

ARTICLES

Determination of Charge and Molecular Weight of Rigid-Rod Polyelectrolytes[†]

U. Böhme, C. Vogel, J. Meier-Haack, and U. Scheler*

Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Received: December 15, 2006; In Final Form: March 29, 2007

Rod-like polyelectrolytes are an interesting model system because their persistence length is independent of the ionic strength and pH of the surrounding medium and they permit the investigation of polyelectrolytes in the absence of conformational degrees of freedom. In this work, rigid-rod poly(aramide) polyelectrolytes were synthesized by the Higashi method. Electrophoresis NMR spectroscopy in conjunction with diffusion NMR spectroscopy has been applied to determine the effective charge of the polymer. The charge was determined from the balance between the force in the electric field and the hydrodynamic friction in the steady-state electrophoretic motion. Because only organic counterions were present, and were identified in the proton NMR spectra, the counterions were investigated as well, and the fraction of condensed counterions was determined directly. From the effective charge per molecule and the knowledge of the fraction of condensed counterions, the total charge per molecule was determined. Finally, from the total charge, the number of repeat units and thus the molecular weight were inferred.

Introduction

Important issues in polyelectrolyte research include counterion condensation and the determination of the effective charge in aqueous solution. In particular, counterion condensation¹ is not yet fully understood. The aim of this study is to contribute to the understanding of the behavior of polyelectrolytes in solution, focusing on counterion condensation. Rod-like polyelectrolytes permit the exploration of polyelectrolytes in the absence of conformational effects.² For this study, rigid-rod polyelectrolytes based on aromatic poly(amides) bearing one sulfonic acid group at each aromatic ring (sulfonated Kevlar) were synthesized. The rigidity of the polymer backbone reduces the variables of chain mobility. As a result of the synthetic route, the polyelectrolyte had pyridinium ions as counterions. From the diffusion coefficient determined by pulsed-field gradient (PFG) NMR spectroscopy,^{3,4} the hydrodynamic size and the hydrodynamic friction coefficient can be derived.⁵ The electrophoretic mobility is determined on the same time scale in electrophoresis NMR.^{6–8} The effective charge on the polymer is the charge not compensated by condensed counterions. Counterions condense on the macromolecule since their thermal energy does not exceed the electrostatic energy, when the density of charges on the macromolecule is too large.¹ Electrophoretic motion in an external electric field is determined by the force on the effective number charges of the macromolecule. On the time scale of the PFG-NMR experiment, which is in the order of tens of milliseconds, a steady state with constant velocity is reached because the velocity dependent friction balances the electrostatic force. Assuming the balance between the two forces, the effective number of charges can be calculated according to equation 1

$$z = \frac{\mu_{\text{el}} k_{\text{B}} T}{eD} \quad (1)$$

using the experimental values of the diffusion coefficient D , the electrophoretic mobility μ , and the temperature T , as well as the Boltzmann constant k_{B} and the elementary charge e .^{8,9} The difference between the nominal charge and the effective charge is the fraction of condensed counterions. The effective charge, that is, the charge available for interactions with other charged molecules or surfaces, can thus be determined directly.

The present case offers the additional advantage that organic counterions are present and contribute to the proton NMR signal. Because series of spectra are recorded in both the diffusion and electrophoresis NMR experiments, the signals originating from the counterions are separated from those originating from the polyelectrolyte by their respective chemical shifts. Thus, the charge of the counterion is determined as well.

On the time scale of the NMR experiments, which is on the order of tens of milliseconds, condensed counterions exchange with free counterions in solution, so that only an average is measured in both diffusion and electrophoretic mobility.¹⁰ From a comparison of measurements of the chloride salt of the pyridinium counterion with the results obtained for the pyridinium cation as a counterion of the poly(aramide), the bound fraction can be determined according to eq 2 below. With the present setup, the precision in the diffusion experiments is superior to that from the electrophoresis experiments; hence, the bound fraction is determined from the diffusion coefficients. The experimentally determined diffusion coefficient D_{obs} is the weighted average of the diffusion coefficient of the free counterions (D_{f}) and the diffusion coefficient of the counterions bound to the polymer (D_{b}), which is the same as that for the polymer.

