NMR Study of the Shell Dynamics and Ionization States of Sodium and Lithium Salts of Poly(methyl methacrylate)-*block*-poly(acrylic acid) Micelles in D_2O

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Received August 20, 1996; Revised Manuscript Received December 27, 1996[⊗]

ABSTRACT: ^{1}H, ^{7}Li, and ^{23}Na NMR spectra and relaxations were measured with Li and Na salts of poly(acrylic acid) (PAAcLi, PAAcNa) and of poly(methyl methacrylate)-*block*-poly(acrylic acid) (PMMA-PAAcLi, PMMA-PAAcNa) micelles at 300 K in D_2O at concentrations from 0.5 to 0.005% w/w. The results show a close similarity in the dependences of polyacrylic chain mobility in PAAcM and PMMA-PAAcM (M = Na, Li) on concentration and indicate that chain stiffness increases with dilution. The analogy of behavior between free linear polyacrylic chains and those bound to a rigid micellar core, which cannot be locally diluted, indicates that the collective interchain and intermicellar interactions have an important effect on the local state on the level of individual monomeric units.

Introduction

In an extensive study using NMR, SANS, and light scattering methods, we are investigating micellization of amphiphilic block copolymers in water and, in particular, solubilization interactions of the resulting polymer micelles with organic substances. The ultimate target of this study is to find optimal copolymer and micellar structures for a controlled uptake and release of solubilized substances with bioactive properties in water.

In our previous paper,[1] we reported on the micellization of the poly(methyl methacrylate)-*block*-poly(acrylic acid) (PMMA-PAAc) copolymers in water or D_2O and on various interactions of the micelles under appropriate conditions. Among other interesting effects, emergence of unimer (or single chain) molecules was observed for higher neutralization degrees of the PAAc blocks and under dilution. As we suspected,[1] this phenomenon is not general and occurs only with rather broad molecular weight distributions of the copolymer. In such cases there occurs even higher chemical composition heterogeneity in the block copolymer and hence higher contents of the methacrylate-poor chains, which, after micellization of the copolymer, presumably are not strongly anchored in the micellar core. With lower polydispersity values, M_w/M_n < 1.4, no significant amount of unimer molecules was observed even with quite short copolymers and under extreme dilution. Another interesting and quite general phenomenon was observed, however, which can be interpreted as a strong dependence of the mobility of the chains of the micellar shell on their neutralization degree and, in particular, on the dilution of the system.

This phenomenon can be divided into two branches. *First*, with concentrations of the block copolymer increasing above 0.5% w/w, progressive immobilization of the shell chains leading to substantial broadening of the NMR signals of their protons can be observed, in particular with their higher neutralization degrees. This effect can be easily interpreted as increasing intermicellar counterion sharing and formation of a "physical net" well-known in the field of linear polyelectrolytes. *Second*, with the concentrations decreasing below 0.2% w/w, more complicated, but generally analogous, changes in the mobility of shell chains can be observed, which should be associated with the changing bonding states of the counterions. As both the mobility and the ionization state of the shell chains influence the dynamics of solubilization,[1] we considered this phenomenon worth this separate study.

Theory

Relaxation of the ^{7}Li and ^{23}Na Counterions and Their Bonding States. Suppose there are only two different bonding states of the counterions, e.g. solvent-separated ion pairs and free ions, in rapid exchange. The time change of the reduced density matrix of the spin states of such quadrupolar ($I = {}^3/_2$) nuclei can then be described (cf. e.g.[2]) by the expression

$$d\sigma_{X,i}/dt = (i/h)[\sigma, \mathbf{H}] + [[F,\sigma], F]/2\tau \qquad (1)$$

where $\sigma_{x,i}$ is the ith basis function of the xth state, **H** is the Hamiltonian, F is the Alexander nuclear transfer function, τ is the exchange correlation time, and the last term in eq 1 contains a double commutator. It must be stressed that this expression and all others derived from it are based on the assumption of adiabatic ("instant") transfer between the corresponding states and of vanishing coupling between exchange and relaxation. Such assumption of zero crossing between states is quite common in spectroscopy in general but could be somewhat wrong in our case. Ignoring this doubt, we can write the Solomon-like equations

$$d\sigma_{F,i} = \Sigma_j (R^F{}_{ij}\sigma_{Fj}) - (\sigma_{F,i}/\tau_F) + (\sigma_{B,i}/\tau_B) \qquad (2a)$$

$$d\sigma_{B,i} = \Sigma_j (R^B{}_{ij}\sigma_{Bj}) - (\sigma_{B,i}/\tau_B) + (\sigma_{F,i}/\tau_F) \qquad (2b)$$

where the subscripts and superscripts F and B refer to the free and bound state, respectively and the τ's are the respective lifetimes. R_{ij} is the corresponding element of the Redfield relaxation matrix. As the diffusion exchange of ions can be considered to be fast even in comparison with rapid quadrupolar relaxation, we can write for the longitudinal relaxation

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S0024-9297(96)01257-0 CCC: $14.00

$$\Delta I_z(t) = \Delta I_z(0)\ [(1/5)\exp(-R_{11}t) + (4/5)\exp(-R_{12}t)] \tag{3}$$

with

$$R_{1i} = p_F r_{1Fi} + p_B r_{1Bi} \tag{3a}$$

where p_F and p_B are the respective populations of free and bound ions and

$$r_{1X,j} = \chi_Q J_{jX}(\omega) \tag{3b}$$

where X = B, F and $j = 1, 2$.

