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Ca^{2+} and Cu^{2+} Induced Conformational Changes of Sodium Polymethacrylate in Dilute Aqueous Solution

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ABSTRACT: The coil contraction of sodium polymethacrylate in dilute aqueous sodium chloride solution (0.1 N, pH = 9) was monitored by static and dynamic light scattering when the Na^+ ions were partly replaced by Ca^{2+} or Cu^{2+} ions. The effect was quantified as a function of polyion and bivalent metal ion concentration. The impact of Cu^{2+} ions on the chain conformation and the solubility of sodium polymethacrylate was observed to be larger than the corresponding effect of Ca^{2+} ions. This difference was ascribed to complexation of the carboxylate group with bivalent metal cations which is larger for the Cu^{2+} than for the Ca^{2+} ion. Even at the largest extent of contraction observed close to the precipitation threshold, the ratio of the radius of gyration and the hydrodynamic radius remained unchanged in contrast to the coil−globule transition observed for neutral polymer systems below the Θ-temperature.

Introduction

For neutral polymers in dilute solution, the solvent quality is modified by variation of the temperature. With decreasing solvation power the chain conformation changes, leading to smaller overall dimensions. If a critical temperature, usually denoted as the Θ-temperature, is reached, the mean square radius of gyration of the coils exhibits a power law dependence on the polymer molecular weight with an exponent of 1. Below this temperature, the solution becomes turbid and a phase highly concentrated with polymer separates. The temperature where phase separation occurs departs from the Θ-temperature by a temperature increment which depends on the molar mass and concentration of the polymer, usually referred to as the metastable regime between the binodal and spinodal curves. This metastable regime provides the kinetic basis for investigating the coil shrinking below the Θ-temperature. Eventually, the single polymer coil collapses[1] rather than precipitates if the concentration is small enough to prevent intermolecular contacts due to Brownian motion.

Polyelectrolytes in dilute aqueous solution exhibit striking analogies to this behavior if an additional salt is present. Now, the solvent quality of the aqueous solution is modified by the concentration of the added salt.[2,3] The salt has to be a low molecular weight electrolyte completely lacking the specific interactions of its ionic components with the polyelectrolyte. If the salt concentration is high enough, precipitation of the polyelectrolyte occurs. Just as the binodal curve borders on phase separation of neutral polymers in solution, the precipitation limit for polyelectrolytes is proximate to a salt concentration where the size of the polyelectrolyte coils is proportional to the square root of the polymer molecular weight.[2] Again, a coil collapse is expected for very dilute solutions, though nothing is known of the existence of a metastable regime in further analogy to neutral polymers.

Halogenides with monovalent alkaline cations are typical representatives of inert, low molecular salts because the respective cations predominantly act as point charges which screen the intra- and intermolecular electrostatic interactions of the polyions. According to Flory[4] the expansion coefficient of the radius of gyration, α_s, depends on a subtle balance of electrostatic and enthalpic contributions of the form

$$\alpha_s^{\,5} - \alpha_s^{\,3} = [{}^1/_2 - \chi + (\text{constant})(\tau f)^2/C_s]N^{1/2} \qquad (1)$$

with N the degree of polymerization, τ the molar fraction of monomers which contain an ionizable group, f the molar fraction of dissociated, ionized groups, and C_s the concentration of the low molecular weight salt. The parameter χ is the Flory interaction parameter of the hypothetically uncharged chain. Typically, ${}^1/_2 - \chi < 0$ for common polyelectrolytes with a hydrophobic main chain. With increasing C_s the term in square brackets becomes zero, leading to Θ-conditions, and eventually attains negative values which induce coil collapse and precipitation.

However, it is well-known and technically utilized that certain metal ions like alkaline earth ions and heavy metal ions do specifically interact with carboxylic groups. If the carboxylic groups are attached to a polymer backbone, as in polymethacrylic acid, this interaction eventually causes the precipitation of the metal polyion "complex" already at low salt concentration. This effect cannot be described in terms of excluded volume theories (i.e. eq 1) as specific interactions become dominant, as discussed in detail below. In the past, several attempts[5−7] have been made to describe the occurrence of polyelectrolyte precipitation in

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terms of a few mechanistic models. Those models are roughly classified into three different types, where each type is related to a characteristic dependence of precipitation on the concentration of the components which are expressed as the molar concentration of cations C_s and as the molar concentration of the monomeric units C_p of the polymer. A star indicates the precipitation limit.