[†] Part of the special issue "International Symposium on Polyelectrolytes (2006)".

* Corresponding author. E-mail: scheler@ipfdd.de

$$D_{\text{obs}} = (1 - x_b)D_f + x_b D_b x_f = 1 - x_b \quad (2)$$

Finally, the polymer is characterized by the effective charge and the fraction of counterions condensed or bound to the polyelectrolyte. From these two values, the total number of charges can be found according to the equation

$$z_{\text{nom}} = \frac{z_{\text{eff}}}{x_f} \quad (3)$$

Because the structure of the polymer with two charges per repeat unit is known, the number of repeat units and thus the molecular weight can be calculated, given the molecular weight of the repeat unit of 557 g/mol. This approach requires neither a molecular weight standard nor any model. It is valid for strong polyelectrolytes, in which all charged groups are dissociated.

Experimental Section

Synthesis. Fully sulfonated poly(aramides) were successfully prepared by application of the Yamazaki–Higashi polycondensation technique from 2,5-diaminobenzene sulfonic acid and sulfoterephthalic acid in the presence of triphenyl phosphite, pyridine, and lithium chloride in *N*-methylpyrrolidone as the solvent.^{11,12} The polymeric amide sulfonic acids were obtained as pyridinium salts. Depending on the concentrations of reactants used, poly(aramides) of different molecular weights were obtained. For further investigation, a sample with weight- and number-average molecular weights of $M_w = 86700$ g/mol and $M_n = 46000$ g/mol was used. The molecular weights were determined by GPC using *N,N*-dimethylacetamide containing water (2%) and lithium chloride (3 g/L) as the solvent and poly-(2-vinyl pyridine) (PVP) as the standard. IR and ¹H NMR spectra are in agreement with the proposed structure.

NMR Spectroscopy. Sulfonated poly(aramide) bis-pyridinium salt was dissolved in D₂O (99.95%, Deutero GmbH), as strong signals of the residual solvent protons would limit the dynamic range and complicate the measurements of polyelectrolyte and counterions at low concentration. The sample concentration was 4 g/L (7 mmol/L repeat units). All experiments were conducted at 20 °C.

Diffusion NMR experiments were performed on a Bruker Avance 500 NMR spectrometer operating at a Larmor frequency of 500 MHz for protons and equipped with a Diff30 probe with a *z* gradient providing magnetic field gradients of up to 11.6 T/m. A stimulated echo pulse sequence was used to measure diffusion. The gradient strength was incremented linearly in 64 steps from 1 to 11.6 T/m, the gradient pulse duration δ was 1 ms, and the diffusion time Δ was 15 ms. From the signal attenuation with increasing gradient strength, the diffusion coefficient was calculated according to the Stejskal–Tanner equation.⁴ For samples exhibiting more than one single diffusion coefficient, it was most convenient to apply an inverse Laplace transform in the dimension of the gradient strength following the Fourier transform generating the spectra, which results in a so-called DOSY (diffusion-ordered) NMR spectrum resolving the diffusion coefficient for each species.⁷

The electrophoresis experiments were performed on a Bruker Avance 300 NMR spectrometer operating at a Larmor frequency of 300 MHz for protons with a micro 2.5 microimaging accessory generating magnetic field gradients of up to 1 T/m. The electrophoresis NMR probe was built in-house.¹⁰ The electrophoresis cell was a U-shaped tube with the NMR coil on one side of the U. A pair of platinum electrodes placed on top of the U-tube permitted gaseous products of the electrode