The quadrupole coupling constant is $\chi_Q = (1/10)(1 + \eta^2/3)(e^2qQ/h)^2$, and the spectral density $J_{jX}(\omega) = \tau_X/(1 + (j\omega\tau_X)^2)$ if the correlation function is a simple exponential (cf. below). In analogy, for the transverse relaxation

$$\Delta I_+(t) = \Delta I_+(0)\exp(-i\omega t)\ [(3/5)\exp(-R_{21}t) + (2/5)\exp(-R_{22}t)] \tag{4}$$

$$R_{2i} = p_F r_{2Fi} + p_B r_{2Bi} \tag{4a}$$

$$r_{2Xj} = 0.5\chi_{QX}\{J_{(j-1)X}(\omega) + J_{jX}(\omega)\} \tag{4b}$$

For free ions, $r_{1F1} = r_{1F2} = r_{2F1} = r_{2F2} = 1/T_{1F}$, so that (with r_{ij} now meaning r_{iBj})

$$\Delta I_z(t) = \Delta I_z(0)\exp(-p_F t/T_{1F})\{(1/5)\exp[-(1 - p_F)r_{11}t] + (4/5)\exp[-(1 - p_F)r_{12}t]\} \tag{5}$$

$$\Delta I_+(t) = \Delta I_+(t)\exp(-i\omega t - p_F t/T_{1F})\{(3/5)(1/5) \times \exp[-(1 - p_F)r_{21}t] + (2/5)\exp[-(1 - p_F)r_{22}t]\} \tag{6}$$

In the experimental results in the subsequent part, longitudinal relaxation appears to be always monoexponential. Transverse relaxation, however, sometimes has two exponential components. This can be also observed in the signal shape, which is roughly a superposition of two Lorentzians. In such cases, R_{22} significantly departs from R_{21}.

The general applicability of the exponential correlation function is not self-evident. In the case of quadrupolar ions, translational diffusion in a random direction relatively to the electric field gradient could be important, too. If translational diffusion is the determining motion in relaxation, there is only one corresponding spectral density $J_d(\omega)$ (cf.[3,4]):

$$J_d(\omega) = 2\omega^{-1/2}\tau^{1/2}/\{1 + \omega\tau + (2\omega\tau)^{1/2}\} \tag{7}$$

When discussing the possible impact of changing mobility of the cations or the anion groups of the chain on the relaxation rates, it is practical to consider the theoretical dependence of the individual spectral density increments on the respective correlation times. A relevant section of these is shown in Figure 1. Significant changes of the translational spectral density occur if the corresponding correlation time τ is below 10^{-10} s whereas, among those of the rotational ones for $\omega/2\pi$ being equal to 52.9 (^{23}Na) or 77.7 (^{7}Li) MHz, $J_0(\omega) + J_1(\omega)$ changes significantly in the whole range whereas $J_1(\omega) + J_2(\omega)$ grows up to $\tau \approx 2 \times 10^{-9}$ s or even more (τ being here the rotational correlation time). It is also noteworthy that the two types of the latter ones depart from each other at $\tau \sim 5 \times 10^{-10}$ s, i.e., in the range quite attainable for local motions of the pendant groups on a polymer chain.

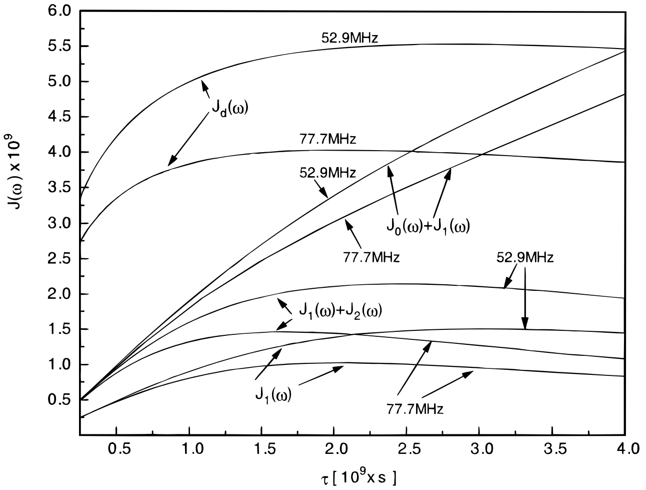

Figure 1. Relevant section of the dependence of individual spectral density increments on their correlation time.

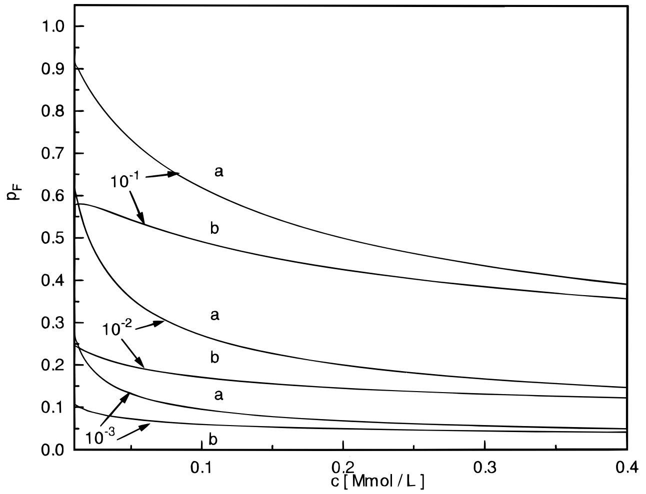

Figure 2. Dependences of the free ion population on monomole concentration according to (a) eq 8 and (b) eq 11. Values of K_0 are indicated.