(i) Charged polyions may be "salted out" according to eq 1 with the ionic groups of the polyion remaining fully or almost fully dissociated. The concentration of the cations at the precipitation limit is nearly independent of the polymer concentration.

$$C_s^* \sim O(C_p) \qquad (2)$$

Here, the concentration of the cation required to reach the precipitation limit is high, and precipitation is denoted as H-type. Unlike to the other two types, the metal cations usually are monovalent.

(ii) In an L-type precipitation, the concentration of cations at the precipitation limit, C_s^*, is generally low and proportional to the polymer concentration C_p^*

$$C_s^* \sim C_p^* \qquad (3)$$

This type of precipitation was investigated systematically by Michaeli[8] as early as 1960. Michaeli interpreted the precipitation of polymethacrylate (PMA) as a function of the degree of ionization and of the concentration of an inert monovalent electrolyte in terms of a stoichiometric complex between the divalent cations and anionic groups.

(iii) In a third type, denoted as MA-type, the precipitation was observed to be governed by the law of mass action, leading to a decrease of C_s^* with increasing C_p^*.

$$C_s^* \sim 1/C_p^* \qquad (4)$$

Here, the ionic group of the polymer forms an insoluble salt (called associations throughout the paper) with bivalent cations or cations of even higher valency which, when precipitating, draw the attached chains out of the solution.

The above types can be fitted into a more general scheme of precipitation/gelation of polyions.[9] By simply writing down the concentration of bivalent cations at the precipitation limit as the sum of the concentrations of free cations, $[M^{2+}]_f$, and bound cations, $[M^{2+}]_b$,

$$C_s^* = [M^{2+}]_f^* + [M^{2+}]_b^* \qquad (5)$$

the following equation was derived which includes L-type and MA-type as limiting cases

$$C_s^* = f^*\tau C_p^*/2 + f^*/[2K_B\tau C_p^*(1 - f^*)^2] \qquad (6)$$

In eq 6, K_B is the equilibrium constant of ion association/complexation and f^* is the molar fraction of dissociated, ionized groups at the precipitation limit. The magnitude of K_B, τ, and f^* determine whether L-type (1. term of eq 6 dominates) or MA-type precipitation occurs (2. term of eq 6 dominates).

Two recent theoretical approaches[10,11] succeeded in semiquantitatively reproducing some of the characteristic features of the precipitation of highly charged polyelectrolytes in solution induced by multivalent gegenions.

In view of the scenario described above, the question arises whether L- or MA-type ionic interactions do induce a coil shrinking close to precipitation in addition to the excluded volume effects described by eq 1.

Experimental evidence which points in this direction appeared as early as 1954, when Flory and Osterheld[12] showed that Ca^{2+} ions caused a much stronger coil contraction of polyacrylates (PA) than the corresponding amount of Na^+ would do. Since then, further results have been presented for the effect of multivalent cations on the extent of shrinking of polycarboxylates.[13-19] Like Flory and Osterheld, most of the other authors[13-16,18] derived their conclusions at least partially from viscosity measurements in dilute solutions. In a few of those publications,[14,16,18] it could indeed be verified unambiguously that bivalent cations amplify the coil shrinking usually induced by the screening effect of monovalent cations.

Significant technical improvements of scientific instruments analyzing polymer structures in solution allowed extension of the knowledge of conformational changes induced by multivalent cations: By means of an elongational flow technique, Narh and Keller[17] related the chain extensibility of poly(sterenesulfonate) (PSS) to the extent of coil contraction induced by the presence of various additional inorganic salts. Simultaneously, it could be shown by combined viscosity and static and dynamic light scattering measurements[18,19] that Ca^{2+} ions induce a strong coil shrinking of PA. This coil shrinking precedes precipitation, and the Ca^{2+} concentration required to reach coil shrinking depends on the PA concentration as expected for L-type precipitation. Along the line of these two preceding papers[18,19] on the interaction of alkaline earth metal ions with quite polydisperse PA, the present paper focuses on the conformational change of uniform PMA upon addition of Ca^{2+} or Cu^{2+} ions close to the precipitation limit.

