Cooperative Interactions of Unlike Macromolecules: 3. NMR and Theoretical Study of the Electrostatic Coupling of Sodium Polyphosphates with Diallyl(dimethyl)ammonium Chloride−Acrylamide Copolymers

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Electrostatic coupling of sodium polyphosphates (polymerization degrees 15 and 65) with statistical copolymers of diallyl(dimethyl)ammonium chloride (DADMAC) and acrylamide (AA) of variable charge densities was studied using theoretical models, quantum chemical calculations, ^{1}H and ^{23}Na NMR spectra, relaxations, and pulsed-gradient-stimulated-echo (PGSE) experimental methods. Sodium polyphosphates with polymerization degrees 15−65 are readily coupled with DADMAC−AA statistical copolymers, containing 8−73% mol of the DADMAC ionic groups. The quantum-chemical prediction that even polycations with low density of ionic groups can be linked to densely charged polyphosphates in a ladder-like fashion is in accordance with the experimental results. Despite the predicted decrease in stabilization energy with increasing coupled sequence, the systems show a definitely cooperative behavior with the polyphosphate sequence of about 15 monomeric units, already sufficient for the full effect. Longer polyphosphate chains and higher charge densities on the DADMAC−AA copolymer cause a theoretically predicted pseudo-irreversible coupling in less advantageous positions (*parking problem*) leading to larger complex particles and slightly lower coupling degrees. As predicted by theory, this effect can be alleviated by a slight increase in the ionic strength. This effect is a further evidence of a true (or second-order, nonlinear) cooperativity in the system. Electrostatic energy is clearly an important factor in the over-all Gibbs energy balance but the driving force of cooperative coupling is probably the entropy gain caused by liberation of the small Na^+ and Cl^- counterions and a part of the hydrating water molecules.

Introduction

Cooperative interactions, which are known to be crucial in the self-assembly of macromolecules into functional supramolecular complexes, are of growing theoretical[1−7] as well as experimental[8−10] interest. Few authors have put them to a systematic and detailed scrutiny, however. Our recent studies[11,12] of electrostatic coupling of complementary polyions or ionomers, apparently a simple case of cooperative self-assembly, indicated a competition of reversible (enthalpy and entropy) as well as irreversible or pseudo-irreversible (kinetics, microphase separation) factors. Strong cooperativity in the interaction of complementary polyions, both relatively well-matched (polyphosphates with poly[2-(trimethylammonio)ethyl methacrylate chloride]-*block*-poly[(*N*-(2-hydroxypropyl)methacrylamide)][11]) and as apparently mismatched in ion distribution (poly(styrenesulfonate)s with statistical diallyl(dimethyl)ammonium chloride−acrylamide copolymers[12]), indicated that the entropy change due to liberation of small counterions and partly water molecules is the main driving force of the process. The complexity of various factors influencing polyion coupling, indicated by our results, calls for a much wider exploration of the subject. We thus plan a broad systematic study varying the chemical nature of the ionic groups and the density of their distribution in the polymer as well as the flexibility and hydrophilicity of the polyanion backbones. Along with polyphosphates, poly(vinylbenzenecarboxylic acid), poly(acrylic acid), poly(methacrylic acid), poly(glutamic acid) anions are to be explored. In this part of the study, we present an experimental as well as theoretical investigation of the electrostatic coupling of statistical copolymers of diallyl(dimethyl)ammonium chloride (DADMAC) with acrylamide (AA), already studied[12−17] in connection with poly(styrene sulfonates), with commercially available sodium polyphosphates (phosphate glasses) of a defined polyion length. The coupling is schematically shown in Scheme 1.

Experimental Section

Sample Preparation. 0.02% wt solutions of poly{[*N*-diallyl(dimethyl)ammonium chloride]−*co*-acrylamide} (COP*XX*, *X* denoting the mol % of DADMAC) and sodium polyphosphate glasses (PG15 and PG65, Sigma products S 6003 and S 6253, used as delivered) in D_2O or 0.05, 0.1, 0.2, and 0.5 M K_2SO_4 in D_2O were prepared by dissolving the given product to 1% wt solution in D_2O and diluting it to 0.02% by the appropriate medium. The complexes were prepared by a slow dropwise addition of the PG*XX* solution to a vigorously magnetically stirred solution of COP*YY*, the ratio of both components being one phosphate group per one DADMAC group. The mixing

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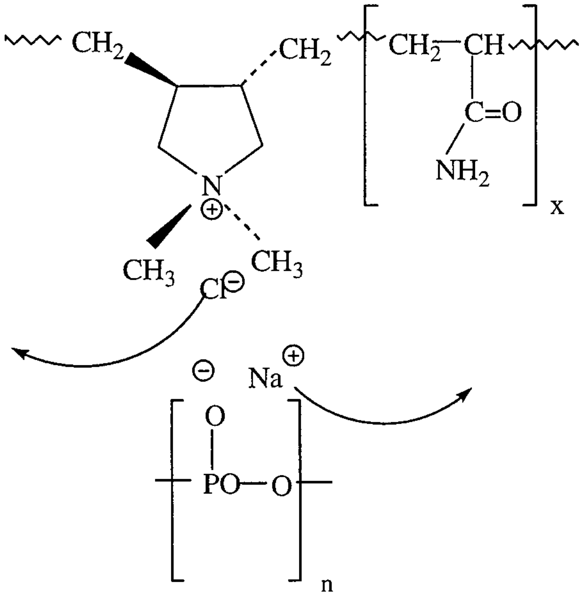
SCHEME 1



and storing was done at ambient temperature (295 K) and the solutions were measured within 6 h after preparation. Some of the samples were measured again after two or three days, some of them showing mobility changes in their PAA part.

