

Water-soluble cationic poly-*p*-phenylene polyelectrolytes with an exceptionally high charge density

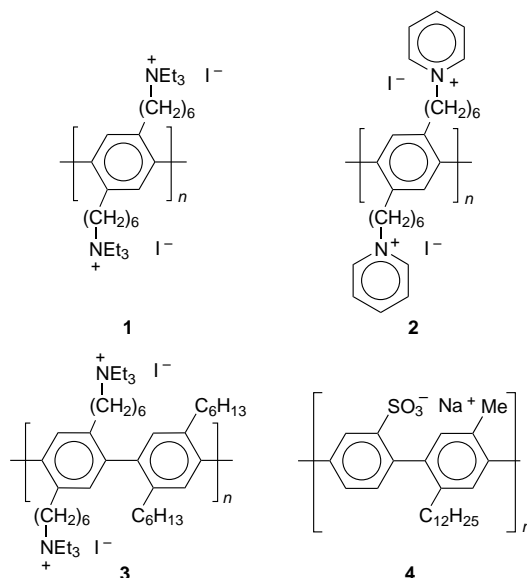
Matthias Wittemann and Matthias Rehahn*†

Polymer-Institut, Universität Karlsruhe, Kaiserstrasse 12, D-76128 Karlsruhe, Germany

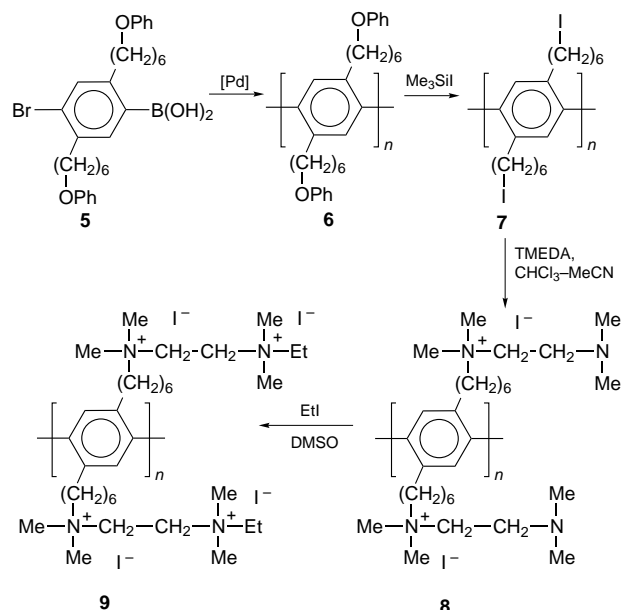
Rod-like poly-*p*-phenylene polyelectrolytes bearing four quaternized tetraalkylammonium functionalities per *p*-phenylene repeating unit are easily available *via* conversion of poly[2,5-di(6-iodohexyl)-1,4-phenylenes] with a large excess of TMEDA followed by the quaternization of the second TMEDA amino group with EtI.

Understanding polyelectrolyte behaviour in dilute solutions of low ionic strengths is an important objective in macromolecular science.^{1–3} Despite much effort, however, a conclusive theoretical description of experimentally observed phenomena such as the polyelectrolyte effect is unavailable so far. One of the reasons for this is the fact that, in the case of the commonly investigated flexible-chain polyelectrolytes, various effects influence the measured quantities simultaneously whose contributions are difficult to separate properly. When, for example, measurements are carried out as a function of ionic strength, the radii of gyration of the polyelectrolytes change over the course of the experiment because the intramolecular Coulomb interactions change. However, not only do the radii of gyration increase with decreasing ionic strength but so also does the distance up to which the charged macromolecules repulse one another intermolecularly. For a more reliable interpretation of the obtained data it is therefore advantageous to additionally study polyelectrolytes which cannot change their shape. Because conformational and excluded volume effects are ruled out here, only the intermolecular Coulomb interactions will determine the solution properties. Based on these considerations, numerous studies have been performed using naturally occurring rod-like polyelectrolytes such as DNA.⁴ At very low ionic strengths and at elevated temperatures, however, these systems fail because they lose their rod-like shape. Moreover, variation of the charge density, *i.e.* the number of ionic groups per unit length, is not possible with these biopolymers. To overcome the latter limitations, efficient routes to synthetic rod-like polyelectrolytes such as the poly(*p*-phenylene) (PPP) derivatives **1–3**⁵ and **4**⁶ have been developed which take advantage of both the concept of solubilizing side chains⁷ and the efficient Pd-catalyzed aryl–aryl coupling reaction.^{8–10} The polymers thus available combine exceptional hydrolytic, thermal and chemical stability with a high charge density of up to two ionic groups per *p*-phenylene repeating unit.