Experimental Section

The sodium salt of a poly(methacrylic acid) standard sample was used to investigate the specific interactions of PMA with Ca^{2+} and Cu^{2+} ions. As specified by the supplier, PSS Co., Mainz, Germany, the molar mass of the sample is M_w = 600 000 g/mol with $M_w/M_n < 1.1$. In order to have a reliable set of reference data, the PMA sample was first characterized by static (SLS) and dynamic light scattering (DLS) in an aqueous solution of 0.1 M NaCl at pH $\approx$ 9. The SLS parameters were evaluated according to Zimm's classical equation

$$Kc/\Delta R_\theta = (1 + R_g^2q^2/_3)/M_w + 2A_2c \qquad (7)$$

where the SLS parameters M_w, R_g^2, and A_2 are the weight averaged molecular weight, the *z*-averaged mean squared radius of gyration, and the osmotic second virial coefficient, respectively, of the polymer sample. The SLS signal, expressed in terms of the Rayleigh-ratio ΔR_θ was measured as a function of the scattering vector $\mathbf{q}$ (or scattering angle θ) and the PMA concentration *c*. The constant *K* in eq 7 is the so called contrast factor, which includes the refractive index increment d*n*/d*c* of the polyelectrolyte in solution. A value of d*n*/d*c* is estimated to 0.18 cm^3/g for sodium PMA in 0.1 M NaCl in order to establish a meaningful connection to the nominal molar mass given by the supplier on the basis of the uncharged poly(butyl methacrylate) "parent" polymer. The exact value is not important for the goal of the present paper.

A relationship, similar to eq 7 was used for the interpretation of the DLS results

$$D = D_0(1 + k_Dc + CR_g^2q^2) \qquad (8)$$

Table 1. Dilute Solution Properties of the PMA Sample from Light Scattering Data, Extrapolated to $c = 0$

M_w*,[a] g/mol	615 000	R_h, nm	35.2
R_g, nm	64.4	k_D, cm^3/g	437
A_2,[a] (cm^3 mol)/g^2	12.3×10^{-4}	ρ	1.83
D, 10^{-8} cm^2/s	6.09		

[a] Data are calculated with $dn/dc = 0.18$ cm^3/g.

In eq 8, D is the reduced first cumulant of the time correlation function of the scattered electric field which was recorded as a function of the PMA concentration c and the scattering vector $\mathbf{q}$. The linear approximation in eq 8 results in an angular dependence, CR_g^2, a concentration dependence, k_D, and a limiting value, D_0, of the reduced first cumulant. The parameter D_0 has the physical meaning of a translational diffusion coefficient of the polymer coils which, by application of the Stokes–Einstein relationship, can be transformed into an effective hydrodynamic radius R_h. The molecular parameters of the PMA sample are summarized in Table 1.

Polyion concentrations c were expressed in gram per liter of the sodium salt of PMA. The minor letter c is used for the polyion concentration in gram per liter in order to distinguish it from the molar concentration of the monomeric units of the polyion, C_p. In the present investigation, C_p was assumed to be very close to the molar concentration of carboxylate groups, $[COO^{\ominus}]$.

The PMA was dissolved in aqueous sodium chloride solution. Before adding defined amounts of aqueous $CaCl_2$ solution (based on $CaCl_2 \cdot 2H_2O$, FFC grade, Merck), the pH-value of the aqueous solution was set to pH ≈ 9–10 in order to ensure complete dissociation of the carboxylic groups. All samples were cleared from dust by filtration with Millex GS (0.22 μm) filters prior to the light scattering measurements. Except for a few examples, measurements were performed one day after the solutions were prepared. Data represented by (◇) and (△) in Figure 5 were received within 5 days after preparation of the solutions. The pH-value of the final solution was observed to change by filtration of the solution and on the standing time of the solution in the closed cuvette, thereby affecting scattering results significantly if the standing time lasted longer than a week. Light scattering measurements were usually performed at pH-values around 9. No significant influence of the pH-value on the light scattering results was noticed in the range $7 < \text{pH} < 9$. This was verified by a series of test measurements of $Kc/R_{\theta=0}$ and R_g^2 in the pH range of $7 < \text{pH} < 9$. Aqueous $CuCl_2$ solution was added to an aqueous sodium chloride solution of poly(methacrylic acid) at pH = 7 in order to avoid precipitation of $Cu(OH)_2$. Copper ion solutions were made from $CuCl_2$, 99.999% pure, from Aldrich Chemical Co.

All solutions were adjusted to a constant 0.1 M concentration of cationic charges, i.e. $[Na^+] + 2[M^{2+}] = 0.1$ M, where the content of M^{2+} is expressed by

$$r_{M^{2+}} = 2[M^{2+}]/(2[M^{2+}] + [Na^+]) \qquad (9)$$

In eq 9, $r_{M^{2+}}$ represents the molar fraction of charges from bivalent cations to the total number of cationic charges.