Ion Dissociation in a System of Polyelectrolyte Chains. Let us consider first a simple equilibrium between ion pairs and free ions of a monomer unit of sodium or lithium polyacrylate without respect to complicating polyelectrolyte effects . The equilibrium constant K_0 is then related to the probability p_F to find a cation as a free ion. Let c be the equivalent monomole concentration of the salt, i.e. the number of moles of monomeric acrylic acid salt units per liter (without respect to the polymerization degree of the polymer to which they belong or to their molecular surroundings). Then the molar concentration of free ions (cations or anions) is $p_F c$ and the relation of p_F to K_0 is $K_0 = p_F^2 c/(1 - p_F)$; hence

$$p_F = \{-K_0 + [K_0(K_0 + 4c)]^{1/2}\}/2c \tag{8}$$

In such case, p_F grows (and relaxation slows down) with $c^{-1/2}$ as shown in Figure 2a. This, however, cannot be a very realistic model of the system of collective interaction between hundreds of adjacent anions and a statistical cloud of corresponding counterions. A very simple approach suggested by Manning and Oosawa[5,6] assumes the equilibrium between free and “sedimented” or bound counterions to be given by a balance between thermal energy and electrostatic pair interaction between adjacent anions, i.e. $p_F = a\epsilon k_B T/q^2$, where a is the distance between anions, ϵ is the dielectric constant, T is the absolute temperature, and q is the elementary charge. This is clearly a very crude approximation which is perhaps tenable for very dilute systems. For our purposes, its chief defect is its failure to account for the shielding effect of the counterions, i.e. for concentration dependence. On the other hand, a really adequate description of this problem appears to be rather inaccessible. Even the Poisson–Boltzmann equation, which is difficult to solve, can fail for systems where the average distance between the ions is not larger than several Bjerrum lengths; Monte Carlo simulations including all interactions represent a formidable task for large systems. The compromise we propose for our problem is the following approximation.

Let us consider the fractional area of a system of polyacrylic salt chains containing n monomeric (i.e. acrylic salt) units, i.e. n anions and, in a first approximation, n cations either free or bound. Assuming that ion pairs contribute in no way to the overall electrostatic energy (which is a rather gross approximation that can be removed later on) and that Debye–Hückel principle holds, we can write (cf.[7,8])

$$nk_BT \ln [p_F^2 n/(1 - p_F)] = -(q^2/\epsilon)p_F^2 n^2 \sum_{ij}\{1 - \exp [-(\epsilon k_B T/n)^{1/2} r_{ij}]\}/r_{ij} \tag{9}$$

where r_{ij} is the distance between the ith and jth anion. In the summation, *all* anions, i.e. both free and bound, have to be considered. In the first approximation, only some of the i,j pairs in eq 9 change their distances with dilution (assuming the shape of a single chain does not change; again, this simplification can be removed). We can thus write

$$\ln [p_F^2 n/(1 - p_F)] = \ln K_0 - np_F^2 (q^2/\epsilon k_B T)\sum_{ij}^{\text{var}} \{1 - \exp[-(\epsilon k_B T/n)^{1/2} r_{ij}]\}/r_{ij}\} \tag{10}$$

where the term K_0 is concentration-independent and the summation $\sum_{ij}^{\text{var}}$ goes over pairs with distances changing with concentration. Assuming that the relative change between the distances in the second term is not very significant in comparison with their collective concentration change, we can substitute all r_{ij} by a mean distance $r_m \approx (3n/4\pi c)^{1/3}$. Hence

$$\ln [p_F^2 n/(1 - p_F)] = \ln K_0 - p_F^2 (q^2/\epsilon k_B T) n^2 (n - 1)(4\pi c/3n)^{1/3}\{1 - \exp[-(\epsilon k_B T/n)^{1/2}(3n/4\pi c)^{1/3}]\}/2 \tag{11}$$

Simulated dependences of p_F on c for numerical solutions of eq 11 (taking the averages of the results for $n = 4, 6, 8$) are given in Figure 2b.

One can see that the second curve is less steep; nevertheless, p_F grows with decreasing concentration. Refining the approximations would probably lead to an even less steep concentration dependence. It is our belief, however, that no refinement could invert the tendency, i.e. make the ions dissociate less with increasing dilution. The concept of "ion sedimentation" is of a heuristic value but has a relative meaning only.

The problem is even more complicated for polyanion chains bound to a relatively rigid micellar core. In such a case, (i) there is a natural steep gradient of the equivalent monomole concentration along the radius of the micellar shell, (ii) but this gradient cannot be significantly changed by dilution of the system. The task to simulate in any detail the concentration change of a system of micelles containing at least 20 000 monomer units in the micellar shell each is a huge one. Our experiments (see below), however, show a striking analogy of behavior between linear PAAc salts and PMMA-PAAc salt micelles. Therefore, we will use the above approximations in further considerations.