NMR Measurements. ^{1}H and ^{23}Na spectra and relaxations were measured with a Bruker Avance DPX300 spectrometer (^{1}H resonance frequency 300.13 MHz), using a multinuclear broad-band probehead (minimum 640 scans per one spectrum) for ^{23}Na, or inverse *z*-gradient multinuclear probehead for ^{1}H spectra and PGSE experiments in extremely dilute solutions (minimum 800 scans per one spectrum). In ^{1}H spectra, the residual HOD signal had to be suppressed using the Watergate pulse sequence[20,21] attached to all the other sequences used. All methods of zero, single, and multiple quantum coherence relaxation measurement and evaluation were described in our previous studies.[11,18,19] PGSE experiments were done using the Stejskal-Tanner sequence[22] with constant delays and variable *z*-field gradient (12.5 to 50 G cm^{-1}). Trial ^{1}H MAS NMR spectra were measured at 15 kHz with a Bruker DSX200 spectrometer using ZrO rotor with a spacer; due to very poor signal-to-noise ratio, 8640 scans (12 h experiment) had to be collected for one 1D spectrum. Very poor spectra unsuitable for quantitative intensity evaluation were obtained.

From ^{23}Na NMR relaxation, the coupling degree α was obtained as in previous studies,[11,18,19] i.e., using the formula

$$\alpha = \frac{R_2 - R_{2F}}{R_{2B} - R_{2F}}$$

where R_2, R_{2F}, and R_{2B} are relaxation rates in the observed system and in the equivalent solutions of NaCl and the parent polyphosphate, respectively.

Quantum Chemistry Calculations. The structures of lithium polyphosphates, DADMAC−A copolymers and of the corresponding 1:1 coupling products were calculated using the MNDO method in the Gaussian 98 program package.[23] For the dimeric coupling product, the optimized molecular structure was recalculated using the DFT method at the B3LYP/6-31G(d) level, finding no significant changes in the optimal geometry. All calculations were done in C_1 symmetry.

Theory and Simulations

Mathematical Model of Reversible and Pseudo-Irreversible (kinetically controlled) Cooperative Coupling in the Presence of Added Free Ions. Let us assume an electrostatic coupling of two equally *n*-valent complementary polyions $\mathbf{Ca}_n$ and $\mathbf{Ac}_n$, where **C**, **a**, **A**, and **c** denote the polycation, counteranion, polyanion, and countercation, respectively. For simplicity, consider ordered coupling only and let the rate constants of coupling and decoupling depend only on the number of already coupled neighboring groups. These simplifications facilitate mathematical description and give a clearest image of the interesting cooperative effects.

Let us consider first a purely reversible coupling, i.e., equilibrium states. Assuming ordered coupling starting always with the respective first (or last) ionic groups, we can write:

$$\mathbf{Ca}_n + \mathbf{Ac}_n \overset{K_1}{\rightleftharpoons} \mathbf{Ca}_{n-1}\mathbf{Ac}_{n-1} + \mathbf{a} + \mathbf{c}$$

$$\mathbf{Ca}_{n-j+1}\mathbf{Ac}_{n-j+1} \overset{K_j}{\rightleftharpoons} \mathbf{Ca}_{n-j}\mathbf{Ac}_{n-j} + \mathbf{a} + \mathbf{c}$$

We are interested in the effect of an added electrolyte **ca** (e.g., NaCl if $\mathbf{c} = \mathrm{Na}^+$ and $\mathbf{a} = \mathrm{Cl}^-$) on the coupling degree α. Such an addition could in fact have a 2-fold nature: (i) considering the coupling as an ordinary reversible reaction, the added ions **c** and **a** simply shift the equilibrium to the left according to K_j (without affecting the value of K_j); (ii) considering the coupling as an electrostatic interaction, the added ions increase the ionic strength and thus have a screening effect, i.e., the value of K_j can be affected. Types (i) and (ii) are practically indistinguishable in experiment but can be separated in theory. In the following, we consider the effect (i) only.

For $[\mathbf{Ca}_n]_0 = [\mathbf{Ac}_n]_0$, $[\mathbf{a}] = [\mathbf{c}]$ always holds and the actual concentration of the counterion of one kind is always $[c] = c_{ad} + [\mathbf{a}] = c_{ad} + n\alpha[\mathbf{Ca}]_0$, where c_{ad} is the concentration of the added ions of one kind and α is the coupling degree. Inspecting the corresponding equilibria, the concentration of the coupling product with *j* groups already coupled is

$$[\mathbf{Ca}_{n-j}\mathbf{Ac}_{n-j}] = [\mathbf{Ca}_n]^2 \frac{\prod_{i=1}^{j} K_i}{[c]^{2j}} \tag{1}$$

and the coupling degree α (expressing the ratio of the coupled ionic groups to all original ones) is

$$\alpha = \frac{\prod_{j=1}^{n} j[\mathbf{Ca}_{n-j}\mathbf{Ac}_{n-j}]}{n[\mathbf{Ca}_n]_0} = \frac{S_n\{-1 + \sqrt{1 + 4Q_n[\mathbf{Ca}_n]_0}\}^2}{4nQ_n^{\;2}[\mathbf{Ca}_n]_0} \tag{2}$$

where

$$Q_n = \sum_{j=1}^{n} \frac{\prod_{i=1}^{j} K_i}{\{c_{ad} + n\alpha[\mathbf{Ca}_n]_0\}^{2j}} \tag{3a}$$

and

$$S_n = \sum_{j=1}^{n} \frac{j \prod_{i=1}^{j} K_i}{\{c_{\mathrm{ad}} + n\alpha[\mathbf{Ca}_n]_0\}^{2j}} \tag{3b}$$

Simulations of the dependences of α on the concentration of added ions c_{ad} using eq 2 and a sigmoidal dependence of K_n on n

$$K_n = K_1 + K_{\max} \exp\{-\exp[-\kappa(n-\beta)]\} \tag{4}$$

(where κ and β express the value and position of the highest slope) are for $\kappa = 0.3$ and $\beta = 5.0$ given in Figure 1, where the values of the parameters were chosen to be close to the experimental conditions and to clearly illustrate the cooperative effect. The increase in initial α as well as its resistance to added ions with higher n is a direct manifestation of cooperativity included in the model via eq 4.