It is important to note that a correct evaluation of M_w would require experiments to be performed at constant chemical potentials of NaCl and $CaCl_2$ in solution instead of at constant concentrations.[20] Unfortunately none of the solutions containing bivalent metal cations could be dialyzed to an equilibrium state because calcium as well as copper ions bind to the polyion, which would continuously shift the equilibrium to the bound state until precipitation occurs in the dialysis hose. Thus, we could not measure refraction index increments which are appropriate for the evaluation of absolute molar masses, and the reduced scattering intensity plotted in Figure 4 is given in arbitrary units, accordingly.

Although this unavoidable lack of dialysis equilibrium prevents access to absolute molecular weight data, it does not introduce any errors on the evaluation of R_g and R_h. Still we should keep in mind that the lack of dialysis may impose a certain ambiguity on the exact values of the chemical potentials of NaCl and $CaCl_2$ in solution which in turn may modify dimensions of the polyelectrolyte chains. Only, we consider this modification to be of minor importance because within the concentration range applied, equilibrium dialysis would change the overall ionic strength by a few percent at the most.[20]

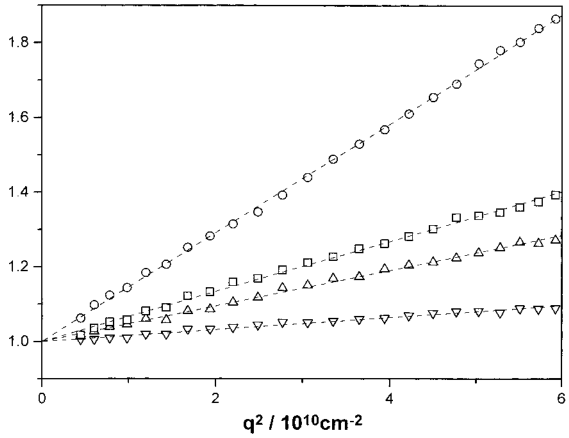

Figure 1. Inverse particle scattering factors at a PMA concentration of 0.04 g/L for four different copper contents: (○) $[Cu^{2+}]/C_p = 0$; (□) $[Cu^{2+}]/C_p = 0.0846$; (△) $[Cu^{2+}]/C_p = 0.169$; (▽) $[Cu^{2+}]/C_p = 0.338$.

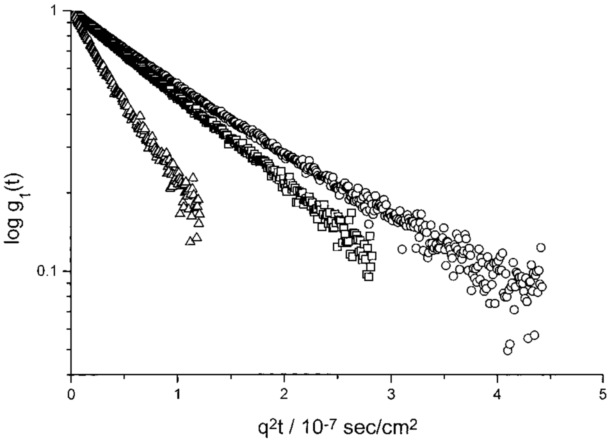

Figure 2. Logarithm of the electric field correlation functions from DLS at a scattering angle of 50° for three different bivalent metal ion contents: (○) $[M^{2+}]/C_p = 0$; (□) $[Ca^{2+}]/C_p = 5.4$; (△) $[Cu^{2+}]/C_p = 0.338$. The PMA concentration is 0.04 g/L for all three curves.

It is also evident from the data shown in Figures 3–6 that the scatter of the data is significantly larger than that usually encountered even for measurements in aqueous solution. This scatter reflects the poor reproducibility of the sample preparation, such as precise control of pH, the filtration procedure, and adsorption of the complexes on various glass surfaces. Although the filter units were “preconditioned” with an aliquot of the respective solutions, adsorption on the filter material and glassware cannot be fully excluded which, however, would not falsify the measured R_g and R_h values (but M_w) if no size fractionation of the possible formation of aggragates occurs. As demonstrated in Figures 1 and 2, there is no indication for aggregate formation detectable in either of the curves, i.e., no downward curvature in the static light scattering plots (Figure 1) and no increased deviation of non-exponentiality for the correlation functions as compared to the M^{2+} free PMA solution. Also, unlike the data shown in Table 2 where aggregation did occur, no effect of filter size (i.e., 0.2 vs 0.45 mm) was found for solutions, the results of which are displayed in the figures.