Nevertheless, further PPP polyelectrolytes having an even higher charge density would be important as well. We have now developed an efficient two-step quaternization route leading to PPP polyelectrolytes **9** with as many as four tetraalkylammonium groups per *p*-phenylene repeating unit and thus every 4.5 Å. Poly[2,5-di(6-iodohexyl)-1,4-phenylene] precursor PPP **7**, which is readily available *via* Pd-catalyzed polycondensation of 4-bromophenylboronic acid derivative **5** followed by an ether cleavage reaction, is first reacted with a 400-fold molar excess of TMEDA (Scheme 1). The large excess of TMEDA is essential in order to suppress quaternization of both TMEDA nitrogen atoms in this first step, which would lead to structural irregularities and crosslinks. Representative samples of the reaction mixture were analyzed at regular intervals using NMR spectroscopy to determine the reaction time required for a quantitative conversion. When the reaction was found to be



complete, solvents and the excess of TMEDA were removed by distillation. The residue was redissolved in water, and the last traces of organic solvents and TMEDA were carefully separated off by ultrafiltration using distilled water. Finally, PPP **8** was freeze-dried from the resulting aqueous solution. In order to quaternize the second TMEDA amino groups of **8**, the brownish, foamy materials thus obtained were redissolved in DMSO and heated in the presence of a slight excess of EtI. Here also the progress of the conversion was monitored using NMR spectroscopy. A prolonged reaction time and forcing conditions



Scheme 1

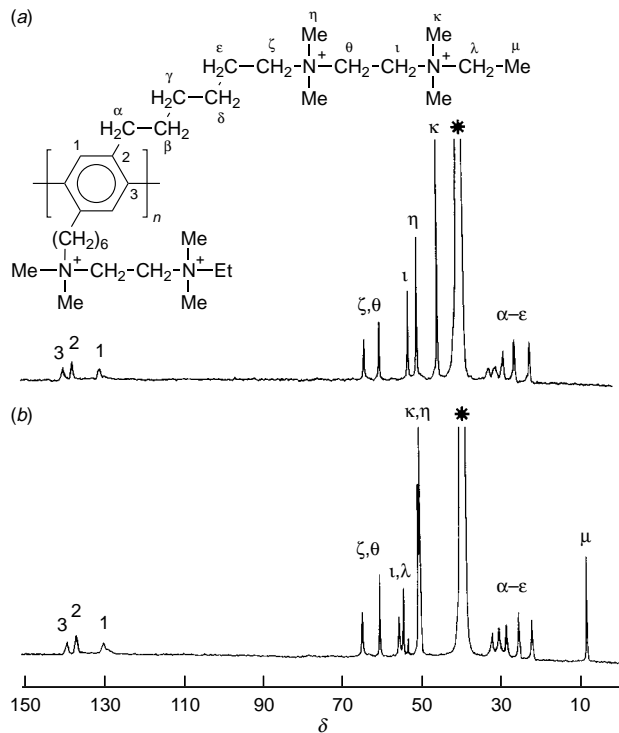


Fig. 1 100 MHz ^{13}C NMR spectra of (a) polymer **8** and (b) polymer **9** recorded in $[\text{2H}_6]\text{DMSO}$ (*) at room temperature. The signal assignment is based on the numbering given for polymer **9**.

were found to be necessary here to achieve complete conversion. Nevertheless, after heating the solutions to 60 °C for two days, complete conversion was reached. The obtained slurries were first diluted with DMSO to redissolve the formed precipitate, and a 20-fold excess of water was then added. Subsequently, the resulting polyelectrolyte solutions were purified by ultrafiltration and freeze-dried to give dark brown, foamy solids **9**.

