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NMR as a Probe into the Local and Semilocal Order in Cooperative Interactions of Polyelectrolytes

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Summary: Polyelectrolytes such as poly(*N*-diallyldimethylammonium chloride) (PDADMAC) exhibit some local and semilocal order both in their conformation dynamics (dynamic correlations) and the average density of their counterion cloud (the radial density distribution). Both aspects of order are subject to cooperative fluctuations as well as mutual reinforcement. They can be observed in particular in dilute solutions, i.e. at concentrations of the charged groups less than 5 mmol/L. At such dilution, ^{1}H NMR is the method of choice for the study of conformation dynamics. In addition to the recently published analysis of transverse relaxation and saturation transfer experiments, relaxations of double-quantum coherence, pseudo-solid echo and solid echo responses and exchange 2D spectra are reported here. For the radial distribution of counterions with spin-3/2 nuclei (^{7}Li, ^{23}Na, ^{35}Cl, ^{81}Br), the relaxation model proposed by Halle, Wennerstrom and Picullel is applied and the use of either combined longitudinal and transverse relaxation or DQC ($\mathbf{T_2^3}$) relaxation is shown. The results show that the counterion condensation, i.e. relative ordering of the counterion cloud, decreases in less densely charged polyions and vanishes for the charge separation about 2.5 nm.

Keywords: conformations; counterions; dynamic order; NMR; polyelectrolytes; relaxations

Introduction

Order in a macromolecular system can adopt various degrees from simply non-random, over more or less correlated up to permanent or periodical positions, motions or even functions of its various parts. It can exist on local, semilocal or global level. In most cases, various levels influence each other in the sense that global order is built up from the local and semilocal levels and conversely imposes restrictions on the lower levels of structural hierarchy through various long- and short-range interactions. In dilute polymer solutions, only local and semilocal levels of order are usually important.

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Both local and semilocal order has a significant importance in the interactions of charged macromolecules. Polyions or polyelectrolytes with complementary charges engage in electrostatic coupling leading to variously organized electrostatic complexes[1]. In most cases, such interactions are cooperative[2-5] and thus sensitive to local and semilocal order. Our first results[4-6] indicate that NMR can serve as a powerful probe into such order in polyelectrolytes such as *poly(N-*diallyldimethylammonium chloride) (PDADMAC) or sodium polymethacrylate (PMANa). In a recent study[6], PDADMAC was shown to exhibit cooperative fluctuations of the form of a local chain collapse, with an average lifetime of about 60 ms. The existence and lifetime of such fluctuations were mainly based on the analysis of ^{1}H NMR transverse relaxation and of specially devised saturation-transfer experiments. In the present study, more attention is given to the actually unperturbed majority of the PDADMAC chain and to its counterions, using a variety of different NMR methods.

In order to specify the aim of this study, the meaning of local (and semilocal) order in a polymer chain or its vicinity should be clarified. Although entropy can always serve as a collective measure of disorder in the system, its meaning could be somewhat vague locally. Let us assume that the monomer units of a polymer such as PDADMAC can be represented planar forms attached to a common axis so that their relative conformations can be characterized by a set of angles θ_1, θ_2 .... The local order can then be expressed by the correlation function $< G(\theta_1\theta_2\theta_3....) >$ integrated over time and the whole ensemble. In the absence of very strong long-range interactions, such function can be expressed, at least in approximation, as a product of pair correlation functions,

$$< G(\theta_1\theta_2\theta_3....) >= \prod_{i=1}^{n-1} < G(\theta_i\theta_{i+1}) > . \tag{1}$$

If there is some strong interaction depending on θ_i (such as electrostatic repulsion) between the adjacent monomer units, the correlation function will depend on the rotational energy profile:

$$< G(\theta_i\theta_{i+1}) > \approx 1 - \int_0^{2\pi} \mathrm{d}\varphi \exp[-\Delta E(\theta_i + \varphi)/kT] . \tag{2}$$