Static and dynamic light scattering measurements were performed with an ALV SP 86 goniometer in combination with an ALV 3000 correlator as described elsewhere.[21] Tempera-

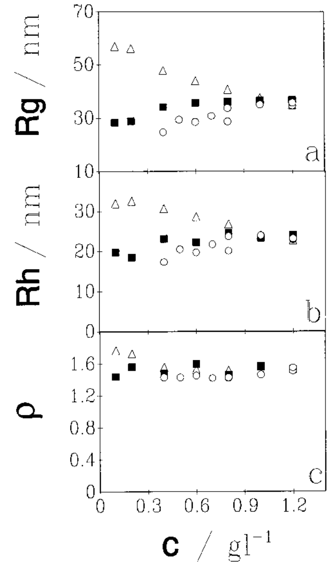

Figure 3. Apparent radius of gyration (a), the hydrodynamic radius (b), and the ratio of radius of gyration over the hydrodynamic radius (c) vs the concentration of the sodium salt of PMA. The symbols have the following meaning: (△) at $r_{Ca^{2+}} = 0.0$, (■) at $r_{Ca^{2+}} = 0.08$, and (O) at $r_{Ca^{2+}} = 0.10$.

Table 2. Radii for the PMA/Cu^{2+} System in the Polymer Concentration Range of $c > 0.1$ g/L

pore size of filter, mm	$r_{M^{2+}}$	c, g/L	$[M^{2+}]/C_p$	R_g, nm	R_h, nm
	0.04	0.6	0.36	precipitation	
0.22	0.02	0.6	0.18	38.5	24.1
0.45				42.6	26.3
	0.02	0.2	0.54	precipitation	
0.22	0.01	0.2	0.27	81.4	42.8
0.45				90.5	57.5
0.22	0.005	0.2	0.135	79.8	59.1
0.45	0.005	0.2		99.7	74.0
0.22	0	0.2	0	56.3	32.7

ture was set to 20 °C. The light source was a krypton-ion laser (Spectra Physics, Model 2065-11) operating at 647.1 nm wavelength at an output power of 500 mW. Values of R_θ were referred to toluene as a standard scatterer with an absolute scattering intensity $R_T = 1.27 \times 10^{-5}$ cm^{-1} at $T = 20$ °C.

Results and Discussion

In Figure 3a,b, the concentration dependencies of the apparent radius of gyration measured by SLS and of the apparent hydrodynamic radius derived from the apparent diffusion coefficient as determined by DLS are shown as a function of the polyion concentration c for different calcium contents. The term “apparent” means that the corresponding quantities are evaluated at a finite concentration c.

In qualitative agreement with earlier investigations[18,19] on polyacrylic acid, the apparent dimensions are significantly reduced with increasing Ca^{2+} concentration of the solvent. Eventually at very low polyion concentrations, i.e., large $Ca^{2+}/COO^{\ominus}$ ratios, precipitation occurs. Figure 4 displays the inverse apparent molar mass $M_{app}^{-1} = (Kc/\Delta R_{\theta=0})$ vs polyion concentration. The solutions without Ca^{2+} do show a pronounced second virial coefficient A_2 as expected, whereas A_2 is close to zero when Ca^{2+} is added. No intermolecular aggregation is evident from the data in Figure 4.

If Ca^{2+} is replaced by Cu^{2+} at similar polyion concentration, strong aggregation effects are observed, as evident from Table 2. The data clearly indicate that aggregation and precipitation prevent access to a set of light scattering data, which would be comparable to the results received from the Ca^{2+} ions, as represented in Figure 3 for PMA and reported in refs 18 and 19 for PA. Intermolecular aggregation with Cu^{2+} ions, however, is avoided if the polyion concentration is reduced to $c \leq 0.04$ g/L as shown by Figure 5a,b, where R_g and R_h are plotted versus the molar ratio $[Cu^{2+}]/C_p$, respectively.

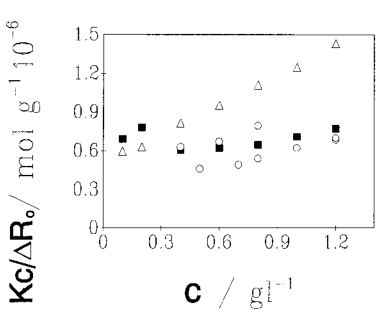

Figure 4. Reduced scattering intensity $Kc/\Delta R_0$ at zero scattering angle. The symbols have the following meaning: (△) at $r_{Ca^{2+}} = 0.0$, (■) at $r_{Ca^{2+}} = 0.08$, and (○) at $r_{Ca^{2+}} = 0.10$.

