



NMR on polyelectrolytes

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ABSTRACT

Nuclear magnetic resonance (NMR) is a versatile tool for the investigation of structure and molecular mobility in soft matter. It is a standard technique for structure determination of polymers and polyelectrolytes. In addition NMR provides information on both the polyelectrolyte, the counterions and often valuable information originating from the surrounding medium. High-resolution NMR spectroscopy enables the observation of counterion interaction in particular π interactions as well as the information about spatial proximity of functional groups in polyelectrolyte complexes. Combinations of PFG NMR and electrophoresis NMR permit the direct observation of counterion condensation. Cryoporometry showed different states of water interacting with polyelectrolytes in multilayers. Solid-state NMR has been applied to investigate both packing effects and local molecular dynamics in polyelectrolyte multilayers. The current research in the field is reviewed.

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1. Introduction

NMR is a versatile tool for the investigation of structure and molecular mobility in soft matter in solution, in dispersion and in the solid state. The focus of the present paper is beyond its indispensable role for structure characterization in modern chemistry. The full range of information from NMR experiments on structure, molecular arrangements and mobility, size and conformation is utilized. The information derived from NMR spectra is inherently element selective, besides that spectroscopic resolution facilitates the assignment of particular properties to specific sites or components of the complex system. Experiments sensitive to internuclear distances have been utilized both in solution and in the solid state probing interactions to counterions or ligands as well as for the study of packing effects in multilayers and complexes. Specific NMR techniques have been applied or developed for polyelectrolytes. In particular pulsed-field gradient (PFG) NMR techniques have been applied to study motion of polyelectrolytes in solution as well as motion of solvent molecules around the molecules or trapped inside layers.

2. Polyelectrolyte conformation

Diffusion measured using PFG NMR has been used to study the solvent-induced transition between random coil and rod conformation of poly(β -benzyl L-aspartate) [1]. The conformation of this particular polymer is adjusted by the solvent, i.e. mixtures of

chloroform and trifluoro acetic acid of different compositions. From the dependence of the observed diffusion coefficient on the polymer concentration the transition between the two conformations has been deduced.

Double quantum NMR in solution has been applied to poly(diallyldimethyl ammonium chloride) to study the local order and motion in solution [2]. Observed residual dipolar coupling is interpreted as a result of local restrictions of motion as expected from the extended conformation of the polyelectrolyte. The relaxation rate of ^{35}Cl from the counterions is interpreted in terms of mobility of the counterions which is an additional indication of counterion condensation.

Phase transitions in hydrogels of poly(N-isopropylmethacrylamide-co-sodium methacrylate) copolymers have been studied by ^1H solution NMR and transverse relaxation [3]. In the solution spectra only the phase-separated fraction contributes to the signal. Thus the fraction of phase-separated polymer is derived from the total signal integral. The time evolution of the transverse relaxation time of the solvent suggests binding of the water inside the gel globules.

3. Counterion effects

The nature of polyelectrolytes as charged macromolecules requires the presence of counterions in the system. As a result the charge of a polyelectrolyte in solution usually is significantly lower than its nominal charge expected from the structure because of the effect of counterion condensation [4]. Simply saying the thermal energy of each counterion is insufficient to escape the electric field generated by the sum of the charges on the macromolecule. Therefore the charge of the polyelectrolyte is lowered by condensation of a fraction of the

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counterions, the thermal energy of the rest is sufficient to escape. The remaining charge of the combined system comprised of the macromolecule and the condensed counterions is called effective charge.

An interesting aspect of the interaction of counterions with the macromolecules has been observed for organic counterions containing aromatic parts [5]. High-resolution solution-state NMR has been applied to study the interaction between the counterions and the polymers. Nuclear-Overhauser spectroscopy (NOESY) gives information on spatial proximity of between the spins. The close proximity found has been interpreted in terms of π - π interaction [6^{**}]. This approach has been extended to different water soluble polymers under variation of their hydrophobic effects, where the pK_a of a small molecule with pharmaceutical activity (chlorpheniramine maleate) has been tuned [7].

²³Na solution-state NMR has been applied to study the binding of Na as a counterion to a polyacrylate gel [8]. Both the line width in the ²³Na NMR spectrum and the chemical shift suggest, that there is tight binding of ion pairs between sodium and carboxylic acid groups. The increase in line width is interpreted as restrictions in the ion mobility. The data found are compared to measurements of the swelling behaviour of gel particles.

Counterion condensation has directly been proven by electrophoresis NMR, where a fluorinated counterion (fluorinated succinic acid) has been used with poly(diallyldimethylammonium chloride), detecting the polyelectrolyte in the ¹H signal and the counterion in the ¹⁹F signal [9]. More recently there have been major developments in electrophoresis NMR, so that limitations and experimental problems have been overcome and it may be used routinely now [10]. There are a number of applications to polyelectrolytes as well as to other charged systems [11]. A comparison to capillary electrophoresis and numerical simulation has shown, that the effective charge of small polyelectrolytes can directly be derived without any model [12].