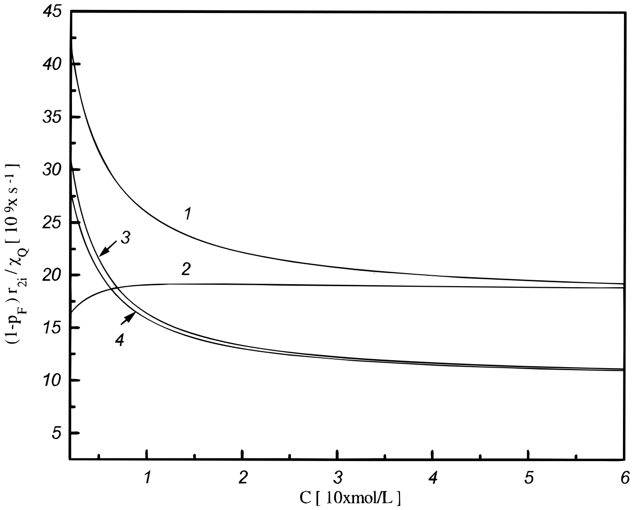

Figure 3. Simulation of the dependence of $(1 - p_F)r_{2i}/\chi_Q$ (i = 1, 2) on monomole concentration: 1, 3, R_{21}; 2, 4, R_{22}. For 1, 2: $\tau = 10^{-8}$ s; $\omega = 2\pi \times 52.9$ MHz. For 3, 4: $\tau = 10^{-9}$s; $\omega = 2\pi \times 77.7$ MHz.

Concentration Dependence of ^{7}Li and ^{23}Na Relaxation Rates. So far, our considerations have concerned the part of the relaxation rate–concentration dependence given by the free ions–ion pairs equilibrium. There is, however, another and probably even more important part given by the dependence of the local polyanion chain mobility on the ionic strength and thus on concentration. In the simplified models of Manning[2] and Oosawa,[3] the *chain stiffness*, characterized by persistence length, is given by a relation of the Bjerrum length, the distance of the anions, and the ion strength. Although such a model describes the overall chain behavior fairly well, it has a limited bearing on *local* mobility. We thus adopt a phenomenological approach to this problem which has some relation to their models.

Suppose that the relaxation rate of ions in pairs depends on the local motions of the chain. One of the simplest phenomenological expressions for the dependence of the energy barrier of such motions on ion strength, i.e. on local concentration, is $\vartheta \approx \vartheta_0 + 1/(\vartheta_m^{-1} + \kappa c)$. This relation converges both for low and high concentrations and the coefficients ϑ_0, ϑ_m and κ have the following intuitive physical meanings: even at very high cation concentration c, there remains some barrier ϑ_0; on the other hand, at vanishing concentration, the barrier does not diverge but reaches a value ϑ_m. κ is the coefficient expressing the relation between ion screening and the barrier. It seems physically reasonable to expect the decorrelation rate to be proportional to $\tau_0^{-1}e^{-\vartheta}$ and thus the corresponding correlation time to be proportional to its inverse. The illustrative simulations of the relaxation rate components $(1 - p_F)$ r_{2i}/χ_Q, i = 1, 2, using eq 11 with $K_0 = 10^{-2}$ and $\tau = \tau_0 \exp[0.07/(0.04 + c)]$, with $\tau_0 = 10^{-9}$ and 10^{-8}, are given in Figure 3. The aim of these simulations is to show that in diferent ranges of τ, the two relaxation components (and thus the two relaxation times) can show very different behaviors.

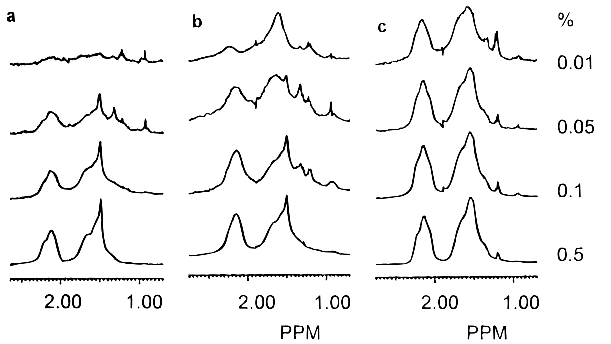

Figure 4. 300.1 MHz ^1H NMR spectra of (a, b) PMMA-PAAcNa micelles (molar ratio of Na acrylate to MMA: (a) 1.6; (b) 3.0) and (c) PAAcNa solution in D_2O. Concentrations are (starting from the bottom) 0.5, 0.1, 0.05, and 0.01% w/w.

Experimental Section

Chemicals. Poly(methyl methacrylate)-*block*-poly(acrylic acid) copolymers (PMMA-PAAc) were prepared as reported earlier[1] by successive group transfer polymerization of methyl methacrylate and *tert*-butyl acrylate (both purified from the Aldrich commercial products), purifying the product by repeated precipitation in methanol, selective acidolysis of the acrylate groups with *p*-toluenesulfonic acid, dialysis of the product with water, and freeze drying. All our products were directly soluble in D_2O. The Na or Li salts were prepared by dissolving the calculated amount of solid NaOH or LiOH in a 0.5% w/w D_2O solution of PMMA-PAAc. Partly neutralized samples were prepared by mixing solutions of PMMA-PAAc and its corresponding salt in appropriate proportions.