More interesting effects can be predicted if the kinetics of coupling and decoupling is introduced. Assume a reaction of $\mathbf{Ac}_5$ with $\mathbf{Ca}_5$ at equal initial concentrations with and without added **c** and **a**. To avoid confusion due to rapidly increasing complexity of the reaction system, let us symbolize the products by vectors of the structure $\{a_1\ a_2\ a_3\ ....\}$, where the subscript i of the component a_i denotes the position of the anionic group in the polyanion and the value of a_i is either 0 for an uncoupled group or an integer between 1 an n denoting the position of the coupled cationic group in the polycation. Thus {00000} means the original five-valent polyanion, initially reacting to {10000} (statistical factor $\gamma = 4$), {01000} ($\gamma = 4$), {00100} ($\gamma = 2$), {20000} ($\gamma = 4$), {02000} ($\gamma = 4$), {00200} ($\gamma = 2$), {30000} ($\gamma = 2$), {03000} ($\gamma = 2$), and {00300} ($\gamma = 1$). The coupling, characterized by a rate constant k_1, is reversible, so that any of these products can produce the original components with a rate constant $k_{-1} = k_1/K_1$. Identifying the concentrations of the products with their symbols, we can write

$$\frac{\mathrm{d}\mathbf{Ac}_5}{\mathrm{d}t} = \frac{\mathrm{d}\mathbf{Ca}_5}{\mathrm{d}t} = -25k_1\mathbf{Ac}_5\mathbf{Ca}_5 + k_{-1}\mathbf{c}\cdot\mathbf{a}[\{10000\} + \{01000\} + \{00100\} + \{20000\} + \{02000\} + \{00200\} + \{30000\} + \{03000\} + \{00300\}] \tag{5}$$

The further development of the system is obvious if ordered coupling is strongly preferred by cooperativity. Thus both {10000} and {02000} produce {12000}, {01000} gives {01200}, etc., with a rate constant $k_2 > k_1$ and the reverse reaction has a rate constant $k_{-2} < k_{-1}$. We assume ordered coupling only and the same value of k_i and k_{-i} for any product containing $i - 1$ ionic couplings. The whole reaction scheme up to the final product {12345} is described by a system of 34 partly nonlinear differential equations, which have to be solved numerically. At larger cooperativity ($k_4 \gg k_1$, etc.), the system becomes stiff. In the simulations, we used the Adams-Moulton or Gear's BDF methods included in the IMSL library Fortran procedure IVPAG. The degree of cooperativity was expressed by a sigmoidal dependence of k_i on i analogous to eq 4, i.e.,

$$k_i = k_a + k_{\max} \exp\{-\exp[-\kappa(i-\beta)]\} \tag{6}$$

where $k_a = k_1$ and $k_{\max}$ is a variable parameter for the coupling reactions ($i = 2-5$), whereas $k_a = k_{-1}$ and $k_{\max} = -k_{-1}$ for the reverse cleavage reactions. The coupling degree α was considered to be "final" (denoted α_f) if $[\alpha_f(t_2)/\alpha(t_1) - 1] < 10^{-4}$, $t_2 = 2t_1$. Figure 2 shows the simulated dependences of α_f of $[\mathbf{Ca}_5]_0 = [\mathbf{Ac}_5]_0 = 10^{-3}$ mol/L, $k_1 = 1.0$ mol^{-1} s^{-1}, $k_{-1} = 10^{-3}$ mol^{-2} s^{-1}, $\kappa = 1.5$, $\beta = 3$, and $k_{\max} = 50$, 150, and 500. This illustrative example shows that smaller amounts of added ions (increased ionic strength) can have a beneficial effect on α_f at higher cooperativity. By closer scrutiny of the final concentrations of the individual products, one can see that this effect is brought about by increased reversibility of the early coupling stages, alleviating thus the tendency to pseudo-irreversible unfavorable couplings (in other words, easing the so-called *parking problem*). The effect is subtle in our case and disappears when giving the system a very long time to evolve. However, we believe that it should increase and become more stable for substantially larger n such as met in experiment.

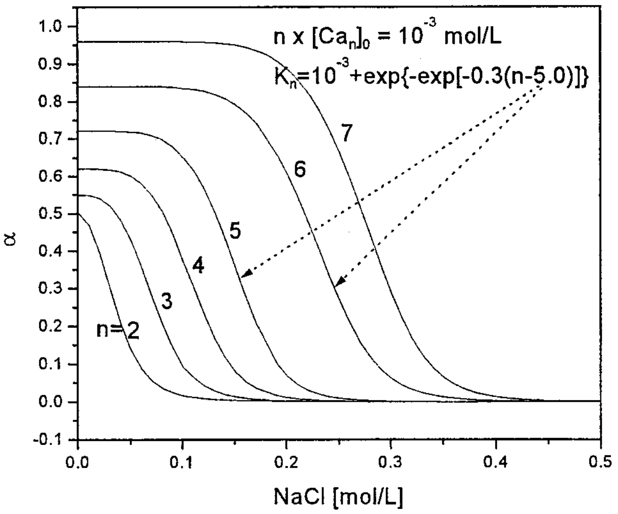


Figure 1. Simulated dependence of the degree of equilibrium coupling (α) of complementary polyions (concentration of ionic groups of one kind 10^{-3} mol/L) on the concentration of added monovalent electrolyte.

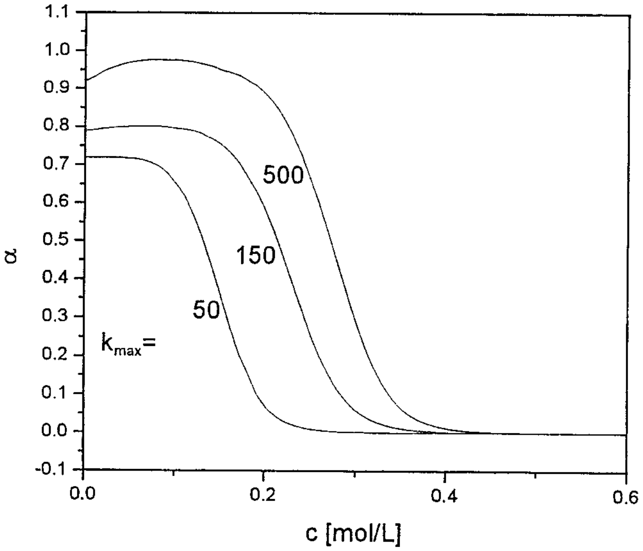


Figure 2. Simulated dependence of the degree of pseudo-irreversible coupling (α) of complementary penta-ions (concentration of ionic groups of one kind 10^{-3} mol/L) on the concentration of added monovalent electrolyte for increasing cooperativity ($k_{\max}$ in eq 4).