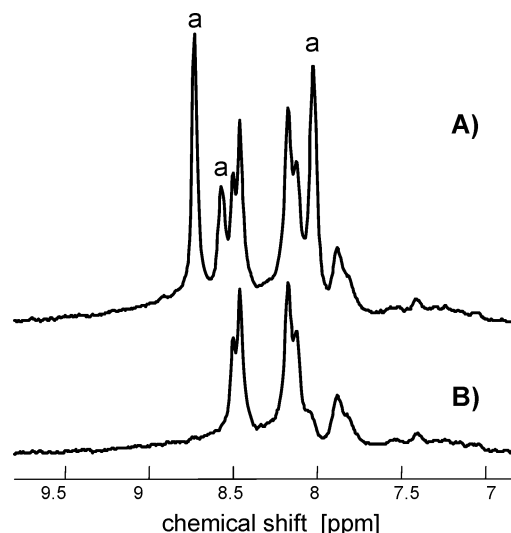


Figure 1. Proton NMR spectra taken from a PFG-NMR experiment, showing (A) the total spectrum of poly(aramide) and pyridinium counterion and (B) the poly(aramide) only. The peaks of the pyridinium cation are labeled with the letter “a”.

reactions to escape without disturbing the NMR experiments and were connected to a custom-made dc amplifier producing a maximum of ± 1000 V¹³ driven by one of the gradient channels of the spectrometer synchronous with the NMR experiment. More details of the electrophoresis NMR equipment, measurements, and processing can be found elsewhere.^{8,9} For the measurement of electrophoretic mobility, a stimulated echo pulsed-field gradient NMR experiment with an applied electric field in the time between the beginning of the first gradient pulse and the end of the second gradient pulse has been used. The stimulated echo has the advantage that, during the diffusion time, only longitudinal relaxation is acting, which, for large molecules, is significantly longer than the transverse relaxation time. In the electrophoresis NMR experiments, the gradient strength was kept constant at 50% of the maximum gradient strength, and the electric field was incremented in 16 steps between 127 and -127 V/cm. Appropriate to the diffusion behavior of the sample, the time constants used were 3 ms for δ and 15 ms for Δ .

Coherent motion of spins in the PFG-NMR experiments results in pure phase modulation, which can be evaluated directly. In cases where the electrophoretic mobility shows a distribution or when not all lines are well-resolved in the spectral dimension, a modified two-dimensional Fourier transform according to ref 8 permits the model-free determination of the electrophoretic mobility for each species. Data processing was performed in MATLAB using MatNMR¹⁴ and in-house-written scripts.

Results and Discussion

Rigid-rod polyelectrolytes based on sulfonated poly(aramides) were synthesized in this work. The high number of ionizable groups results in good water solubility of the polymer. GPC data in *N,N*-dimethylacetamide are comparable to those of poly-(2-vinyl pyridine) (PVP) with a molecular weight of (M_w) 87000 g/mol.

In Figure 1, a section of an NMR spectrum taken from diffusion NMR experiments is shown. The peaks at 8.7, 8.6, and 8.0 ppm are attributed to the pyridinium cation, and the peak groups at 8.5, 8.2, and 7.9 ppm result from the polymer.

Figure 2 presents a diffusion-ordered NMR spectrum in which the diffusion coefficients obtained from an inverse Laplace

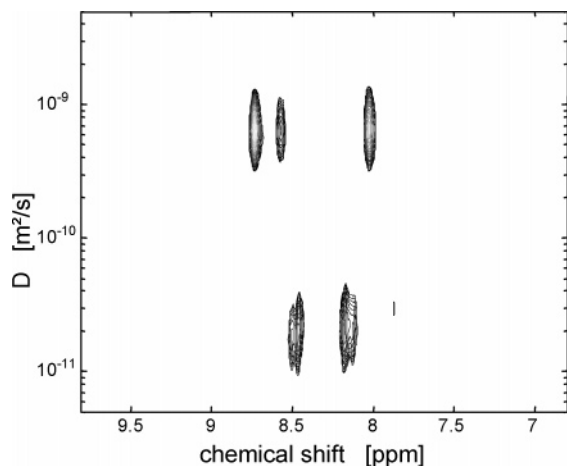


Figure 2. Diffusion-ordered (DOSY) NMR spectrum resolving poly(aramide) and pyridinium counterions by their respective chemical shifts and diffusion coefficients.

