Macromol. Symp. **2004**, *211,* 87-92

Counterion Mobility and Effective Charge of Polyelectrolytes in Solution

*Ute Böhme, Ulrich Scheler**

Institute for Polymer Research Dresden e. V., Hohe Strasse 6,
D-01069 Dresden, Germany

Summary: Polyelectrolytes are macromolecules containing dissociable or charged groups. The charge, that is effectively accessible, is determined by counterion condensation, which is strongly influenced by the ionic strength of the solution under study. In general a rapid exchange between free and condensed counterions is expected. In the present study diffusion and electrophoretic mobility of poly(diallyldimethylammoniumchloride) and perfluorinated succinic acid have been monitored simultaneously. Condensation of the perfluorinated succinic acid to the macroion shows in the electrophoretic mobility of succinic acid monitored by pulsed field gradient NMR. In the concentration dependence of the averaged diffusion coefficient and electrophoretic mobility an exchange fast on the time scale of the NMR experiment is manifested.

Keywords: counterion condensation; effective charge; electrophoretic mobility; polyelectrolytes; pulsed field gradient NMR

Introduction

Polyelectrolytes are polymers containing charged groups, therefore their solution properties are strongly determined by the electrostatic interaction between these charges. However, the effective charge of strong polyelectrolytes is determined by counterion condensation rather than the nominal charge. If the charge-charge interaction would exceed the thermal energy, counterions condense onto the macromolecule, generating the force balance.[1] Condensation of counterions is enhanced upon the addition of salt to a solution of polyelectrolytes.[2]

Pulsed field gradient NMR (PFG NMR)[3, 6] is applied to probe molecular displacements of both the macromolecules and counterions in solution.[7] From the diffusion experiment the friction coefficient for the velocity-proportional friction is derived according to the Einstein equation. The electrophoresis NMR experiment yields the electrophoretic mobility.[8, 9] From both the effective charge of the macromolecules can be determined assuming, that the molecules are free draining, which is justified because of the fractal dimension of the polymers well below 2.[10] In the following a qualitative picture is discussed where the selectivity of the NMR is utilized with a special emphasis on the counterions.

DOI: 10.1002/masy.200450706

Experimental

The experiments have been performed on a Bruker Avance 300 NMR spectrometer, operating at Larmor frequencies of 300 MHz and 282 MHz for protons and fluorine respectively. The spectrometer is equipped with a micro imaging accessory providing magnetic field gradients up to 1 T/m. The electrophoresis NMR system is in-house built and is described elsewhere in more detail.[7] The new system, permitting the investigation of small molecules simultaneously, consists of a U-shaped tube with the NMR coil on one side of the U. Any possible NMR signal from the other side is blocked by an concentric rf shield around the rf coil. The electric field is generated by a pair of platinum electrodes on top of the U. Placing the electrodes on the top permits any gas produced by a possible electrode reaction to escape without disturbing the experiment. The electrodes are connected to a custom made DC amplifier which is driven by one of the gradient channels of the spectrometer to synchronize the DC field with the NMR experiment.

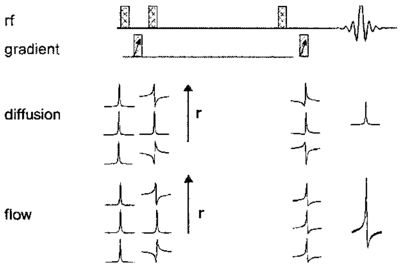

Figure 1. Schematic illustration of the pulsed field gradient stimulated echo NMR experiment. On the bottom the signal phase for three locations is shown schematically indicating the resulting signal attenuation in the case of incoherent motion and phase modulation in the case of coherent motion respectively.

A stimulated echo pulsed field gradient NMR experiment has been used to measure diffusion. From the echo attenuation the diffusion coefficient is derived using the Stejskal-Tanner equation.[6] In the electrophoresis NMR experiment the duration of the gradient pulses is kept constant and the strength of the electric field as the driving force for the electrophoretic motion is incremented.[10, 7]

For ^{1}H-diffusion measurements z-field gradients varied in 32 or 64 steps from 0.12 T/m to 0.98 T/m with 6 ms gradient pulse and 40 ms diffusion delay were applied. For ^{19}F-diffusion measurements the z-field gradients were incremented from 0 T/m to 0.98 T/m for all solutions containing PDADMAC and from 0 T/m to 0.5 T/m for samples without it, respectively. The gradient pulse duration δ was 4 ms and the diffusion delay Δ 20 ms. All electrophoresis experiments were performed incrementing the electric field in 16 steps from -120 V/cm to +120 V/cm or conversely. ^1H was measured with a gradient pulse duration δ of 6 ms, a diffusion delay Δ of 28 ms and a constant magnetic field gradient of 0.8 or 0.9 T/m. For ^{19}F-electrophoresis experiments the same time constants as for diffusion have been used. The applied z-field gradient varied from 0.3 to 0.9 T/m, depending on the diffusion behaviour of the sample.