This certainly is the case of polyion such as PDADMAC if the adjacent charges are not effectively screened off by the counterions. However, correlation functions of these types are rarely accessible experimentally in NMR. As a rather poor substitution, many authors use the popular order parameter S introduced by Wennerström[7] and made very popular by Lipari and Szabo[8],

$$S_2 = (1/2)\overline{(3\cos^2\theta - 1)}\ , \qquad (3)$$

where θ is the angle between the vector connecting two interacting nuclei and the local director. Like $< G(\theta_1\theta_2) >$, S_2 adopts values from 0 (lack of correlation and order) to 1 (full correlation, local order). Its higher values can lead both to dynamic broadening[8] and residual static dipolar interactions[9].

In contrast to the polyion chain, the order of the counterion cloud can be described in semilocal rather than local scope. Assuming that the polyion can be taken as a charged rod, radial density distribution $\rho(r)$ of the counterions can be expressed. Giving the entropy of the counterions the symbol S_C (to distinguish it from the order parameter), one can write

$$S_C \approx k\int_a^\infty \rho(r)\ln[\rho(r)]\,\mathrm{d}r\,. \qquad (4)$$

S_C is considerably lower for steeper decrease of $\rho(r)$ at larger r (counterion condensation). This phenomenon has been shown[3-5] to have a direct connection with the cooperative interactions of polyions.

Experimental

^{1}H, ^{23}Na and ^{35}Cl NMR spectra and relaxations were measured with an upgraded Bruker Avance DPX300 spectrometer (^{1}H resonance frequency 300.13 MHz) except for ^{1}H MAS NMR spectra, which were measured with a Bruker Avance DSX200 spectrometer. Double-quantum coherence (DQC)[10] was measured with the pulse sequence $\pi/2_{\phi 1} - [\tau - \pi_{\phi 2} - \tau]_n - \pi/2_{\phi 1} - \delta - \pi/2_{\phi 1}$, where δ was 50 μs and τ was 0.5 ms. Pseudo-solid-echo (PSE)[11] pulse sequence was adopted to fit the compared transverse decay, i.e. $\pi/2_y - [\tau/2 - \pi_y - \tau/2]_m - \pi/2_{-x} - [\tau_1/2 - \pi_{\pm y} - \tau_1/2]_n$, both τ and τ_1 being 1 ms. Solid-echo (SE) evolution[12,13] pulse sequence was $\pi/2_x - [\tau - \pi/2_y - \tau]_n$, τ being varied from 0.1 to 0.5 ms. Exchange spectra[14] were measured with the usual NOESY sequence $\pi/2_x - d0 - \pi/2_x - \delta - \pi/2_y$ but with δ shortened to 0.1 ms so that no exchange in the form of cross-peaks was observed. 1028 points and 256 increments were measured in quadrature detection and sine-bell weighting function was used in both directions. ^{1}H magic angle spinning (MAS) spectra were measured in a 8 mm rotor with the spinning frequency 2, 5, and 8 kHz. ^{23}Na and ^{35}Cl NMR spectra and relaxations were measured with a 5 mm broadband probe, using 2048 points in quadrature detection. Inverse-recovery (T_1) experiments used the usual pulse sequence

$\pi_x - d - \pi/2_x$ with d incremented. Transverse ($\mathbf{T_1^1}$) relaxation was measured with the standard $\pi/2_x - (\tau/2 - \pi_{\pm y} - \tau/2)_n$ sequence, τ being 1 ms. Double quantum ($\mathbf{T_2^3}$) relaxation was measured with the sequence $\pi/2_x - \delta - \pi_x - \delta - \pi/2_\varphi - (\tau/2 - \pi_{\pm y} - \tau/2) - \pi/2_\varphi$, with $\delta = 0.2$ ms and $\tau = 1$ ms (φ means proper phase cycling for DQC selection).