As both the intermediate **8** and the doubly quaternized polyelectrolyte **9** readily dissolve not only in pure water but also in polar organic solvents, their homogeneous molecular constitution could be proved using NMR spectroscopy. Fig. 1 displays the ^{13}C NMR spectra of polyelectrolytes **8** and **9** together with the full signal assignment, which is based on tabulated increments and model compounds.

As is evident from these spectra, all observed absorptions are in full agreement with the expected polymer structures, and no absorptions can be detected which would point towards the formation of structural irregularities. However, not only is the homogeneous constitution of the polyelectrolytes of importance for the planned investigations, but so also is their molar masses. We therefore determined the degrees of polycondensation of precursor PPPs **6** using osmometry. Because no evidence of chain degradation was found during the conversions $\mathbf{6} \rightarrow \mathbf{7} \rightarrow \mathbf{8} \rightarrow \mathbf{9}$, the only process that might result in a change of the molar masses is diffusion of low-molecular-weight polymer fractions through the membranes used for ultrafiltration. We therefore ensured that no polymeric material passed through the membranes, and we can thus also rule out any fractionation in the course of the polymer work-up processes. Consequently, the obtained polyelectrolytes **8** and **9** have the same degrees of polycondensation as the precursor PPPs **6** used for their preparation,¹³ *i.e.* PPP polyelectrolytes became available in the

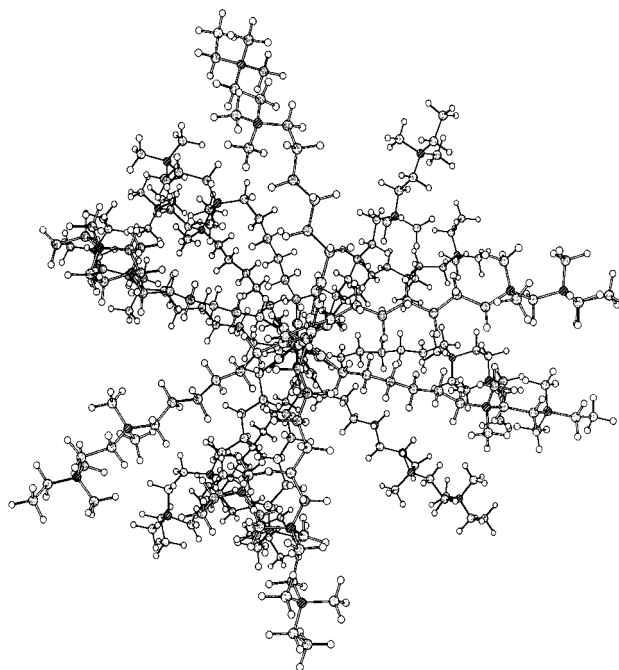


Fig. 2 Schematic illustration of the cylinder-like shape of polymers **9** (viewed along the polymer main chain), sketched according to the results of preliminary SAXS studies performed in salt-free aqueous solutions

present work with average degrees of polycondensation of $P_n = 20\text{--}70$ ($M_n = 15\,000\text{--}50\,000\text{ g mol}^{-1}$).

Finally, we would like to emphasize that PPP polyelectrolytes **8** and **9** are very soluble in water, despite their highly hydrophobic skeleton. This is presumably due to the fact that these macromolecules represent cylinders of an average length of $l_c = 90\text{--}300\text{ \AA}$ and a diameter of $d_c \approx 10\text{ \AA}$ whose hydrocarbon core is covered by the highly polar and thus hydrophilic shell of tetraalkylammonium groups (Fig. 2).

Presently, we are investigating the behaviour of PPP polyelectrolytes **8** and **9** in solution as a function of solvent, temperature, ionic strength and counter ion. The obtained results will be compared with those of other PPP polyelectrolytes such as **1–4** to gain a deeper insight into polyelectrolyte behaviour in dilute solution.

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Notes and References

† E-mail: rehahn@polyibm2.chemie.uni-karlsruhe.de

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