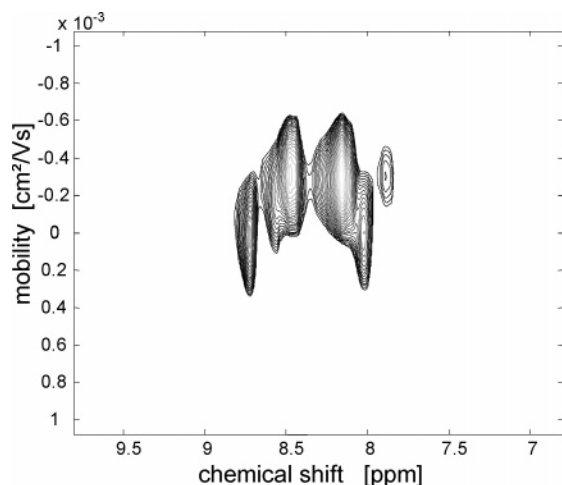


Figure 3. Two-dimensional electrophoresis NMR spectrum resolving poly(aramide) and pyridinium counterions by their chemical shifts and electrophoretic mobilities.

transform are correlated with the respective chemical shifts. There is a strong water signal in the slices with weak gradients that dominates the DOSY spectrum; therefore, only an enlargement of the spectrum not including the chemical shift of water is shown. Two diffusion coefficients are resolved: $6.3 \times 10^{-10} \text{ m}^2/\text{s}$ for the pyridinium counterion and $2.3 \times 10^{-11} \text{ m}^2/\text{s}$ for the polymer. The value obtained for the pyridinium cation is significantly lower than the value of $8.9 \times 10^{-10} \text{ m}^2/\text{s}$ obtained for the free pyridinium cation, because it is the average between the free and condensed states. With a knowledge of both values, the fraction of condensed counterions is calculated to be 30%. Condensation of counterions does not change the hydrodynamic size of the polymer significantly.

In Figure 3, a two-dimensional electrophoresis NMR spectrum correlating electrophoretic mobility with chemical shift is shown. Again, two species are resolved. The electrophoretic mobility of the polymer is $-3.2 \times 10^{-4} \text{ cm}^2/(\text{V s})$, and that for the pyridinium ion is $+1 \times 10^{-4} \text{ cm}^2/(\text{V s})$. Because there is remaining overlap in the chemical shift range, the slice for the pyridinium ion was fitted in the mobility direction to obtain the mobility values. The mobility observed for the pyridinium ion is again the average between the values of the free and condensed species, which is identical to the mobility of the polymer. The electrophoretic mobility of the polymer is determined by the effective number of charges, that is, the

number of charges not compensated by condensed counterions. This number of charges was determined according to eq 1 from the experimental values for the electrophoretic mobility of $-3.2 \times 10^{-4} \text{ cm}^2/(\text{V s})$ and the diffusion coefficient of $2.3 \times 10^{-11} \text{ m}^2/\text{s}$ to be -35 . The same approach yields a charge of $+1$ for the free pyridinium cation. The Bjerrum length calculated for the solutions used here is 0.7 nm. The charge–charge distance for the polymer was estimated to be 0.6 nm from an analogue of one-half the charge density.¹⁵

Given the fraction of condensed counterions of 30%, the total number of charges per molecule was calculated to be -50 in the present case. Because there are two acid groups per repeat unit and because both are dissociated at the given pH of ~ 3.5 , the molecule was determined to contain 25 repeat units and have a molecular mass of 14000 g/mol.

This value differs from that obtained by GPC, as expected because the PVP standard is not optimal for stiff molecules and does not take into account that the polymer is rigid. Under the elution conditions, the PVP standard is a statistically coiled polymer,¹⁶ and its hydrodynamic behavior is significantly different from that of a rigid rod, which is incapable of changing its shape and size depending on the solvent and salt content. The measured diffusion coefficient of sulfonated polyaramide in water is comparable to that of poly(styrene sulfonate) with a molecular weight of about 40000 g/mol, which adopts a more coiled conformation.