For each value of the gradient strength or the electric field respectively an NMR spectrum has been detected. Thus components of the solution are identified from the spectrum. In the proton NMR spectrum signals from the polymer and a residual signal from H_2O in D_2O have been observed. In the fluorine spectrum only perfluoro succinic acid has been observed.

Poly(diallyldimethylammoniumchloride) (PDADMAC, Mw = 240kg/mol, Polyscience) and the perfluorinated acid (perfluorinated succinic acid PFSA, Aldrich) have been used as received without further purification. A 5.2 mmol/l (monomer) solution of the polyelectrolyte in D_2O was used for all experiments. Starting from this solution, small quantities of a high concentrated perfluorinated succinic acid solution were added, so that the volume expansion could be neglected. The concentrations of the dibasic acid PFSA adjusted were 1.3, 1.9, 2.6 and 3.9 mmol/l, resulting in 2.6, 3.9, 5.2 and 7.8 mmol/l equivalent charges, respectively.

Results

Typical NMR spectra of poly(diallyldimethylammoniumchloride) and perfluorinated succinic acid are depicted in Figure 2.

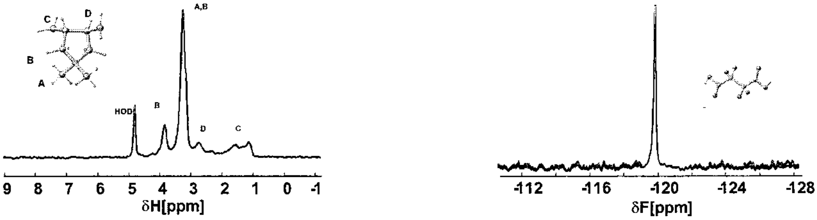

Figure 2. One-dimensional NMR spectra of poly(diallyldimethylammoniumchloride) (left) and perfluorinated succinic acid (right).

Although the resolution in these spectra is not comparable with that in high-resolution NMR spectra, it is sufficient for signal assignment. In the following the selection will be based on the observed nucleus, where in the proton spectra signals from poly(diallyldimethylammoniumchloride) and in the fluorine spectra the signal from perfluorinated succinic acid are observed respectively.

Figure 3 depicts two-dimensional electrophoresis NMR spectra correlating chemical shift with electrophoretic mobility. According to Ref. [10], a model-free data evaluation based on a two-dimensional Fourier transform permits the assignment of the electrophoretic mobility and its sign.

The electrophoretic mobility of the polycation by definition is positive. The mobility of the fluorinated acid in the free solution is negative. If the acid is added to the solution of the polycation in a concentration well below theoretical charge compensation, the effective mobility, that is measured for the acid, is positive as well. This reversal of the effective electrophoretic mobility is a direct proof of the condensation of the perfluorinated succinic acid as a counterion onto the polycation.

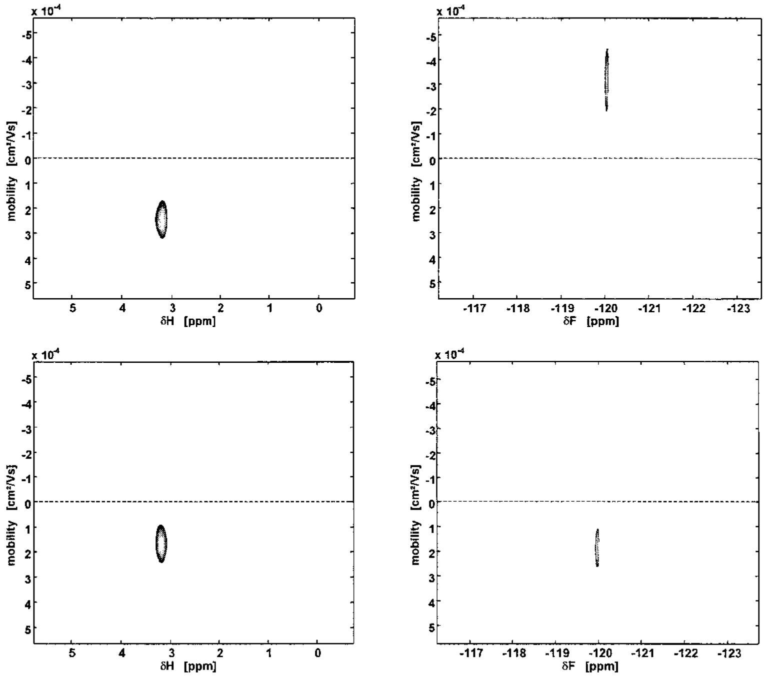

Figure 3. Two-dimensional electrophoresis NMR spectra of 5.2 mmol/l (monomer) PDADMAC (left) and 2.6 mmol/l perfluorinated succinic acid (right) for the free components (top) and a mixture of 5.2 mmol/l (monomer) PDADMAC with 1.3 mmol/l perfluorinated succinic acid, that represents compensation of half the charges of the polycation by the acid (bottom).