Quantum Chemical Simulations. The cooperativity of coupling could depend on the charge densities on the complementary polyions in two different ways:[12] (i) the entropy gain due to the liberation of small counterions increases with charge density because of the polyelectrolyte effect; (ii) a gross ion mismatch due to a large difference in charge densities could

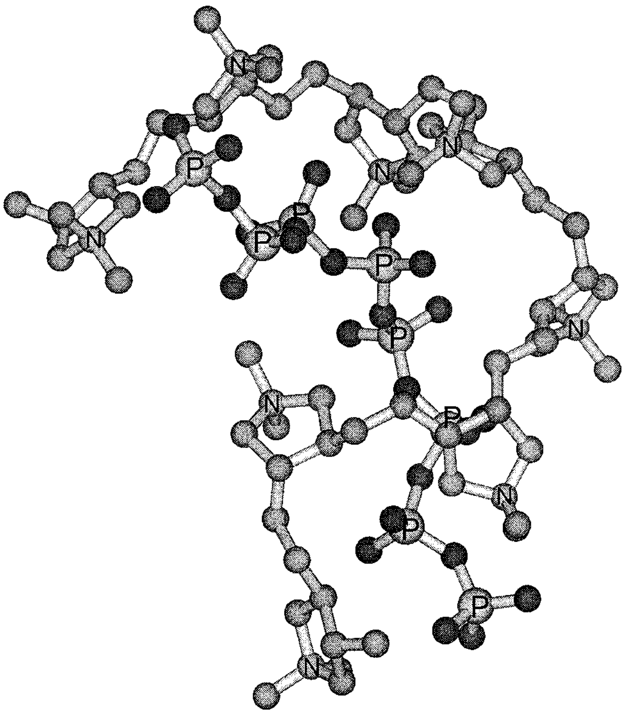


Figure 3. MNDO optimized structure of the complex of *hepta*-DADMAC with a *hepta*-phosphate (phosphorus and cation-bearing nitrogen atoms are signed by P and N, respectively).

lead to geometric impossibility of complementary ions to achieve contacts not only in ordered, ladder-like structures but even in chaotic *scrambled egg* structures. The latter case was assumed[12] for the coupling of poly(styrenesulfonates) with copolymers containing longer AA sequences interlaying between the ionic DADMAC groups. However, polyphosphates with as dense charge distribution as one can get in polyanions were shown[11] to be able to form ladder-like coupling products with apparently poorly matched polycations. Therefore, we simulated the structures of the coupling products of polyphosphates with DADMAC homopolymer and its copolymers, containing 1, 2, and 4 equally distributed AA units per one DADMAC group. Because of the size of the structures, the simulations up to the octamer were done using the semiempirical quantum-chemical method MNDO/2. However, the dimeric structure was re-optimized using a high-precision ab initio-DFT format. No substantial changes in molecular geometry or charge distribution in comparison with MNDO/2 were found so that no serious artifacts are produced by the latter method. Two examples of the optimized structures of coupling products are shown in Figures 3 and 4: octaphosphate with $[\mathrm{DADMAC}]_8$ (Figure 3) and heptaphosphate with $[\mathrm{DADMAC\text{-}AA}_4]_7$ (Figure 4). Both structures correspond to true energy minima and have to be considered to be stable. Figure 5 shows the main lowest distances between N and P atoms for $[\mathrm{PO}_3]_n[\mathrm{DADMAC{-}AA}_x]_n$, $x = 0, 1, 2, 4$ and $n = 1, 2,...0.8$. As can be seen, these distances are reasonably short, i.e., correspond to contact distances, and do not markedly change for increasing x or n. Thus interlaying DADMAC groups with AA groups does not produce a serious mismatch, according to the simulations. However, the stabilization energy per one bond, as also shown by Figure 5, steadily decreases with increasing n. This is in accord with our earlier findings on the coupling of polyphosphates with 2-(trimethylammonio)ethyl methacrylate copolymers.[11] According to quantum chemistry, stabilization energy thus is not the source of the cooperative effect in our case, even though its level is important in the over-all Gibbs energy balance of the coupling process.

Results and Discussion

Like poly(styrenesulfonates),[12] polyphosphates coupled in equi-ionic ratio with DADMAC−AA copolymers tend to flocculate and even precipitate at medium-low concentrations of the reactants. All NMR observations reported here thus had to be done at 0.02% wt concentrations of the reactants, which reduced the pool of observable nuclei to ^{1}H, ^{23}Na, and conditionally ^{31}P. Of these, ^{31}P was observable in the polyphosphates but gave no observable signal in their coupling products, probably due to extreme broadening.[11] For a single 1D ^{1}H NMR spectrum, at least 800 scans had to be collected with a highly sensitive inverse-detection probehead. Additionally, the residual HOD signal of the 99.9% D_2O used as the medium had to be suppressed using the Watergate sequence (simple presaturation was not sufficient). Accordingly, the Watergate suppression was added to all the other sequences used.

Due to extreme dilution of the samples, a number of techniques used in modern NMR more or less fail due to their poor sensitivity. In particular, ^{1}H MAS NMR with the spinning frequency 15 kHz gave a recognizable but very poor spectrum after 12 h of accumulation (8640 scans), which could be used for a qualitative demonstration of the presence of some residual quasi-static dipolar interactions in the spin system. Similarly, a double quantum ^{1}H NMR spectrum could be obtained after 12 h of accumulation but the poor quality of the spectrum excluded its quantitative use. Notwithstanding these difficulties, valuable information could be obtained using more conventional single quantum spectra as shown below.