The motion of condensed counterions with the oppositely-charged macromolecule has been found directly in pulsed-field-gradient (PFG) NMR for the measurement of diffusion. One of the major advantages of diffusion NMR over other techniques for the determination of the diffusion coefficient comes into play, the fact, that the measurement is site specific. The diffusion coefficients of the macromolecule and the counterion are determined simultaneously. Comparison between the diffusion coefficient of the counterion with a low-molecular weight salt and with the macromolecule yields a difference. Assuming that there are two states only, a free and a bound state, the bound fraction is simply determined from the weighted average, that is measured in the PFG NMR experiment. Condensation of an additional counterion does not alter the diffusion coefficient of the macromolecule, therefore the diffusion coefficient of the condensed counterion is equal to that of the macromolecule, while that of the free counterion has been measured separately. This approach has been taken further, in a case, where the effective charge of the polyelectrolyte has been determined using electrophoresis NMR together with the fraction of condensed counterions. This permits the calculation of the nominal charge of polyelectrolyte. In the particular case the structure of the repeat unit, its molecular weight, and number of nominal charges per repeat unit have been known. Therefore the molecular weight of the polyelectrolyte had been determined [13^{**}], while chromatographic techniques failed in the particular case for two reasons: There is no standard for the chromatography of stiff polymers and the charge of the polyelectrolyte is the source of an additional interaction between the solute and the column.

Poly(styrene sulfonate) has been used to study the effect of the degree of polymerisation [14], the ionic strength [15] and of the dielectric constant of the surrounding solvent [16^{**}] on counterion condensation using electrophoresis NMR. At low molecular weight there is as expected no counterion condensation. In an intermediate range the effective charge follows that expected from Manning's theory [4], at larger molecular weight additional factors come into

play. With increasing ionic strength there is more counterion condensation, the effective charge of the molecule decreases. A reduced effective charge results in weaker repelling electrostatic interaction along the polyelectrolyte chain and thus in a more compact conformation. From the hydrodynamic size as a function of the molecular weight a fractal dimension, describing the use of space in the fictitious growth of the polymer, is derived. This fractal dimension increases accordingly with increasing ionic strength [17]. The influence of the dielectric constant is more complex, because it affects the conformation of the polyelectrolyte via the electrostatic repulsion. The effective charge of the polyelectrolyte decreases with decreasing dielectric constant, at until the repulsion of the charges along the chain becomes too weak. Then the polymer abruptly goes into a coiled conformation with a simultaneous sudden decrease in the effective charge.

4. Polyelectrolyte complexes

Diffusion and electrophoresis NMR have been applied to polyelectrolyte complexes as well. The effective charge of these particles follows the trend of the composition. The most interesting point is the change in the hydrodynamic size of the complexes [18]. The charge brings the polyelectrolyte into a more extended conformation compared to an uncharged polymer [19]. Increasing the ionic strength results in partial screening of the charge and thus a more compact conformation. If the same ionic strength is adjusted by a polyelectrolyte of opposite charge, the resulting conformation is even more compact, because the oppositely charged polyelectrolyte acts as a crosslinker for the long-chain polyelectrolyte. The heterogeneity in the diffusion of PDADMAC in coacervates with Bovine serum albumin (BSA) has been interpreted in terms of heterogeneities in the coacervate [20]. However, the detailed discussion is complicated, because a number of factors resulting from the polymer conformations in the coacervate influence the polymer conformation and thus NMR relaxation times. This results in different weighting of various sub-ensembles in the NMR signal.

An interesting class of complexes has been formed from block copolymers containing a charged and a hydrophilic block. If such polymers with block of opposite charge are mixed, they spontaneously form micelles with a charge-compensated core formed from the oppositely-charged blocks and a corona from the hydrophilic uncharged block [21,22]. While light scattering has been used to proof the formation of the micelles and to estimate their size, solution-state NOE NMR has been used to gain insight into the local structure [23] from internuclear distance information. There is as expected tighter packing in the core than in the corona. A similar behaviour has been found for block copolymers from poly(styrene) and poly((sulfamate-carboxylate)isoprene [24], where mostly mobility information from the linewidth in the ¹H NMR spectra has been evaluated.

5. Polyelectrolyte multilayers and capsules

Polyelectrolyte multilayers are used for surface modification and for the formation of hollow capsules with the aim of controlled release.

Two-dimensional diffusion exchange NMR has been applied to investigate transport through hollow capsules formed from multilayers from poly(styrene sulfonate) and poly(diallyldimethylammonium chloride) [25^{**}]. Dextran of high molecular weight exhibits two distinct diffusion coefficients indicating a fraction being confined in the capsule, while there seems to be no confinement for dextran of low molecular weight. In a two-dimensional experiment consisting of two diffusion encoding steps based on a stimulated echo pulsed-field-gradient NMR experiment [26], which are separated by a mixing time in the order of hundreds of milliseconds the exchange between ensembles of different diffusion coefficients is monitored. Unlike other two-dimensional NMR experiments the diffusion exchange experiment requires a

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