When the concentration of the acid is increased a decreasing effective electrophoretic mobility is observed. The term effective is emphasized here, because in the NMR experiment the average between the condensed and free acid is observed, when the exchange between the two populations is rapid on the time scale of the experiment, which here is in the order of 10 ms. Although increasing the total concentration of the fluorinated acid by more than a factor of four will lead to enhanced counterion condensation[2] most of the additional acid will increase the population of the free acid in the solution. Therefore the effective electrophoretic mobility shifts towards the mobility of the free acid. The same is true for the effective, exchange averaged diffusion coefficient as depicted in Figure 4. The diffusion coefficient and the electrophoretic mobility of poly(diallyldimethylammoniumchloride) remain nearly unchanged.

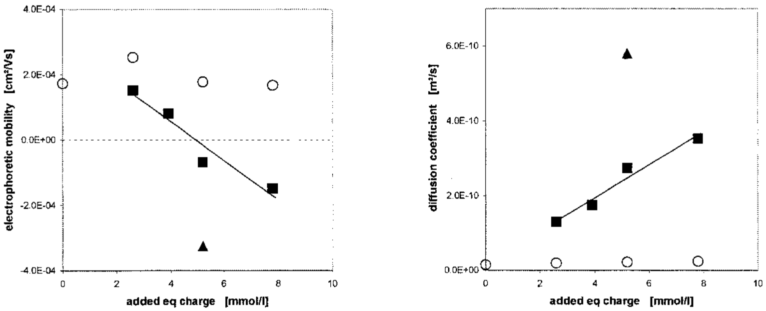

Figure 4. Effective electrophoretic mobility (left) and diffusion coefficient (right) of (■) perfluorinated succinic acid, (▲) perfluorinated succinic acid without PDADMAC and (○) PDADMAC, measured as a function of the charge added.

Conclusions

It has been demonstrated, that the electrophoretic mobility of both, poly(diallyldimethylammoniumchloride) and a perfluorinated acid are determined simultaneously in an electrophoresis NMR experiment. Both compounds in pure solution exhibit electrophoretic mobility of opposite signs. If the perfluorinated acid is added to the polymer in a concentration well below charge compensation, an effective electrophoretic mobility close to that of the polymer is detected, indicating that the perfluoro succinic acid replaced the originally condensed counterions on the polymer. Increasing the concentration results in a shift of both the electrophoretic mobility and the diffusion coefficient towards the value of the free acid. The fact, that a single component in both is detected at all concentrations proofs, that there is fast exchange between free and condensed acid on the time scale of the pulsed field gradient NMR experiment.

Acknowledgement

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) under grant SCHE 524/2-2.

[1] G. S. Manning, in *"Polyelectrolytes"*, E. Sélégny, M. Mandel, U. P. Strauss, Eds., D. Reidel Publishing Company, Dordrecht-Holland 1974.

[2] U. Böhme, U. Scheler, *Colloids and Surfaces A* **2003**, *222*, 35.

[3] P. T. Callaghan, *"Principles of Nuclear Magnetic Resonance Microscopy"*, Oxford University Press, Oxford 1991.

[4] R. Kimmich, *"NMR Tomography, Diffusometry, Relaxometry"*, Springer, Berlin, Heidelberg 1997.

[5] J. Kärger, in *"Diffusion in Condensed Matter"*, Kärger, Heitjans, Haberland Eds., Vieweg, Braunschweig 1998.

[6] E. O. Stejskal, J. E. Tanner, *J. Chem. Phys.* **1965**, *42*, 288.

[7] S. Wong, U. Scheler, *Colloids and Surfaces A* **2001**, *195*, 253.

[8] M. Holz, *Chem. Soc. Rev.* **1994**, *23*, 165.

[9] C. S. Johnson, in *"Encyclopedia of Nuclear Magnetic Resonance"*, D.M. Grant, R.K. Harris Eds., John Wiley & Sons, Chichester 1996, and references therein.

[10] M. Ullner, in *"Handbook of Polyelectrolytes and Their Applications"*, S. K. Tripathy, J. Kumar, H. S. Nalwa Eds., American Scientific Publishers 2002, Vol. 3, 271.

[11] U. Scheler, in *"Handbook of Polyelectrolytes and Their Applications"*, S .K. Tripathy, J. Kuma, H. S. Nalwa Eds., American Scientific Publishers 2002.