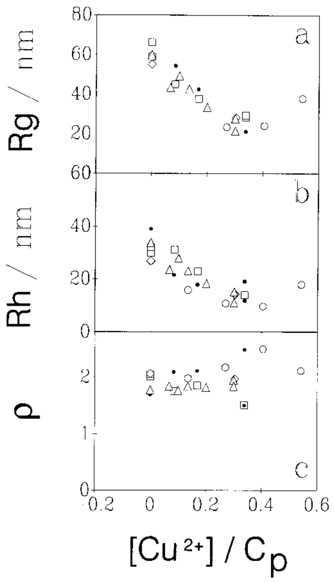

Figure 5. Apparent radius of gyration (a), the hydrodynamic radius (b), and the ratio of radius of gyration over the hydrodynamic radius (c) vs relative concentration of Cu^{2+} ions (molar concentration of Cu^{2+} ions devided by PMA concentration in moles of monomeric units) at various PMA concentrations. The symbols have the following meaning: (◊) $c = 0.01$ g/L, (□) $c = 0.02$ g/L, (●) $c = 0.04$ g/L, (○) $c = 0.04$ g/L, and (△) $c = 0.04$g/L.

In contrast to Figure 3, in each of the three series of measurements shown in Figure 5, the polyion concentration was kept constant and the amount of added bivalent metal cations was varied. Both the radius of gyration and the hydrodynamic radius became significantly smaller with the increasing ratio of $[Cu^{2+}]/C_p$ until precipitation occurred at a molar ratio of approximately 0.5. Within experimental error no effect of the absolute polyion concentration was observed.

The maximum extent of shrinking borders precipitation very much like it does for the PA/Ca^{2+} and PMA/Ca^{2+} systems. However, for copper ions precipitation approximately occurs at a molar ratio of 0.5, resembling the isoelectric point as one Cu^{2+} ion is bound to two carboxylate groups. Similar results were already re-

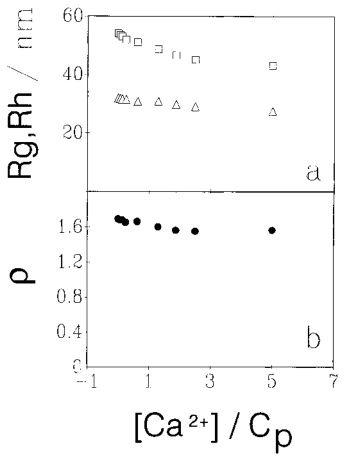

Figure 6. Apparent radius of gyration and hydrodynamic radius (a), where (□) represents R_g values and (△) represents R_h values; the ratio of the radius of gyration over the hydrodynamic radius (b) vs the relative concentration of Ca^{2+} ions (molar concentration of Ca^{2+} ions divided by PMA concentration in the moles of monomeric units).

ported by Mandel and Leyte in 1964 on a similar PMA/Cu^{2+} system, where the authors based their conclusion on potentiometric[22] and viscometric, electrophoretic, and spectrophotometric[13] evidence.

For direct comparisons, the shrinking of the polyion dimension with added amount of Ca^{2+} in the low polyion concentration regime of $c \leq 0.04$ g/L is shown in Figure 6a. The smallest value of R_g in Figure 6a is 42.5 nm, which is significantly larger than the smallest values represented in Figure 5a for the system PMA/Cu^{2+}. At the same time, the solution remained stable up to a 10-fold excess of Ca^{2+} ions compared to $COO^{\ominus}$ groups. For the higher polyion concentration shown in Figure 3, the stability limit is shifted to a smaller ratio of $[Ca^{2+}]/C_p$.

L- vs MA-Type Precipitation. This extension of the stability regime toward larger ratios of $Ca^{2+}/COO^{\ominus}$ at $c \leq 0.04$ g/L can at least qualitatively be explained in terms of eq 6 and corresponds to a transition from L-type to MA-type precipitation: As has been shown by Gregor et al.,[23,24] the binding constant of carboxylate groups to the M^{2+} ion, K_B, for the system PA/Cu^{2+} is larger than for the system PA/Ca^{2+} by a factor of 6×10^3. Notwithstanding the fact that K_B depends on the molecular weight of the polyion and that K_B for the system PA/M^{2+} differs from the corresponding value for the system PMA/M^{2+}, an increase of K_B, similar to the one observed by Gregor et al. for PA/M^{2+}, might be expected for the system PMA/M^{2+} when exchanging Ca^{2+} by Cu^{2+}.