Due to rather complex intensity changes observed in ^{1}H spectra, which will be discussed later, the coupling degree α could be established by a single method only, namely ^{23}Na NMR longitudinal relaxation,[11,12] as outlined in the Experimental part. Two remaining quantities discussed below, transverse relaxation rate R_{21} (leading term in a polyexponential decay) and hydrodynamic radius R_H, are related to *visible* ^{1}H NMR signals.

As in our previous papers,[11,12] PG*XX* means phosphate glass with *XX* ± 3 phosphate atoms and COP*YY* means DADMAC−AA statistical copolymer with *YY* % mol of DADMAC throughout the text.

Figures 6 and 7 show the coupling degrees α to be close to 1.0 and surprisingly insensitive to the DADMAC content both with PG65 and PG15. In contrast, the intensities of CH_3 (DADMAC) and CH_2 (AA), expressed relative to the corresponding intensities in the corresponding copolymer in 1 M NaCl, exhibit rather dramatic changes both with increasing content of DADMAC and between the PG65 and PG15 complexes. The same is true for the leading term in the transverse relaxation rate of the CH_3 groups.

The decrease in signal intensity (due to extreme broadening of a signal component) as well as increase in transverse relaxation rate of the visible signal is usually a sign of hindered mobility of the corresponding group. If the correlation time of the main motion of the group exceeds the inverse of the intensity of the main dipolar spin−spin interaction (expressed in frequency units), the transverse relaxation rate increases steeply and, in consequence, the signal broadens. If the broadening exceeds about 1 kHz, the signal is invisible due to sensitivity (the signal is drowned in noise) or other instrumental reasons. From the fact that only a part of the intensity is lost in all our

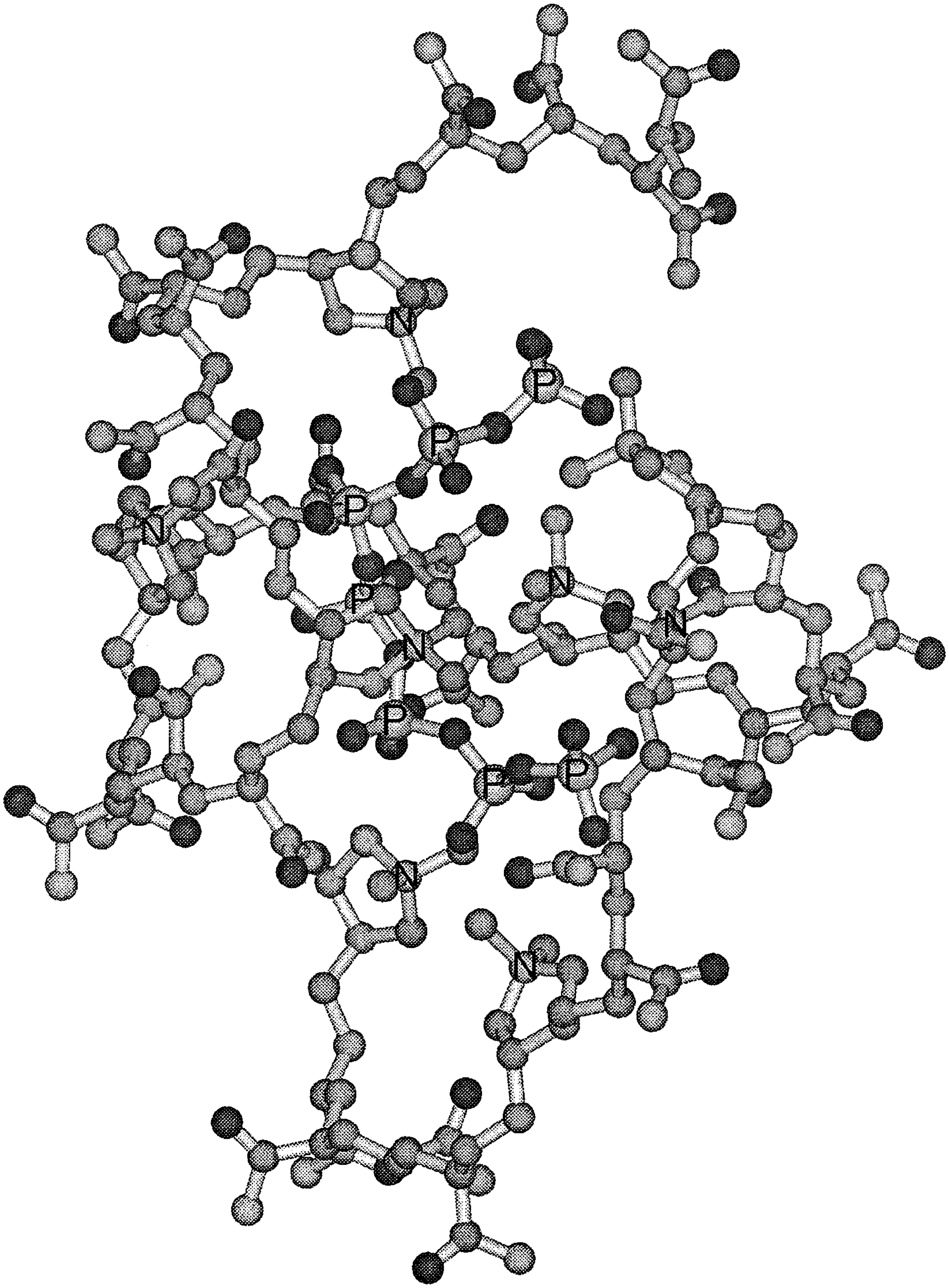


Figure 4. MNDO optimized structure of a complex of a *hepta*-DADMAC-*co*-AA oligomer (AA/DADMAC = 4) with *hepta*-phosphate (phosphorus and cation-bearing nitrogen atoms are signed by P and N, respectively).

experiments, a distribution of mobilities of analogous groups (such as CH_3) in the complex can be deduced. Such conclusion is also evidenced by (i) the polyexponential shape of the decay curves in transverse relaxation of the visible signal and (ii) the progressive narrowing of the visible signal during transverse relaxation. In accordance with expectation, the complexes with the largest loss of signal intensity (i.e., with the largest parts of relatively immobilized groups) also exhibit the largest relaxation rates of the visible signals. The spectroscopic behavior of the complexes of PG65 and PG15 is more complex, however.

