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Polyelectrolytes with Defined Molecular Architecture I

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Polyelectrolytes with Defined Molecular Architecture I

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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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New Polyelectrolyte Architectures

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Abstract This chapter reviews recent advances in the synthesis of polyelectrolytes. New results are presented for linear polymers with stiff and flexible backbones and with star-shaped and randomly branched structures. Block and graft copolymers containing both charged ionic and hydrophobic monomer units are also discussed. Homo- and block copolymers of carbobetaines complete the variation of molecular architecture. Synthetic approaches mainly use anionic, controlled radical, and macromonomer polymerization techniques, and the Suzuki reaction, to synthesize reactive precursors which are subsequently transformed into the final products. Results from physicochemical characterization of the new polymers are also mentioned.

Keywords Polyelectrolytes · Polycarbobetaines · Block copolymers · Graft copolymers · Reactive precursors

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1

Introduction

Polyelectrolytes play a major part in nature and find manifold application in industrial processes and daily life. Because they are both macromolecules and electrolytes they represent a unique class of polymer. The special properties of these polymers are determined by their electrochemical and macromolecular parameters and their chemical structure. Charge density and charge strength result in variable long-range electrostatic interactions, which are mainly responsible for the physicochemical properties of polyelectrolytes and their peculiarities in aqueous solution. These interactions and the formation of complexes driven by attractive Coulomb forces between charged macromolecules and oppositely charged macroions, surfactants, colloid particles, or solid surfaces are of central importance in the life sciences and in most technical applications. However, the typical properties of polyelectrolytes do not depend exclusively on the electrostatic forces. Differences between the flexibility of the polymer chain and, especially, a molecular architecture supporting the formation of H-bonds or hydrophobic interactions also play a major role in questions of scientific interest and practical importance.

Due to the comparatively high structural variability of polyelectrolytes an increasing number of applications with high practical relevance has been established, but up to now the fundamentals of many of these processes are not well understood. Also many topics in the life sciences, where polyelectrolytes are involved, bear similar open questions. To support any research in this field tailor-made polyelectrolytes with well defined molecular architecture and molecular parameters are required. Additionally, new polymers with adjusted properties may contribute to the optimization of known applications of polyelectrolytes and to the opening of new applications.

This chapter deals with the synthesis and properties of polyelectrolytes bearing a new molecular architecture. The following structures are included:

- rodlike poly(*p*-phenylene) polyelectrolytes
- ionically charged block copolymers and polycarbobetaines
- nonlinear polyelectrolyte topology
- amphipolar graft copolyelectrolytes.

2

Synthesis of Rodlike Poly(*p*-phenylene) Polyelectrolytes

To tailor-make polyelectrolytes for a specific aim, profound understanding of their structure–property relationships is required. This understanding, however, is not yet available, despite intense research during recent decades [1–3]. To fill the gaps in our knowledge, comprehensive consideration of:

1. the intramolecular electrostatic forces,
2. their intermolecular counterparts,
3. the osmotic effects, and
4. possible conformational changes occurring in aqueous polyelectrolyte solutions

is necessary. All these parameters have to be correlated with the chain's architecture and the composition of the respective solution. Unfortunately, such an analysis is very difficult for flexible polyelectrolytes. In these systems, both the intramolecular and intermolecular coulomb forces depend on the ionic strength. Hence the coil dimensions and the range of intermolecular electrostatic repulsion change simultaneously with changing ionic strength, but according to unknown rules. As a consequence, the different parameters contributing to the macroscopically observed polyelectrolyte behavior cannot be determined individually. Thus it is hardly possible to develop the required theoretical understanding just by analyzing flexible systems. Conformationally rigid, rodlike polyelectrolytes, on the other hand, are much easier to understand because they do not change their shape as a function of the ionic strength. Since conformational changes can be neglected here, all effects observed on changing the ionic strength can be attributed to electrostatics. Once this special aspect of polyelectrolyte behavior of rodlike systems is understood, it should be much easier to describe flexible polyelectrolytes also when conformational changes have to be taken into account. Therefore rodlike polyelectrolytes are considered to be ideal model systems for developing the required full understanding of polyelectrolytes in solution.