Local order of the PDADMAC chain

^{1}H NMR had to be used exclusively due to sensitivity as the concentration of the DADMAC groups used in this study was $1 - 5 \times 10^{-3}$ mol/L. In addition to the previously reported[6] transverse relaxation, the following methods probing the local order were used: double-quantum coherence (DQC) evolution[10], pseudo-solid-echo (PSE) evolution[11], solid-echo (SE) evolution[12,13], exchange spectra[14], magic angle spinning (MAS).

DQC evolution. The result compared with transverse decay is shown in Figure 1.

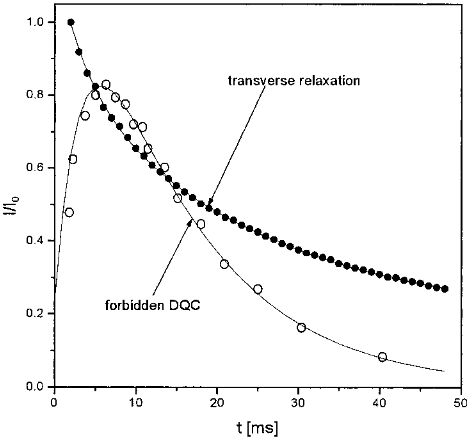

Figure 1. Time dependence of DQC (indirectly detected) and transverse magnetization of *N*-methyl protons in PDADMAC (2.0×10^{-3} mol/L in D_2O, 300 K)

The existence of DQC in a magnetically isolated methyl group is a clear evidence of a hindering[10] of the overall methyl motion, probably leading to residual dipolar interactions. The course of DQC decay indicates that only some of the groups detected in transverse magnetization give rise to DQC.

PSE evolution. Pseudo-solid-echo decay was measured under the same conditions as in the previous case. The results, compared to transverse decay, are shown in Figure 2.

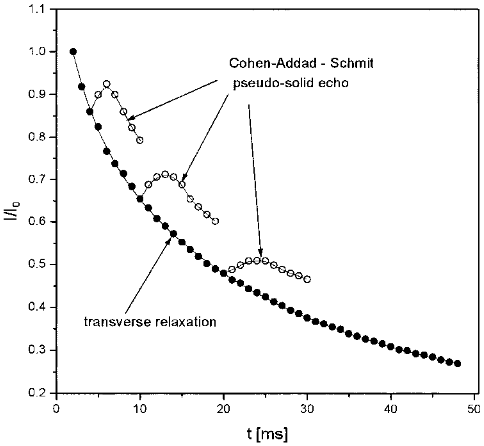

Figure 2. PSE decays compared with transverse relaxation decay in *N*-methyl protons in PDADMAC (2.0×10^{-3} mol/L in D_2O, 300 K)

The existence and course of PSE decay clearly indicate the presence of residual static dipolar interactions, i.e. motion not only hindered but possibly restricted (for discussion, see below). The decreasing intensity of PSE at longer times also indicates that some of the groups suffer lower hindering[6].

SE evolution. The solid-echo response should decay exponentially, $I = I_0 \exp(-R_{2e}t)$, R_{2e} being

$$R_{2e} = \frac{\overline{\omega^2} J(0)}{4}\left[1 - \frac{\tanh(\tau/\tau_c)}{\tau/\tau_c}\right], \tag{5}$$

where τ_c is the correlation time of main motion and the remaining terms are the dipolar interaction and the zero-frequency spectral density. Figure 3 compares semi-logarithmic time dependences of transverse and SE intensities. Non-linearity of the former dependence was recently[6] suggested to be a sign of a mobility distribution in *N*-methyl groups. Non-linearity (although slighter) of the SE dependence indicates a distribution either of τ_c or of residual dipolar interactions (or both).

