estimate when and in which frame this simple theory is applicable, and in which directions the theory needs to be improved.



Scheme 2 Chemical structure of polyelectrolyte **PPP-2**

The review is organized as follows: While Sect. 2 gives an overview over the relevant polyelectrolyte theory, Sect. 3 describes the synthetic routes that lead to the polyelectrolytes **PPP-1** and **PPP-2**. Then, in Sect. 4, the solution properties of **PPP-1** and **PPP-2** are discussed. Here the electric birefringence showed for the first time that the polyelectrolyte **PPP-1** forms molecularly disperse solutions. Moreover, transport properties in general can be compared to the results obtained by birefringence. The osmotic coefficient as well as small-angle X-ray scattering have been chosen as further experimental observables to be discussed because they give the most conclusive insight into the distribution of the counterions around the cylindrical macroion. Our conclusion will summarize the results obtained so far on stiff-chain polyelectrolytes and we briefly mention the direction of further research in Sect. 5.

2
Theory

In general, one of the characteristics of rod-like polyelectrolytes is the charge (Manning) parameter ξ which for monovalent counterions is defined through the ratio of the Bjerrum length λ_B to the contour distance per unit charge b [22–24]:

$$\xi = \frac{\lambda_B}{b} \tag{1}$$

with λ_B being defined through

$$\lambda_B = \frac{e^2}{4\pi\varepsilon_0 \varepsilon k_B T} \tag{2}$$

where e is the unit charge, ε the dielectric constant of the medium and ε_0, k_B and T have their usual meanings. In the following we only consider strongly charged polyelectrolytes with $\xi > 1$. To keep the treatment as simple as possible, we mostly consider salt-free solutions. Moreover, we consider the macroion to be infinitely stiff, *i.e.*, all effects due to flexibility or curvature of the macroion are not taken into account.

2.1
Poisson-Boltzmann Theory for the Cylindrical Cell Model

The cell model is a commonly used way of reducing the complicated many-body problem of a polyelectrolyte solution to an effective one-particle theory [24–30]. The idea depicted in Fig. 1 is to partition the solution into sub-volumes, each containing only a single macroion together with its counterions. Since each sub-volume is electrically neutral, the electric field will on average vanish on the cell surface. By virtue of this construction different sub-volumes are electrostatically decoupled to a first approximation. Hence, the partition function is factorized and the problem is reduced to a single-particle problem, namely the treatment of one sub-volume, called "cell". Its shape should reflect the symmetry of the polyelectrolyte. Reviews of the basic concepts can be found in [24–26].

For a solution of N rod-like polyelectrolytes with density $n=N/V$ and rod length L this gives a cylindrical cell with the cell radius R_0 being fixed by the condition $\pi R_0^2 LN/V=1$ (for the definition of these quantities, see Fig. 1). The theoretical treatment is much simpler after neglecting end effects at the cylinder caps. This is equivalent to a treatment of rods of infinite length after mapping to the correct density. The analytical description of this model proceeds within the Poisson-Boltzmann (PB) approximation: the ionic degrees of freedom are replaced by a cylindrical density $n(r)$ that describes the radial distribution of counterions around the macroion. The distribution $n(r)$ is locally proportional to the Boltzmann factor [24–30]. In doing so all correla-

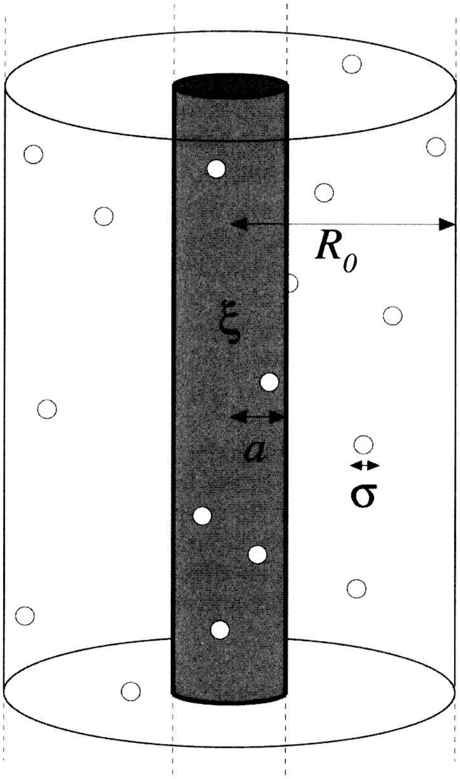


Fig. 1 Scheme of the PB cell model: The rod-like macroion with radius a is confined in a cell of radius R_0 together with its counterions. The charge density of the macroion is characterized by the charge parameter ξ (see Eq. (1)). See Sect. 2.1 for further explanation

tions among the counterions are neglected and the counterions behave as pointlike objects.

The PB-differential equation may be solved analytically for salt-free solution [27, 28], and $n(r)$ is given by [28]

$$\frac{n(r)}{n(R_o)} = 2\left\{\frac{\beta}{\kappa r \cos[\beta \ln(r/R_M)]}\right\}^2 \tag{3}$$

From the known parameters ξ, R_o, and the radius of the macroion a, the first integration constant β has to be obtained through a numerical solution of the transcendental equation

$$\arctan\left(\frac{\xi-1}{\beta}\right) + \arctan\left(\frac{1}{\beta}\right) - \beta \ln\left(\frac{R_o}{a}\right) = 0 \tag{4}$$