Poly(acrylic acid), its salts, and solutions were prepared in a quite analogous manner to ensure comparability of the results.

Glutaric acid was an analytical grade commercial product of Aldrich.

NMR Measurements. ^1H NMR spectra and relaxations were measured under presaturation of the remaining H_2O signal at 300.13 MHz with a Bruker ACF 300 spectrometer. The presaturation period used was 3 s; the number of accumulated scans varied according to the sample concentration from 80 (0.5% w/w) to 3200 (0.005% w/w). Before FT, exponential weighting with lb = 2.0 was used. ^7Li and ^{23}Na were measured at 77.7 and 52.9 MHz , respectively, with a Varian Unity 200 spectrometer. Again, the number of accumulated scans varied with concentration: from 32 to 800 (no weighting before FT) for ^7Li and from 128 to 1600 (exponential weighting with lb = 2.0 before FT) for ^{23}Na. All measurements were done at 300 K.

For T_1 measurements, the conventional inversion−recovery sequence was used. T_2 values were measured using the Carr−Purcell−Meiboom−Gill sequence with the delay between the π pulses equal to 2 ms. For $T_{1\rho}$ measurements with varying spin-lock power, pulsed spin-lock was used with 2 μs pulses separated by 10 μs delays.

Results and Discussion

In ^1H NMR spectra of D_2O solutions of Li and Na salts of PMMA-PAAc and PAAc progressively diluted with a 1.0 mol/L D_2O solution of LiCl or NaCl, i.e. with the ion strength kept constant, no important concentration changes in the spectra are observed. In contrast to that, quite dramatic changes occur if the system is diluted with pure D_2O as illustrated in Figure 4. Here and throughout the remaining text, the concentration is always in moles of the monomeric unit of acrylic acid salt per liter, without respect to molecular surroundings along the chain or to the polymerization degree of the incident polymer. The changes in the ^1H spectra of PMMA-PAAcLi and PAAcLi are quite analogous.

In the case of PMMA-PAAc, the spectra contain merely the signals of the backbone protons of the shell poly(acrylate) chains because the PMMA core blocks are in a quasi-glassy state.[1] With decreasing micellar concentration, there can be observed changes of both the chemical shift and the shape of the signals, which are parallelled by analogous but much less pronounced changes in the corresponding spectra of poly(acrylic acid) salts. The chemical shifts of the CH_2 groups vary in an even more pronounced way than those of CH. From the shape of the signals in CH_2 region (1.3−1.9 ppm) it follows that, in comparison with the acid form of PMMA-PAAc (cf.[1]), the protons of the isotactic dyad in PMMA-PAAcNa or PMMA-PAAcLi are shifted toward equivalence even at the concentration of 0.5% w/w, indicating thus a marked change in conformation. With dilution of the system, this trend appears to continue (although the changes are less pronounced and less easy to detect because of the general broadening of the signals). The increasing signal half-width is chiefly caused by homogeneous broadening and not by the chemical shift distribution, as can be demonstrated by saturation of the signal by a train of selective pulses at its various parts. Hence, it must be caused by an increasing transverse relaxation rate as will be shown later on.

Both PMMA-PAAc and PAAc contain residual *tert*-butyl ester groups (about 3% mol in PMMA-PAAc and 1% mol in PAAc) left after selective hydrolysis as an indicator of the poly(acrylic salt) conformation. In the spectra of PMMA-PAAcNa in Figure 4, the originally sharp *tert*-butyl signal superimposed on the broad CH_2 signal at 1.49 ppm is split, giving rise to a new, relatively increasing signal at 1.35 ppm (the other minor sharp signals are partly spikes and partly resonances of impurities). Both signals are progressively broadened at concentrations below 0.1% w/w. Considering the well-known sensitivity of proton chemical shifts in (meth)acrylic polymers to the changes in the enviroment, we interpret the splitting of the *tert*-butyl signal as a sign of a major change in the PAAcNa chain conformation.

The concentration effects just mentioned suggest changes in the ion bonding states or ion screening or both. Considering the first possibility, let us start with the categorization customary in physical chemistry, i.e. the discrete states of contact and solvent-separated ion pairs and free ions. The extrapolated T_1 values for $^7Li^+$ and $^{23}Na^+$ free ions are 38 and 0.56 s, respectively. In most of our systems, the T_1 values of $^7Li^+$ ions are in the range 1−4 s and those of $^{23}Na^+$ ions are between 0.01 and 0.04 s. Thus, a substantial part of the ions must exist in pairs with the respective anions or reside in some less defined bonding state in the vicinity of the polyanion chain. On the other hand, ^7Li and ^{23}Na NMR spectra show a single signal mostly of Lorentzian shape (with the exception of very dilute systems with Na^+ counterions) with its chemical shift changing slightly under dilution of the system. Highly populated contact ion pairs with appreciable lifetimes are thus not very probable. In agreement with this, infrared and Raman spectra of all our systems show exclusively absorption bands characteristic of carboxylic ions (1570 cm^{-1} asymmetric and 1410 cm^{-1} symmetric carboxyl vibrations). Moreover, extensive *ab initio* SCF calculations (6-31G** basis set) predict separated ion pairs for both lithium and sodium acetate in water (Figure 5). In the case of lithium, the counterion is predicted to be tightly solvated