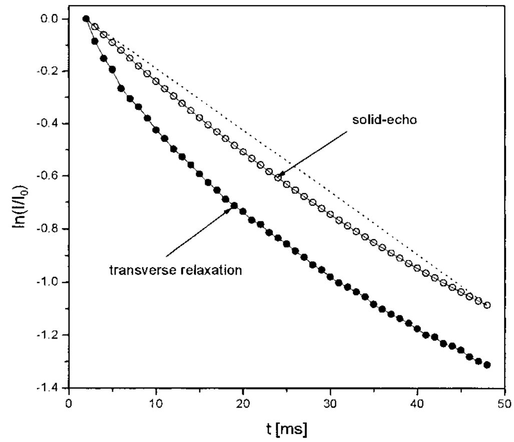

Figure 3. SE decay compared with transverse relaxation (logarithmic scale) in *N*-methyl protons in PDADMAC (2.0×10^{-3} mol/L in D_2O, 300 K).

2D-exchange spectra. As shown by Ernst et al.[14] and Spiess et al.[15], the ratio of the diagonal and transverse width of a diagonal peak in exchange spectra under very short mixing times reflects the extent to which residual dipolar interactions take part in the overall broadening of the signal. Figure 4 shows the *N*-methyl diagonal peak of PDADMAC under 0.1 ms mixing time (no cross-peak is observed). The spectrum could not be obtained with a better resolution than 5.86 Hz/point because of fast transverse decay during the evolution period. Therefore, the contours were artificially smoothed using spline functions and the ratio of the diagonal-to-transverse width was extracted for each contour. The results are given in Figure 5.

The ratio strongly depends on the contour level showing clear contribution of residual static dipolar interactions at the base of the peak but virtually no such effect near to the summit. This again is a clear sign that components of the signal (and corresponding groups) are variously affected by dipolar interactions.

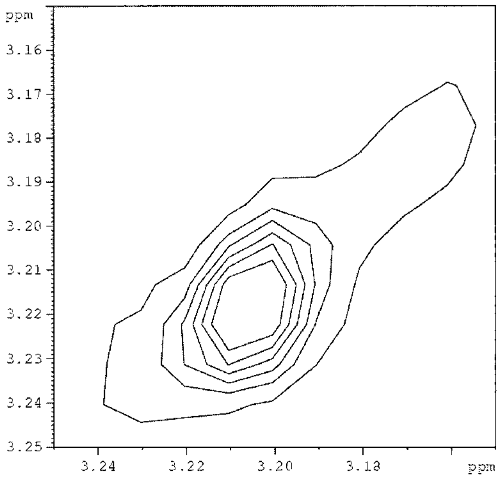

Figure 4. Diagonal peak of *N*-methyl protons in the raw 2D-exchange spectrum of PDADMAC.

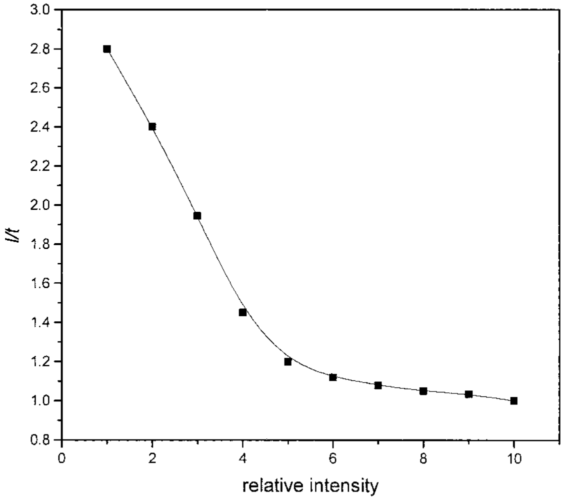

Figure 5. Ratio of longitudinal to transverse width of the diagonal peak contours at various intensity levels (*N*-methyl signal of PDADMAC, 2×10^{-3} mol/L in D_2O, 300 K).

^{1}H MAS spectra. Rotation under magic angle increases the absolute intensity of the *N*-methyl signal up to 3.5 times. Comparing this value with the almost tenfold increase, which can be achieved by increasing the ionic strength of the solution[6], one can see that residual dipolar interactions are not the main source of broadening.