A key to the understanding of this behavior can be found in the collective motion of the complex particles. As we have shown in our previous studies, the transverse magnetization of the nuclei influenced by the dipolar broadening ω_{Di} and by their local and collective isotropic motion (with the respective correlation times τ_{ci} and τ_R) decays according to the expression[18,19]

$$M_x(t) = M_x(0) \sum_i w_i \exp\left\{ -\frac{\omega_{Di}{}^2 \tau_{ci}{}^2}{1 + \kappa_i{}^2 \omega_{Di}{}^{-2} \tau_R{}^{-2}} [t/\tau_{ci} + \exp(-t/\tau_{ci}) - 1] \right\} \quad (7)$$

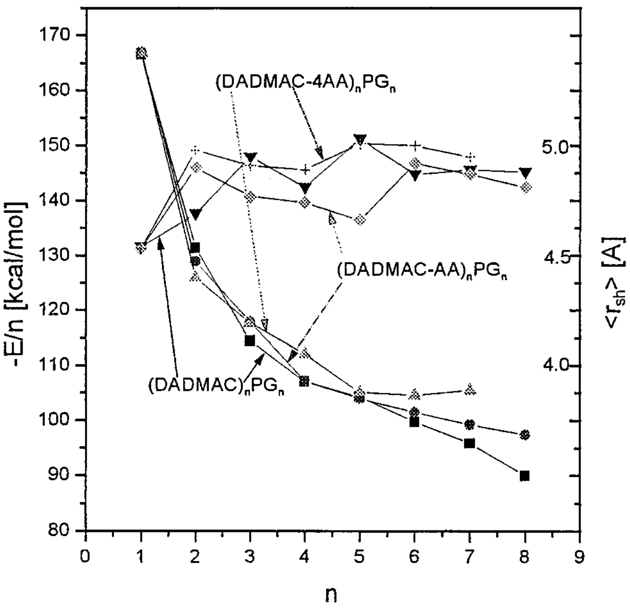


Figure 5. Stabilization energies (lower group) and mean shortest N−P distances (upper group) of MNDO-optimized complexes of $(\mathrm{DADMAC})_n$, $(\mathrm{DADMAC-AA})_n$, and $(\mathrm{DADMAC-4AA})_n$ oligomers with *n*-membered oligophosphates.

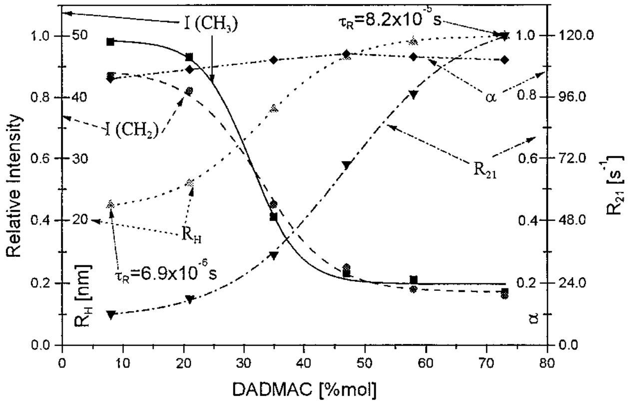


Figure 6. Intensities (relative to the corresponding COP*XX* solution in 1 M NaCl/D_2O) of the CH_3 (DADMAC) and CH_2 (AA) signals, transverse relaxation rates (leading term) R_{21}, coupling ratios α and hydrodynamic radii (PGSE) R_H in the coupling products of COP*XX* with PG65 (0.02% wt in D_2O, 300 K).

The dependence of the signal broadening on τ_R is approximately $1/[1 + \kappa^2\omega_{\mathrm{D}} - 2\tau_{\mathrm{R}} - 2]$, κ being an empirical constant > 50. If $\omega_{\mathrm{D}}\tau_{\mathrm{R}} < 1.0$, the influence of static dipolar broadening disappears, the signal narrows and is restored in the spectrum. For the given medium and temperature, τ_R can be deduced from the hydrodynamic radius of the complex particle, R_H, which can be obtained from the translation self-diffusion coefficient D_T, measured by PGSE, in the following way: according to Einstein-Stokes, $D_T = kT/(6\pi R_H\eta)$, η being viscosity at the given temperature T. The coefficient of rotational diffusion D_R, assuming a spherical shape, obeys the Debye expression $D_R = kT/(8\pi R_H^3\eta)$. Thus the correlation time of rotational diffusion τ_R is

$$\tau_R = \frac{1}{6D_R} = \frac{4R_H^{\ 2}}{3D_T} \tag{8}$$

The values of R_H and some indicative values of τ_R are shown in Figures 6 and 7. For the DADMAC content increasing over 35% mol, the complex particles containing PG65 increase whereas those of PG15 decrease in size. In the latter case, τ_R decreases below 10^{-6} s so that the collective motion is able to average out dipolar broadening of the order of 1.0 kHz. Consequently, there is only a small or vanishing intensity loss for the PG15 complexes and the relaxation rate is relatively low, too. In these cases, no real information about the local mobility can be obtained from NMR spectra unless all residual static spin interactions are removed, e.g., by dipolar decoupling or magic angle spinning. Unfortunately, neither of these techniques can be used with a high-sensitivity probehead.