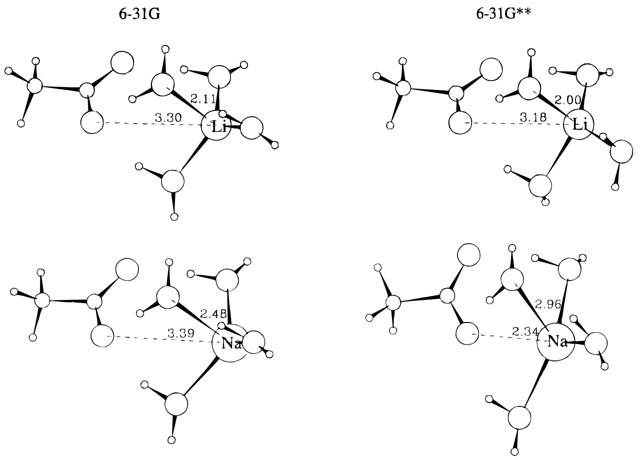

Figure 5. Tetrahydrated lithium acetate and sodium acetate ion pairs according to 6-31G and 6-31G** *ab initio* SCF calculations.

in a roughly cubical shell. The solvation of the sodium counterion, however, is less symmetrical with one of the nearest water molecules being more than 0.5 Å further from Na^+. As is shown in Figure 5, this feature could not be discovered with a poorer if quite extensive basis set, 6-31G.

A realistic description of the hydrated ion pair would call for an inclusion of one or two outer solvation spheres and Monte Carlo evaluation of the probability of their various configurations. This, however, is not practically feasible on a sufficient level of precision. Furthermore, semiempirical quantum calculations indicate that the outer solvation spheres add quite a small energy increment and do not seriously influence the results obtained with the first solvation sphere only.

When only the first hydration sphere is taken into account, the calculations with the 6-31G** basis set predict the tetrahydrated lithium ion in a water-separated ion pair to be only ~0.6 kcal/mol more stable than its sodium analogue (in contrast to 6-31G which predicts the tetrahydration of lithium to be about 7 kcal/mol more stable compared to that for the sodium analogue). Under closer inspection, however, the stabilization in the sodium case is to a considerable extent due to the Coulombic interaction of the counterion with the carboxylic anion, i.e. to a closer similarity of the system to a contact ion pair. In other words, sodium ion appears to be less tightly solvated and can, in spite of its larger ionic radius, thus be effectively smaller and more mobile in short range diffusional jumps.

The predicted stabilization of the solvent-separated ion pairs in both cases of lithium and sodium is in agreement with the above mentioned vibrational spectra which see the carboxylic groups as symmetric anions. The much higher NMR relaxation rates of both ^{7}Li and ^{23}Na in our systems in comparison with those of the corresponding free ions show that most of the ions in all our cases are in a bound state whereas the occurrence of only a single ^{7}Li or ^{23}Na signal which is shifted on dilution shows that the exchange between the bound and the free state of the ions must be fast. This gives us the right to expect a rapid exchange between ion pairs and less populated free ions to be the chief dynamics of the ion system.

According to the deductions in the Theory section, dilution of the system should thus lead to an increase in the relative population of free ions which in turn should cause an increase in both their longitudinal and transverse relaxation times unless complicating factors interfere. Such an increase would be less steep in the case of a polyanion but its absolute lower bound must be zero; i.e. the so-called counterion sedimentation on the polyion could be only relative, i.e. higher than in the case of low-molecular-weight compounds or polyionomers with widely spaced anion groups.

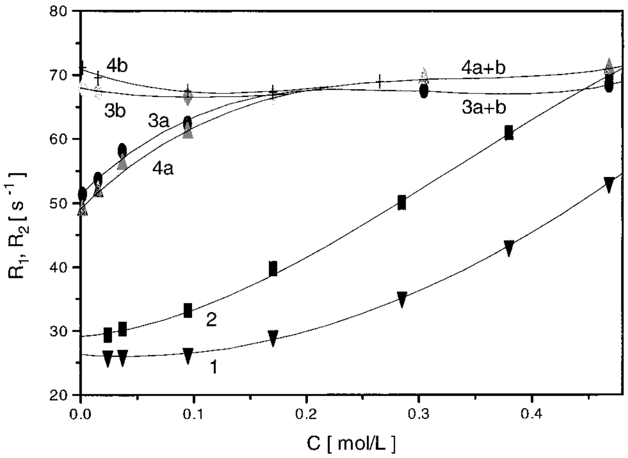

Figure 6. ^{23}Na longitudinal (R_1) and transverse (R_2) relaxation rates in systems with concentration of sodium carboxylate groups changed (i) by dilution [1, disodium glutarate ($R_1 = R_2$); 3, poly(acrylic acid) (3a, R_1; 3b, R_2); 4, PMMA-PAAcNa micelles (4a, R_1; 4b, R_2); (ii) by decreasing neutralization degree α at constant polymer concentration (0.5% w/w) [2, PMMA-PAAcNa micelles ($R_1 = R_2$).