Rodlike polyelectrolytes have been known for a long time. Biological polymers such as DNA [4–8] and xanthane [9–12], or colloidal systems like the ferredoxin virus [13, 14] and the tobacco mosaic virus (TMV) [15, 16], may be the most prominent examples. However, there were also publications on some synthetic rods in the early 1990s when we started our program. Poly(*p*-phenylene-benzobisoxazoles) and poly(*p*-phenylene-benzobisthiazoles) may serve as examples [17–20]. Nevertheless, new rodlike polyelec-

trolytes were developed based on poly(*p*-phenylene) (PPP). This step seemed to be necessary because a system was required which is chemically very stable and rodlike under all the conditions its aqueous solution may be exposed to. PPP fulfils these requirements as it is:

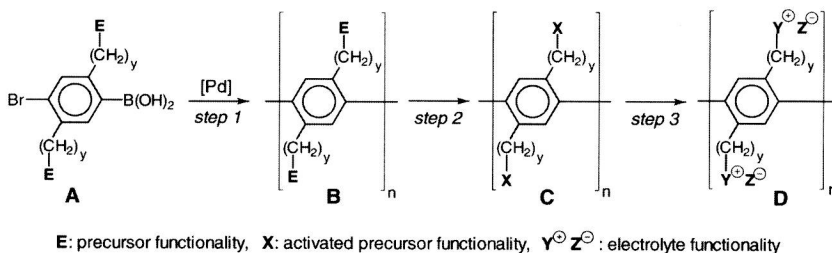
1. intrinsically rodlike (persistence length $l_p \approx 20$ nm [21]) due to its all-*para*-linked phenylene repeating units, and
2. perfectly inert against hydrolysis and all other reactions possible in aqueous media.

Moreover, PPP was selected because the powerful Pd-catalyzed Suzuki coupling reaction in combination with the concept of solubilizing side chains offers many advantages in synthesis.

2.1

PPP Polyelectrolytes via Ether Intermediates

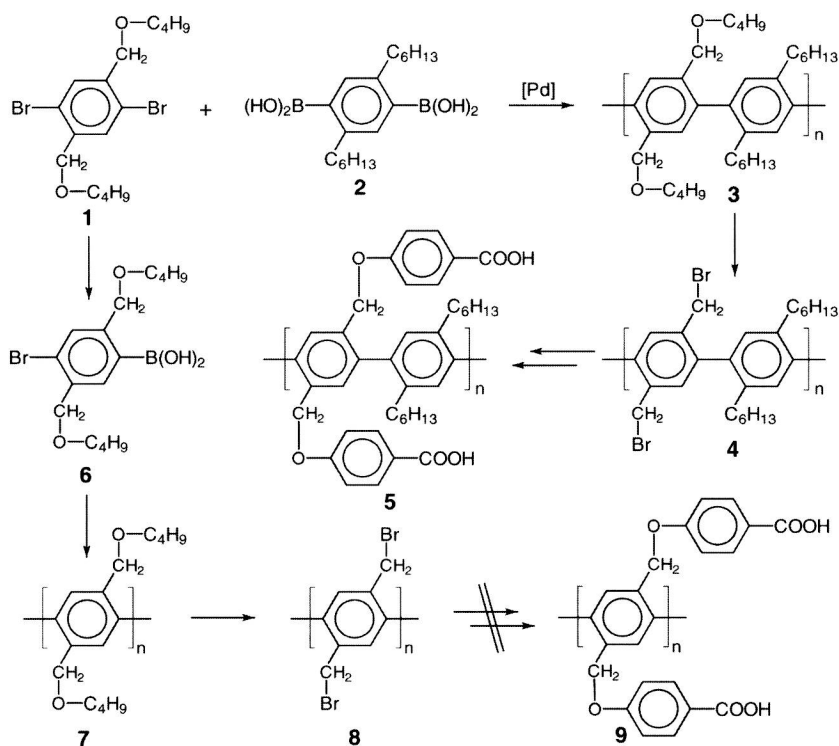
Due to the pronounced tolerance of the Suzuki reaction towards additional functional groups in the monomers, precursor strategies as well as so called direct routes can be applied for polyelectrolyte synthesis. However, the latter possibility, where the ionic functionalities are already present in the monomers, was rejected. The reason is too difficult determination of molecular information by means of ionic polymers. Therefore the decision was to apply precursor strategies (Scheme 1). Here, the Pd-catalyzed polycondensation process of monomers **A** leads to a non-ionic PPP precursor **B** which can be readily characterized. Then, using sufficiently efficient and selective macromolecular substitution reactions, precursor **B** can be transformed into well-defined PPP polyelectrolytes **D**, if appropriate via an activated intermediate **C**.