If K_B increases by 6×10^3, the second term in eq 6 for the system PMA/Cu^{2+} may become negligible at a C_p (or c) value, which is a few orders of magnitude below the corresponding value for the system PMA/Ca^{2+}. As a direct consequence thereof, L-type precipitation extends down to much lower polymer concentrations for the system PMA/Cu^{2+}. In fact, L-type behavior can be inferred from the common minimum in the coil dimensions for all three values of c at $c \leq 0.04$ g/L in Figure 5.

Coil Collapse. The data presented so far suggest that both Ca^{2+} and Cu^{2+} induce a coil collapse, as is observable for neutral polymers when the solvent quality is reduced. Such a coil to globule transition should also be reflected in a significant drop of the ratio $\rho = R_g/R_h$, which is sensitive to structural changes of macromolecules: An expanded coil exhibits a value of $\rho \approx 1.5-1.8$, whereas, for the hard sphere, $\rho \approx 0.8$ only.

The values of ρ for the system PMA/Ca^{2+} at $c > 0.04$ g/L are represented in Figure 3c as a function of C_p and for the Ca^{2+} series and the Cu^{2+} series at $c \leq 0.04$ g/L, in Figures 5c and 6b, respectively, as a function of the ratio $[M^{2+}]/C_p$. In Figure 5c no change at all did occur, and in Figures 3c and 6b only a minor decrease became noticeable. Similar behavior was already reported for the system PA/Ca^{2+} in ref 19.

The key question raised by the observed behavior is the following: How can the dimension of an expanded, flexible coil shrink by a factor of up to 3, if the radial segment density distribution (i.e., probability density) which eventually determines the value of ρ apparently remains unchanged.

For neutral polymers in solution, the decrease in ρ while approaching the collapsed state from an unperturbed coil depends on the extent of shrinking which is expressed by the expansion factor α_s introduced already in eq (1)

$$\alpha_s = R_g/R_g(\mathrm{ref}) \tag{10}$$

where R_g(ref) is the radius of gyration of the chain in its unperturbed state. The behavior of α_s is influenced by the molar mass and subtle thermodynamic conditions. A decrease of ρ from 1.36 to 0.74 was observed when R_g of a polystyrene (PS) sample with $M_w = 2.6 \times 10^7$g/mol decreased by a factor of 0.2 and from $\rho = 1.4$ to 1.25 when R_g of a PS sample with $M_w = 8.6 \times 10^6$g/mol shrank by a factor of 0.75 to name but a few examples.[25,26] Comparable experiments on water soluble poly(n-isopropylacrylamide) chains[27] with $M_w = 1.08 \times 10^7$g/mol revealed a drop of ρ from 1.45 under θ-conditions to values below 1 if the extent of shrinking reaches the range of $0.4 > \alpha_s > 0.3$.

For polyelectrolytes the experimental determination of α_s is somewhat ambiguous because the unperturbed dimensions are not easily accessible. For the presently investigated PMA, for instance, no unperturbed dimensions are available in the literature. Therefore, the extent of shrinking, α_s, for PA and PMA with Ca^{2+} and Cu^{2+} under consideration, had to be related to R_g(ref) values which were extrapolated to $c \rightarrow 0$ at $r_{M^{2+}} = 0$ and which correspond to moderately good solvent condition (see Table 1 for the PMA sample). This shrinking includes potential conformational changes occurring during the transition of an extended coil under good solvent condition to an unperturbed coil under Θ-condition. However, at 0.1 M salt the chain expansion is considered to be not that strong.

For the PA/Ca^{2+} system, a maximum shrinking of 0.55 for the smallest R_g measured is inferred from Figure 5 of ref 19 for $r_{Ca^{2+}} = 0.08$. The corresponding ρ parameter was identical to the one observed for $r_{Ca^{2+}} = 0.0$. For the system PMA/Ca^{2+} the extent of shrinking was 0.39 at $r_{Ca^{2+}} = 0.08$ and the ρ values were slightly lower than the reference value of 1.83 at $r_{Ca^{2+}} = 0.0$ (Table 1). Within experimental error, the value of ρ does not change significantly with C_p, although a slight reduction with decreasing C_p may be anticipated.