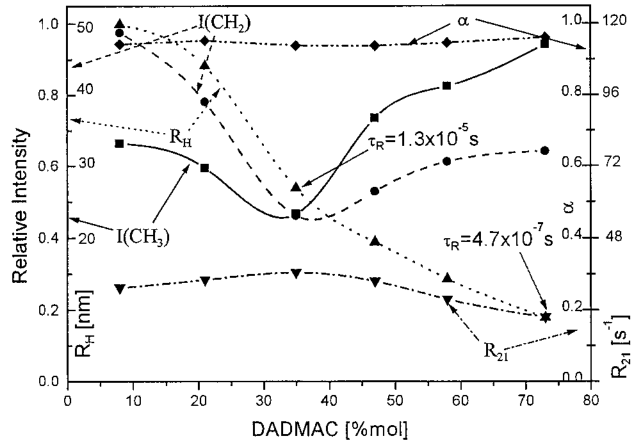


Figure 7. Intensities (relative to the corresponding COP*XX* solution in 1 M NaCl/D_2O) of the CH_3 (DADMAC) and CH_2 (AA) signals, transverse relaxation rates (leading term) R_{21}, coupling ratios α, and hydrodynamic radii (PGSE) R_H in the coupling products of COP*XX* with PG15 (0.02% wt in D_2O, 300 K).

If the DADMAC content is equal or lower than 35% mol, the value of R_H or τ_R could explain the low intensity loss in the complexes of PG65 but not those of PG15. In these cases, relatively high signal intensity and low relaxation rate indicate a less compact structure of these complexes. For PG65 and the DADMAC content exceeding 35%, quite the opposite must be the case. Higher charge density on the polycation (higher DADMAC content) thus probably leads to a more compact structure of the complex with either type of polyphosphate. The very different—in fact complementary—dependence of R_H on the DADMAC content for PG65 and PG15 is rather surprising. A possible explanation is the following. The copolymers with higher DADMAC contents have lower molecular weight[13] and tend to form somewhat smaller complexes[14−17] with poly(styrenesulfonate)s. Due to a weaker *parking problem* (or pseudo-irreversible nonoptimal alignment), PG15 probably tends to form molecular complexes, which are consequently smaller. In the case of PG65, first stages of electrostatic coupling are probably pseudo-irreversible, leaving larger phosphate as well as DADMAC sequences free. In the second stage, these sequences form larger particles. The latter tendency should be larger with higher-charge-density polycations, which is observed.

Another change of the patterns can be observed if PG15 is mixed with COP*XX* in a medium with high ionic strength, viz. 0.5 M K_2SO_4 in D_2O, as shown in Figure 8. The dependence of R_H on the DADMAC content is similar to neat D_2O but it is much flatter spanning a region from 10 to 14 nm. This corresponds to the rotational correlation time τ_R approximately from 0.7 to 1.9 × 10^{-6} s, i.e., the dynamic region in which most of weak static interactions are canceled by the collective tumbling of the complex particle. Consequently, the intensity loss in observable signals is lower than in neat D_2O for low

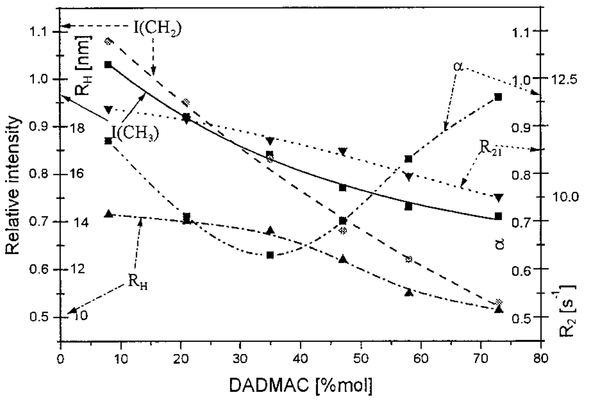


Figure 8. Intensities (relative to the corresponding COP*XX* solution in 1 M NaCl/D_2O) of the CH_3 (DADMAC) and CH_2 (AA) signals, transverse relaxation rates (leading term) R_{21}, coupling ratios α and hydrodynamic radii (PGSE) R_H in the coupling products of COP*XX* with PG15 (0.02% wt in 0.5 M K_2SO_4/D_2O, 300 K).

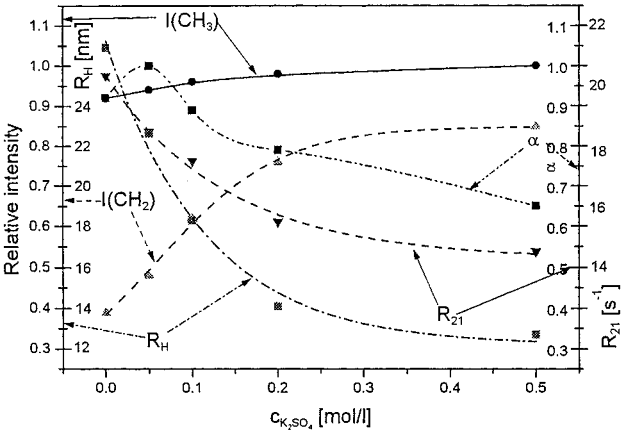


Figure 9. Intensities (relative to the corresponding COP35 solution in 1 M NaCl/D_2O) of the CH_3 (DADMAC) and CH_2 (AA) signals, transverse relaxation rates (leading term) R_{21}, coupling ratios α and hydrodynamic radii (PGSE) R_H in the coupling products of COP35 with PG15 in variously concentrated K_2SO_4/D_2O solutions (300 K).

DADMAC contents and so is the transverse relaxation rate (accordingly, the signals are perceptibly narrower). However, the intensity loss both for CH_3 and in particular CH_2 increases with increasing DADMAC content, in contrast to pure D_2O. Considering the calculated values of τ_R, there must be quite strong static interactions behind this loss, i.e., regions of structure with almost completely arrested internal motion. The only reasonable explanation appears to be that higher ionic strength of the medium leads to less haphazard coupling and thus better alignment to more compact structures. We already observed an analogous phenomenon in the study of coupling COP*XX* with poly(styrenesulfonate). When inspecting the coupling degree α, one can see an expectedly decreasing sensitivity to high ionic strength with increasing charge density on the polycation in the region 35−73% mol of DADMAC. However, the analogous increase in α for the ion groups content below 35% mol cannot be explained in this way.