Dynamic order of PDADMAC backbone. In accord with the recently obtained independent results[6], the experiments reported here reflect a broad distribution of dynamic states expressed in a variety of dynamic and dipolar broadening. The latter are usually connected with restrictions of motion, but it has to be stressed that they apply to space-time rather than space only. As shown for similar cases in one of our earlier works[9], the transverse magnetization decay can be approximated by the formula

$$M_x(t) \cong M_x(0)\exp\left[-\frac{\omega_D{}^2\tau_c{}^2}{1+\omega_D{}^{-2}\tau_R{}^{-2}}[t/\tau_c+\exp(-t/\tau_c)-1]\right], \tag{6}$$

according to which the impact of the dipolar broadening $\omega_D{}^2$ depends on the correlation times of local (τ_c) and semilocal (τ_R) motions. In the present experiments, we have clearly shown that there is a distribution of dipolar broadening in the signal. We thus can conclude that there is also a distribution of dynamic states. Therefore, we can conclude that there is not much dynamic order in the sense of motional correlation in the polymer backbone of PDADMAC.

Semilocal order of the PDADMAC counterions.

Assuming the polyion to be a stiff rod and using the Poisson-Boltzmann equation

$$-\varepsilon_0\varepsilon_r\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left[r\frac{\mathrm{d}\psi(r)}{\mathrm{d}r}\right]=\sum_i z_i e n_i(b)\exp\left[-\frac{z_i e\psi(r)}{k_B T}\right], \tag{7}$$

one can simulate the radial distribution of the counterions $\rho(r)$,

$$\rho(r)=\rho\exp[-z_i e\psi(r)/k_B T] \tag{8}$$

as shown in Figure 6 for various mean charge distances d and for the concentration of charge units 1×10^{-3} mol/L. NMR cannot give the experimental $\rho(r)$ but it can, with the help of the HWP model[16,17] of spin-3/2 quadrupolar relaxation, the value of the probability P

$$P=\int_a^b\rho(r)dr \tag{9}$$

of finding the counterion in the cylindrical area up to a certain radius b not very distanced from the surface of the polyion. According to the HWP model, P is in close relation with the so-called relaxation increment ΔR_2:

$$\Delta R_2 = (2\pi^2/3)[J(0) - J(2\omega_0)] = (\pi^2/20)\overline{\chi_Q}^2 P^2 \tau_{\mathrm{rad}}/(1 - S_2) \qquad (10)$$

where $J(x)$ are the spectral densities at the frequency x, χ_Q is the quadrupolar coupling constant,

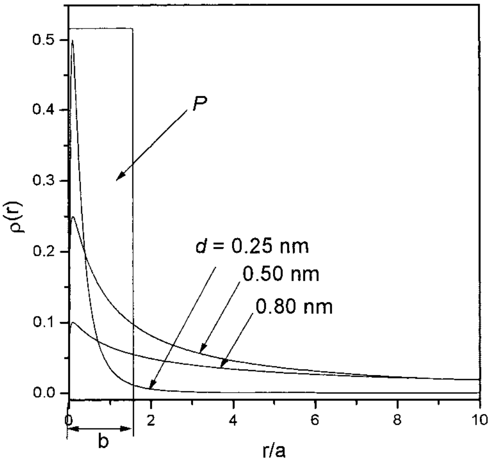

Figure 6. Simulated radial counterion density distribution for a rod-like polyion (5×10^{-3} mol/L) with the indicated distance d of its charges using Equations 7 and 8.

τ_{rad} is the correlation time of diffusion out of the polyion area S_2 is an order parameter (which can be neglected in our case). Owing to the fact that τ_{rad} steeply increases with decreasing concentration, ΔR_2 is a very sensitive measure of the dependence of P^2 on concentration. In low-molecular-weight electrolytes as well as in polyions with lone charged groups, P^2 steeply decreases at concentrations below 5×10^{-3} mol/L and, accordingly, ΔR_2 either decreases or remains constant. In densely charged polyions, the phenomenon of the so-called counterion condensation forces P^2 to stay constant or decrease only slightly, which leads to a sharp increase in ΔR_2 at low concentrations.