Figure 6 illustrates some of this reasoning for the ^{23}Na relaxation rate in micellar and model systems. In the case of disodium glutarate, which is a very rough model of a dyadic unit in poly(sodium acrylate), longitudinal (R_1) and transverse (R_2) relaxation rates are equal and decrease, as expected, properly with dilution. If we decrease the equivalent monomole concentration of sodium carboxylate groups in a 0.5% w/w solution of sodium polyacrylate or a PMMA-PAAcNa micelle by lowering the neutralization degree α, we obtain—in the case of sodium—an analogous even though somewhat less steep dependence (this result is at variance with the findings of Gustavsson et al.[11] who worked with much more concentrated systems). If, however, the equivalent monomole concentration is decreased by dilution of the solution of fully neutralized PAAcNa or PMMA-PAAcNa micelles, the dependence is markedly different.

If the solution of PAAcNa or PMMA-PAAcNa is progressively diluted, R_1 does not decrease markedly except at extreme dilution where, at the same time, R_2 (more exactly, its second component R_{22}) increases. In the case of PAAcNa, our results are in agreement with those of Leyte et al.,[12-14] and the results with PMMA-PAAcNa are analogous but even more radical in the indicated tendencies.

Figure 7 shows the results obtained for the analogous system with the Li^+ counterions. In sharp contrast to the sodium salts, the curves for changing α go through a maximum (in the vicinity of $\alpha = 0.35$) whereas those for progressively diluted solutions show a steep increase in relaxation rate. The results for progressively diluted PAAcLi are in agreement with those of Leyte,[15] whereas those for changing α are interestingly analogous to those obtained by Gustavsson et al. for PMAcNa (cf. ref 11). Again, PMMA-PAAcLi shows an analogous behavior in all specific features.

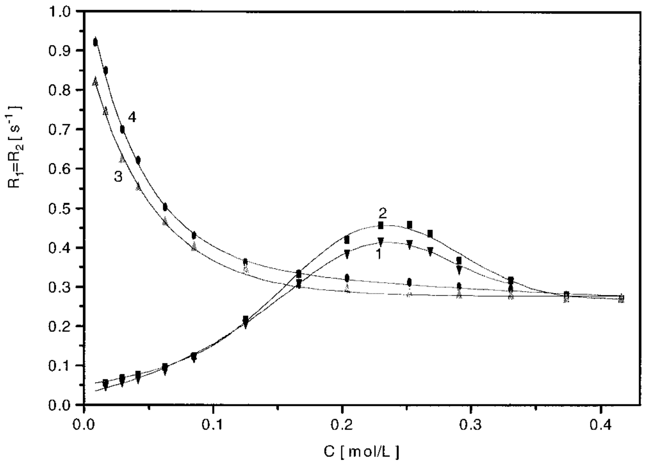

Figure 7. ^{7}Li relaxation rates ($R_1 = R_2$) in systems with the concentration of lithium carboxylate groups changed by (i) decreasing the neutralization degree α (1, 2) at constant polymer concentration (0.5% w/w) or (ii) dilution of the system with fully neutralized PAAc chains (3, 4). Key 1, 3, PAAcLi, 2, 4, PMMA-PAAcLi.

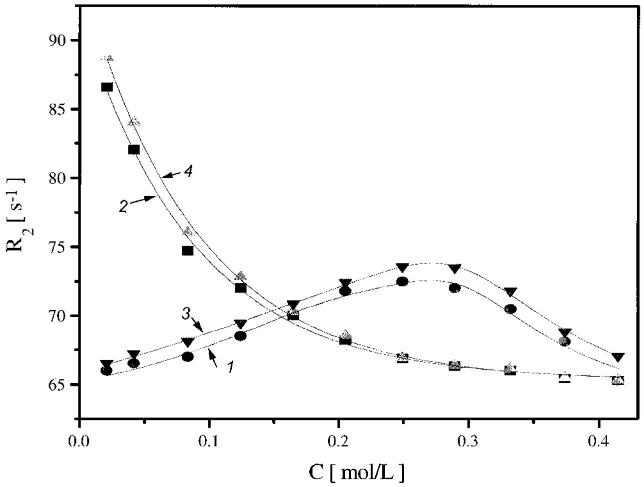

Figure 8. Transverse relaxation rates of the backbone α-protons in micellar PMMA-PAAcLi (1, 2) and PMMA-PAAcNa (3, 4) in dependence on the concentration of lithium carboxylate groups changed by (1, 3) decreasing neutralization degree at constant polymer concentration (0.5% w/w) or (2, 4) dilution of the system with fully neutralized PAAc chains.

Athough the accepted conceptual model of ^{7}Li or ^{23}Na relaxation in aqueous polyelectrolytes takes ion diffusion as the sole decorrelation mechanism, our results indicate that local motions of the charged groups of the polyanion could play a certain role, too. The obvious tool to probe into the possibility is the relaxation of the backbone nuclei. Unfortunately, the measurement of ^{13}C relaxations is out of the question due to low sensitivity. We thus chose ^{1}H transverse relaxation, which is somewhat less easy to interpret due to spin coupling between backbone protons but can nevertheless be considered a crude indicator of chain mobility. Figure 8 shows transverse relaxation rates of backbone α-protons in micellar PMMA-PAAcLi and PMMA-PAAcNa under the same conditions as above. Also, the tendency of R_1 for protons (which is generally 6−10 times that of R_2) is analogous but less pronounced. We do not show it here because R_2 is generally accepted as a better indicator of chain mobility albeit complicated by spin−spin scalar interactions.