In the regime of very low PMA concentrations, i.e., $c \leq 0.04$ g/L, light scattering experiments were performed for varying concentrations of Ca^{2+} or Cu^{2+} ions at constant polyion concentrations of 0.01, 0.02, and 0.04 g/L, respectively. The maximum extent of shrinking, α_s, for the system PMA/Cu^{2+} reached as low a value as

0.32 for relative copper concentrations $[Cu^{2+}]/C_p$ larger than 0.3. Although the corresponding ρ ratios scattered remarkably, they kept well above 1.5 and did not show a significant change. For the system PMA/Ca^{2+} at similar small concentration, α_s values did not fall below 0.66, even at relative calcium contents of $[Ca^{2+}]/C_p$ as large as 5. Yet, a tiny decrease of ρ becomes noticeable with increasing Ca^{2+} concentration and is represented in Figure 6b. Also, the smaller shrinking of PMA with Ca^{2+} ions compared to Cu^{2+} ions may be another indication of the interaction between PMA and Ca^{2+} ions to be much weaker than between PMA and Cu^{2+} ions.

In summary, the quantity ρ for the system PMA/Ca^{2+} varied only slightly and changes of ρ for the system PMA/Cu $^{2+}$ if existent at all were completely hidden by the experimental uncertainty of the data. For both systems, ρ values never decreased below 1.43, which still resembles random coil behavior rather than the conformation of a sphere, i.e., $\rho = 0.77$. Thus, the experimental data do not at all support a bivalent metal induced coil to globule transition of the presently investigated polyelectrolytes.

Large polymer coils have a radial segment density distribution which decreases with increasing distance from the center of mass. In principle, a constant ρ ratio can always be brought into line with a shrinking process of the polyelectrolyte coil which preserves the nonuniform distribution of the segment density. In other words, the structures of the expanded and collapsed coils are self-similar.

Alternatively, a shortening of the effective contour length could be adopted in order to explain the large ρ values. Various mechanisms of such a backbone transformation appear to be conceivable: (1) The bivalent metal cations induce a back-folding of the polyion chain, i.e., form bridges between the monomers in a regular manner, leading to a final contour length which is not shorter than half of the original contour length. However, a complete back-folding of the chain in a Gaussian coil lowers the size of the coil by a factor of $(1/2)^{0.5}$ at the most. Further shrinking down to 0.32 could only be achieved by a simultaneous increase in chain flexibility, which renders the back-folding mechanism rather unlikely. (2) The effective contour length is shortened by the formation of small, successive loops also induced by M^{2+} bridging. The sequence of loops still form a chainlike structure. (3) A cooperative binding mechanism of M^{2+} ions to carboxylate groups leads to the formation of domains of collapsed coil segments comparable to a model suggested by Kantor and Kardar[28,29] and Dobrynin et al.[30] The nodules are connected by polyion segments to a chainlike structure. The linking polyion segments remained in their original structure because they are free of M^{2+} ions and are still in the same thermodynamic environment. This environment is an aqueous solution with 0.1 equiv of low molecular electrolyte. These mechanisms do not necessarily lead to a structure being self-similar to the polyion coil without M^{2+}. Nevertheless, they are also compatible with an invariant ρ ratio.

Conclusions

The radius of gyration for PMA in an aqueous solution of 0.1 N NaCl at pH = 9 strongly decreases when part of the added alkaline cations are replaced by Ca^{2+} ions. This coil contraction borders precipitation in a phase diagram of C_s* versus C_p*. A similar pattern was already observed for PA in an earlier invetsigation.[18,19]

If Cu^{2+} ions are used instead of Ca^{2+} ions, the range of M^{2+} concentration and of PMA concentration, which is accessible to an investigation of conformational changes, is lowered by an order of magnitude. If compared at equal $[M^{2+}]$, Cu^{2+} ions induce a larger contraction of PMA coils than Ca^{2+} ions do.

Although the extent of contraction observed in the present investigation is as large as 0.32, the recorded ρ values remain larger than 1.4. These large ρ values do not indicate a compact spherical structure for the contracted PMA coils. Certainly much more experimental data are required in order to draw a clear picture on the mechanism of M^{2+} induced shrinking of polycarboxylate chains. One important requirement for reaching this goal is detailed knowledge of the unperturbed dimensions of these polyelectrolyte chains.

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References and Notes

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