Scheme 1 General representation of precursor syntheses leading to PPP polyelectrolytes

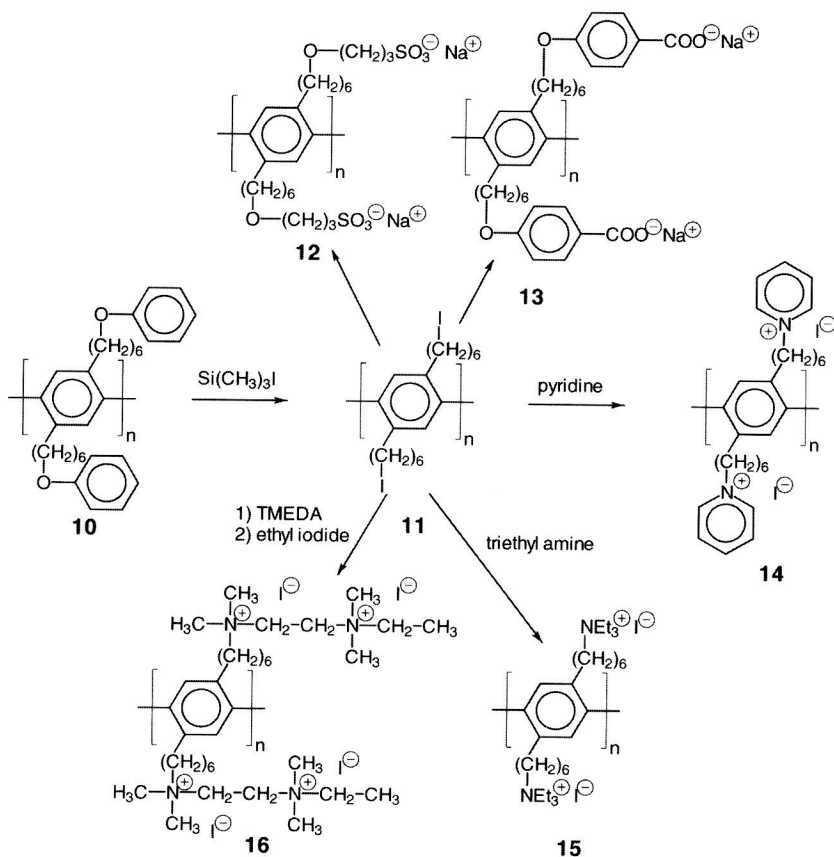
For most of the polymers, ether groups E were selected as precursor functionalities because they are inert under the conditions of the Pd-catalyzed polycondensation reaction but can be converted selectively and completely into reactive groups $-(CH_2)_y-X$ such as alkyl bromides or alkyl iodides that allow the final introduction of the ionic functionalities.

In a first sequence of experiments, butoxymethylene-substituted precursor PPPs **3** were prepared (Scheme 2) [22, 23]. The polycondensation of equimolar amounts of **1** and **2** leads to constitutionally homogeneous products **3** having values of $P_n \approx 60$. The lateral benzylalkyl ether groups were then cleaved quantitatively, leading to the nicely soluble bromomethylene-functionalized activated precursor **4** which was finally converted into, for example, the carboxylated PPP **5**. Unfortunately, this polymer proved to be insoluble in water or aqueous bases. It was reasonable to assume that this is due to the relatively low density of charged groups along the chains, and also to the apolar alkyl side chains attached to every second phenylene moiety causing intermolecular hydrophobic interactions. An attempt was therefore made to make the corresponding homopolymer **7** available. Under very specific conditions it was possible to obtain the required AB type monomer **6**. After successful polycondensation, however, it was no longer possible to transfer precursor PPP **7** into polyelectrolyte **9**. Due to the lack of solubilizing side chains in the activated intermediate **8**, this material was insoluble and could not be converted into a constitutionally homogeneous product.