ΔR_2 is not quite easy to obtain, in particular if the counterions are Cl^- or Br^- anions. In principle, there are two ways. The first one exploits the empirical fact that, for small ions containing nuclei such as ^{7}Li, ^{23}Na, ^{35}Cl, and ^{81}Br, the longitudinal relaxation is usually almost exactly monoexponential,

$$<I_z(t)> = <I_z(0)> \exp(-R_1 t) \qquad (11)$$

and the classical expression for the transverse ($\mathbf{T_1}^1$) relaxation thus can be modified:

$$<I_x(t)> + i <I_y(t)> = [<I_x(0)> + i <I_y(0)>]e^{-i\omega t}\{\frac{3}{5}\exp[-(J(0)+R_1/2)t] + \frac{2}{5}\exp[-R_1 t]\} \qquad (12)$$

The other way exploits the fact, that $\Delta R_2 = R_{23}$, the latter term being the relaxation rate of the double-quantum coherence (third-rank second order tensor $\mathbf{T_2}^3$), which is experimentally accessible in a limited number of cases, however.

Figure 7 shows the concentration dependences of ^{35}Cl ΔR_2 values for a number of DADMAC based polyions with gradually decreasing charge densities achived by interleaving the charged DADMAC groups with sequences of neutral acrylamide groups.

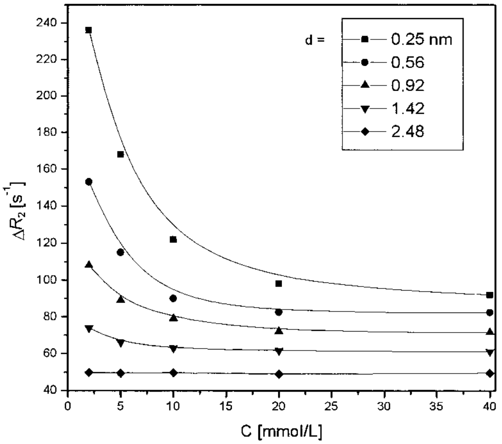

Figure 7. Experimentally obtained concentration dependences of ΔR_2 derived from ^{35}Cl NMR relaxation of the Cl^- counterions in the solutions of DADMAC-AA copolymers (D_2O, 300 K)

As one can see, the steep increase of ΔR_2 at concentrations below 5×10^{-3} mol/L is detected in the cases of relatively dense charge on the polyion, where counterion condensation is predicted by the Poisson-Boltzmann equation. Quadrupolar relaxation of the counterions thus can serve as an efficient probe into the semilocal order of the counterion cloud in this case.

Conclusions

^{1}H NMR double-quantum coherence, pseudo-solid-echo and solid-echo relaxation evolutions as well as 2D-exchange spectra and magic-angle-spinning ^{1}H NMR spectra revealed the existence of both dynamic (homogeneous) broadening and residual static dipolar interactions in a dilute solution (concentration of charged groups below 5×10^{-3} mol/L) of PDADMAC. Thus substantial hindering of skeletal motion must be present. However, the existence of a broad distribution of both homogeneous and inhomogeneous interactions suggests rather a lack of dynamic order in a PDADMAC chain in spite of the possibility to assign a substantially nonzero value of the order parameter S_2 to most of the DADMAC groups. In contrast to it, ^{35}Cl NMR relaxation methods (longitudinal, transverse and DQC) combined to calculated value of ΔR_2 reveal a substantial semilocal order of the density distribution of the counterion cloud (counterion condensation) in dilute solutions provided that the polyion is densely charged. Quite analogous results were obtained for complementary polyions such as sodium polymethacrylate.

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