For further exploration of the dependence of coupling mode and degree on ionic strength, we chose COP35 (where the highest sensitivity was detected). The results are given in Figure 9. As shown, the size of the complexes decreases with increasing ionic strength. The correlated decrease in the relaxation rate as well as the decrease in signal intensity (much steeper for AA CH_2 groups) should be due partly to removing the broadening static interactions by fast collective rotation and partly to the decreasing coupling degree. However, there is an interesting dependence of α on the increasing ionic strength: contrary to intuitive expectations, it starts increasing, goes through a maximum, and decreases as expected. This seemingly bizarre behavior is not limited to COP35 and PG15 but is rather general as seen by comparison with the coupling of COP58 and PG65 in Figure 10. Most plausible explanation of this phenomenon is the easing of the pseudo-irreversible coupling (i.e., of the *parking problem*) by the added ions as explained in the Theory part. Summarizing briefly, this interesting phenomenon is a direct consequence of the cooperative effect. In the absence of additional ions, the first random attachment of the polyions leads to a fast binding in a disadvantageous position; due to cooperativity, this binding is pseudo-irreversible, i.e., α is lowered. When the ionic strength of the medium is increased, cooperativity and pseudo-irreversibility of the first binding steps is decreased due to electrostatic screening and the reactants are thus allowed to find more advantageous, i.e., thermodynamically more stable, positions; hence, α is increased. At relatively high ionic strength, the electrostatic screening decreases the cooperativity of coupling so that α decreases again. The alleviation of the "parking problem" by a medium increase of ionic strength thus amounts to its experimental evidence.

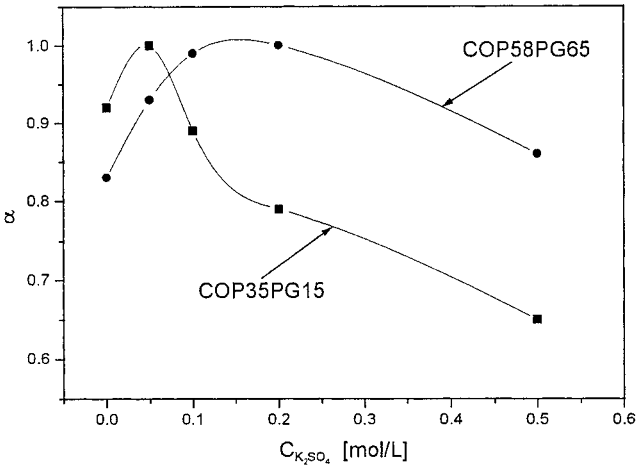


Figure 10. Coupling degrees α of products COP35PG15 and COP58PG65 achieved in media with different ionic strength (K_2SO_4/D_2O).

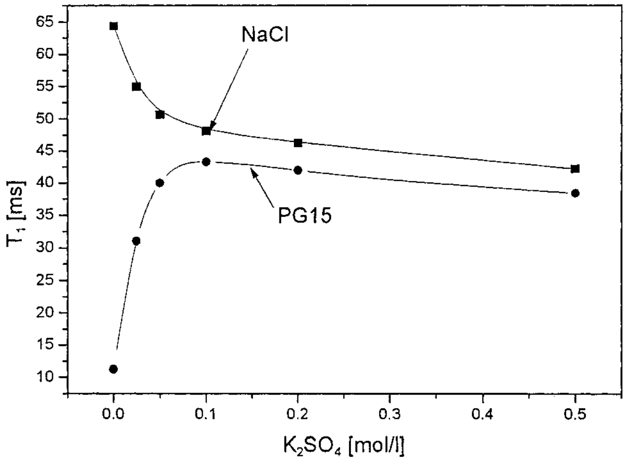


Figure 11. ^{23}Na T_1 relaxation times of 0.02% wt solutions of PG15 and the equimolar solutions of NaCl in different solutions of K_2SO_4 in D_2O (300 K).

Unfortunately, an exact study of this interesting effect is hampered by a decrease in the precision of α measured by NMR relaxation (or any other method based on the activity of liberated counterions) with increasing concentration of added ions. As illustrated in Figure 11, ^{23}Na relaxation times in NaCl (coupling side-product) and original PG15 are inconveniently approximated at K_2SO_4 concentrations higher than 0.05 mol/L. The reason is (i) increased relaxation rate of the free ions due to more frequent collisions with other ions in the first case, and (ii) exchange of Na for K ions in the second case, liberating Na ions into solution. Above the concentration of K_2SO_4 0.1 mol/L, the usual 2−5% relative error in T_1 corresponds to 16−40% relative error in α. Despite the smoothness of the α dependences in Figures 8−10, their detailed shape has to be considered with caution. However, as the first increase in α starts at low ionic strength, where the error in α is about 5%, we believe the observed effect to be at least qualitatively established.

Conclusions

We have demonstrated that sodium polyphosphates with polymerization degrees 15−65 are readily coupled with DADMAC−AA statistical copolymers, containing 8−73% mol of the DADMAC ionic groups. The quantum-chemical prediction that even polycations with low density of ionic groups can link to densely charged polyphosphates in a ladder-like fashion is in accordance with the experimental results. Despite the predicted decrease in stabilization energy with an increased coupled sequence, the systems show a definitely cooperative behavior with the polyphosphate length about 15 monomeric units already sufficient for the full effect. Longer polyphosphate chains and higher charge densities on the DADMAC−AA copolymer cause a theoretically predicted pseudo-irreversible coupling in less advantageous positions (*parking problem*) leading to larger complex particles and slightly lower coupling degrees. As predicted by theory, this effect can be alleviated by slight increase in the ionic strength. This effect is a further evidence of a true (or second-order[12]) cooperativity in the system. As in the previously studied systems,[11,12] the electrostatic energy is clearly an important factor in the over-all Gibbs energy balance. However, the driving force of cooperative coupling must be again the entropy gain caused by liberation of small Na^+ and Cl^- counterions and a part of the hydrating water molecules.

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