A comparison of Figures 7 and 8 clearly shows that the tendencies in relaxation rates are mutually analogous. Both changing the neutralization degree at constant total concentration of the polymer and changing the dilution cause a change in the mobility of polyanion groups, i.e. in the local stiffness of the chain, which goes through an extreme with changing α whereas dilution causes its monotonic increase.

A striking analogy between the concentration dependences of ^{7}Li T_1 (and T_2) and ^{1}H T_2 indicates that the deciding site where $^7Li^+$ ions relax is the ion pairs and that the local motions of the polyanion chain play an important role in the relaxation. The different relaxation behavior of $^{23}Na^+$ and $^7Li^+$ ions described above can be caused by a difference in the basic correlation time τ_0 as indicated by the simulations described in the Theory section (cf. Figure 3) or, in principle, by a more important role of dipolar interaction with the backbone protons in the case of lithium. However, the latter possibility seems not to be very probable. It is well-known that for the free lithium cation in normal water, dipolar interactions provide for about half of the relaxation rate.[16] As shown in Figure 5, the protons in the inner solvation sphere have a distance of about 0.21 nm from the cation whereas the distance of the nearest backbone proton on the polyanion chain must be at least 0.51 nm. Owing to its r^{-6} dependence, the dipolar interaction must thus be at most 5×10^{-3} of that in water, i.e. a tiny fraction of the total relaxation interaction.

As suggested above, even the paired lithium ion is able to be tightly solvated with a high local symmetry which can have, however, important fluctuations caused by slight relative motions of the anion which cannot be expected to exactly correlate with the motions of the bulky solvation sphere. As the symmetry of the electric field around the nucleus and its change is known to be one of the most important factors in quadrupole relaxation, the transient symmetry distortion could be the main mechanism of lithium relaxation. The corresponding correlation time would be significantly shorter than that of the usual diffusion motion. In the case of the sodium ion, the same type of solvation of the ion pair occurs. However, its solvation sphere is less stabilized and hence less organized. Relaxation thus probably is associated with diffusion of the sodium ion in the gradient of the anion electric field, which can be expected to have a slightly different correlation time and different frequency dependence. Even moderate difference in correlation times can be, as shown, the cause of strikingly different relaxation behavior under the resonance conditions used in our study.

However opaque the difference between the ^{7}Li and ^{23}Na relaxations in our systems might be, the fact remains that (i) both types of counterion somewhat change their behavior with the dilution of the system, (ii) this change is correlated with an analogous change in the behavior of the skeletal protons of the polyanion chain, and (iii) all these effects can be considered an indication of a decrease in the local mobility of the chain (or increasing stiffness) with dilution of the system. This could be expected for free PAAcNa or PAAcLi chains (cf. Theory section) but is quite surprising in the case of polymer micelles of our type where no significant local dilution of the chains is possible because of the quasi-glassy state of the core (cf. ref 1). Evidently, there is some analogy in behavior of a single polyacrylate chain and a micelle as a whole. The extent to which polymeric macroions influence each other's counterion clouds is under discussion[9,10] which cannot be considered to be closed. It seems to be clear that even micellar macroions share their counterions to some extent: hence the analogy in behavior between a PAAc coil and a PMMA-PAAc micelle. A scaling principle close to that postulated by de Gennes (cf. ref 17) could operate in the relation between a multichain micellar system and a single polyelectrolyte coil.

Acknowledgment. The authors thank the Grant Agency of the Czech Republic for financial support given under Grant No. 203/95/1319.

References and Notes

(1) Kříž, J.; Masař, B.; Pospíšil, H.; Pleštil, J.; Tuzar, Z.; Kiselev, M. A. *Macromolecules,* in press.
(2) Bull, T. E. *J. Magn. Reson.* **1972**, *8*, 344.
(3) Hubbard, P. S. *J. Chem. Phys.* **1970**, *52*, 563.
(4) Lenk, R. *Brownian Motion and Spin Relaxation*; Elsevier: Amsterdam, 1977.
(5) Manning, G. S. *J. Phys. Chem.***1969**, *51*, 924.
(6) Oosawa, F. *Polyelectrolytes*; Dekker: New York, 1971.
(7) Odijk, T. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 477.
(8) Odijk, T. *Macromolecules* **1979,** *12*, 688.
(9) Sogami, I.; Ise, N. *J. Chem. Phys.* **1984**, *81*, 6320.
(10) Overbeek, J. T. G. *J. Chem. Phys.* **1987**, *87*, 4406.
(11) Gustavsson, H.; Lindman, B.; Bull, T. *J. Am. Chem. Soc.* **1978,** *100*, 4655.
(12) Mulder, C. W. R.; de Bleijser, J.; Leyte, J. C. *Chem. Phys. Lett.* **1980**, *69*, 354.
(13) Levij, M.; de Bleijser, J.; Leyte, J. C. *Chem. Phys. Lett.* **1981**, *83*, 183.
(14) van Rijn, C. J. M.; Jess, W.; de Bleijser, J.; Leyte, J. C. *J. Phys. Chem.* **1987**, *91*, 203.
(15) Leyte, J. C. *Makromol. Chem., Macromol. Symp.* **1990**, *34*, 81.
(16) Harris, R. K.; Mann. B. E. *NMR and The Periodic Table*; Academic Press: London 1978.
(17) de Gennes, P. G. *J. Phys., Lett.* **1978**, *39L*, 299.

MA961257D