Scheme 2 Precursor synthesis of carboxylated PPP polyelectrolytes

This failure forced a change in the synthetic strategy. The two functions of the two different lateral substituents of **3**, i.e. solubilizing the polymer (done by the C_6H_{13} groups) and making possible final introduction of electrolyte functionalities (done by the $CH_2-O-C_4H_9$ groups), were combined in one single type of side chain [24]. This was realized by introducing a larger spacer group between the PPP main chain and the ether functionality. Hexamethylene spacers were sufficient to solubilize the rodlike macromolecules even in the activated state. Due to the longer spacers, however, the ether functionality was no longer in a benzylic position. To nevertheless maintain the selectivity of the ether cleavage process, which must guarantee the formation of 100% halogenalkyl groups and 0% hydroxy groups in the activated polymer—to prevent crosslinking—alkyl phenyl ethers were used as the precursor's functionality.



Scheme 3 PPP polyelectrolytes available from precursor **10**

The synthesis of the required monomer and of precursor polymer 10 proved to be time-consuming but not difficult. The subsequent ether cleavage 10→11 using $(\text{H}_3\text{C})_3\text{Si-I}$ in CCl_4 occurs very homogeneously, and also completely, if strictly water-free conditions are kept (Scheme 3). Rather surprisingly, however, all anionic polyelectrolytes prepared from 11, such as 12 and 13, proved to be insoluble in water or aqueous bases, despite their charge density being twice as high as in polymers like 5 [24]. In contrast to this, cationic polyelectrolytes such as 14–16, easily available via conversion of 11 with a tertiary amine, proved to be molecular-dispersal soluble not only in polar organic solvents but even in pure water [25, 26]. It is believed that this is because the apolar interior of these cylinder-like polyelectrolytes is covered by a sufficiently “dense” shell of hydrophilic cationic groups which prevent intermolecular hydrophobic interactions. In the case of anionic polyelectrolytes such as 12 and 13, on the other hand, the density of the charged groups in the cylinder shell is not high enough due to the longer spacers between the main chain and the electrolyte functionality. Therefore, they are insoluble in water.

Using polyelectrolytes 14–16, a huge number of studies have been performed by means of, for example, viscosimetry, membrane osmometry, small-angle X-ray scattering (SAXS), and electric birefringence. Because selected results are described in the chapter “Stiff-Chain Polyelectrolytes”, we only report here on the key results of viscosity experiments. Salt-free aqueous solutions of the above rodlike polyelectrolytes always display a polyelectrolyte effect which is much more pronounced than that of flexible-chain analogs of comparable chain length. Moreover, the maximum value of $\eta_{\text{sp}}/c_{\text{p}}$ always appears at values of c_{p} approx., one order of magnitude lower than with flexible systems. When salt is added to these solutions, the maximum becomes weaker and shifts towards higher values of c_{p} . Finally, at salt concentrations higher than $c_{\text{s}}=2\times 10^{-4}\text{ mol L}^{-1}$, a linear Huggins plot is obtained which gives an intrinsic viscosity $[\eta]$ nicely corresponding to that of the precursor polymer used for the preparation of the respective polyelectrolyte.

SAXS and osmometry, on the other hand, allow the conclusion that the Poisson–Boltzmann cell model gives a quite realistic description of counterion condensation in rodlike macromolecules. However, prior to a final evaluation, a more profound analysis is required. Here, it will be of particular importance to consider polyelectrolytes with substantially lower charge densities also. Unfortunately, but in accordance with expectations, all polyelectrolytes containing phenylene moieties without charged side groups, such as 20–22, proved to be insoluble in water (Scheme 4).