The resulting molecular weight represents the mass average, because each proton contributes the same to the signal at the respective chemical shift and the integral of the signal is a measure of the number of protons. Information on the molecular weight distribution can be derived from distribution of diffusion coefficients obtained by taking the inverse Laplace transform of the signal decays in the diffusion experiment, which can be transformed into a distribution of hydrodynamic radii, again giving a weight average. To determine the distribution of the electrophoretic mobility, a three-dimensional experiment must be conducted.¹⁷

Conclusions

Rigid-rod poly(aramide) polyelectrolytes have been synthesized. The effective charge of the poly(aramide), the charge that determines the interaction of the polymer with other charged objects, was determined from electrophoresis NMR experiments in conjunction with PFG-NMR diffusion measurements. The charge of the polymer in the present case was determined to be -35 . The total charge on the polymer was determined from the experimentally determined effective charge of the polyelectrolyte and the fraction of condensed counterions. With the knowledge of the molecular weight of a repeat unit, which contains two charged acid groups, the molecular weight of the polymer was calculated in a straightforward manner to be 14000 g/mol.

This approach is by no means limited to rigid-rod polyelectrolytes. The only requirement is an NMR signal from the counterion. Most conveniently, this is a proton signal from an organic counterion.

Acknowledgment. We thank Brigitte Hänel for assistance with some of the NMR measurements. Financial support from the Deutsche Forschungsgemeinschaft (DFG) under Grant SCHE 524/5 is gratefully acknowledged.

References and Notes

- (1) Manning, G. S. In *Polyelectrolytes*; Sélégny, E., Mandel, M., Strauss, U. P., Eds.; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1974; p 9.

- (2) Rehahn, M.; Rau, I. U. In *Concise Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1999; p 1145.
- (3) Stejskal, E. O. *J. Chem. Phys.* **1965**, *43*, 3597.
- (4) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
- (5) Einstein, A. *Ann. Phys.* **1905**, *17*, 549.
- (6) Holz, M. In *Diffusion in Condensed Matter*; Kärger, J., Heitjans, P., Haberland, R., Eds.; Vieweg: Braunschweig, Germany, 1998; pp 245–264.
- (7) Johnson, C. S. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; pp 1886–1895.
- (8) Scheler, U. In *Handbook of Polyelectrolytes and Their Applications*; Tripathy, S. K., Kuma, J., Nalwa, H. S., Eds.; American Scientific Publishers: Stevenson Ranch, California, 2002; Vol. 2, pp 173–189.
- (9) Böhme, U.; Scheler, U. *Colloids Surf. A* **2003**, *222*, 35.
- (10) Böhme, U.; Scheler, U. *Macromol. Symp.* **2004**, *211*, 87.
- (11) Viale, S.; Best, A. S.; Mendes, E.; Picken, S. J. *Chem. Commun.* **2005**, 1528.
- (12) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. A: Polym. Chem.* **1975**, *13*, 1373.
- (13) Rohrer GmbH Mess- und Systemtechnik, München, Germany.
- (14) MatNMR is a toolbox for processing NMR/EPR data using MATLAB and can be freely downloaded at <http://matnmr.sourceforge.net>.
- (15) Taeger, A.; Vogel, C.; Lehmann, D.; Jehnichen, D.; Komber, H.; Meier-Haack, J.; Ochoa, N. A.; Nunes, S. P.; Peinemann, K. *React. Funct. Polym.* **2003**, *57*, 77–92.
- (16) Lederer, A.; Voigt, D.; Appelhans, D.; Voit, B. *Polym. Bull.* **2006**, *57*, 329.
- (17) Böhme, U.; Scheler, U. *J. Magn. Reson.*, manuscript in preparation.