

Influence of counterion valency on the scattering properties of highly charged polyelectrolyte solutions

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Light and neutron scattering measurements on highly charged polyelectrolyte solutions have recently provided firm evidence for the existence of “domain structures” containing many chains, even at rather low-polymer concentrations. In the present paper, we systematically investigate the influence of counterion charge valency Z_c on the scattering properties of sulfonated polystyrene (PSS) solutions in water with monovalent and divalent counterions. This study is part of a larger effort to identify essential factors governing polyelectrolyte domain formation and the geometric properties of these transient structures. Neutron scattering measurements indicate that the interchain correlation length ξ_d within the domains becomes larger by a factor of 1.5–2 for divalent relative to monovalent counterions. This observation is consistent with the Manning model estimate of the change in effective polymer charge density Γ^* with Z_c and with previous observations linking ξ_d [from the peak position in the scattering intensity $I(q)$] with the bare polymer charge density, Γ . Light scattering measurements of the radius of gyration $R_{g,d}$ of the domains indicate that their size becomes *smaller* for divalent counterions and with a reduction of Γ . We observe that the “fractal” dimension of the domains measured from the low-angle scaling of $I(q)$ depends on the chemical structure of the polyelectrolyte. Zero average contrast (ZAC) neutron scattering measurements show that the radius of gyration $R_{g,c}$ of individual polyelectrolyte chains is also reduced for divalent counterions, suggesting that chain rigidity is strongly influenced by Γ^* . Charge valency effects on relaxation times are investigated by dynamic light scattering. As usual, two diffusive modes are observed in the light intensity autocorrelation function, $G(\tau)$. The “fast” mode becomes slower and the “slow” mode becomes faster for the divalent counterion (Mg^{2+}), relative to the monovalent counterion (Na^+). Counterion valence has a large influence on the structure and dynamics of highly charged polyelectrolyte solutions through its influence on Γ^* . © 2001 American Institute of Physics. [DOI: 10.1063/1.1336148]

I. INTRODUCTION

The tendency toward clustering is a ubiquitous phenomenon in colloidal dispersions, polymer solutions, and other complex fluids. In many cases, such as living polymer solutions, micelle solutions, and thermally reversible gels of various kinds, the clusters form and disintegrate in a state of equilibrium so that these are “dynamic” cluster structures.^{1,2} The nature of the interparticle interactions giving rise to these clusters range from weak van der Waals interactions to ionic associations and covalent chemical bonds and in polymeric systems these interactions can also be influenced by subtle interactions having a topological origin. The geometry of these dynamic clusters exhibit a wide variety of forms ranging from globular structures such as micelles or objects having a very specific structure (as commonly found in self-organization of biological forms) to fractal polymeric structures having a linear or branched chain topology. The type of clustering apparently depends on the geometrical form of the molecules, the symmetry and range of the interparticle interactions and the capacity of the clustering species to form multifunctional associations. In practice, it is difficult to pre-

dict the morphology of the domains of clustering particles from molecular information, but there has been recent progress in this direction in the case of charged particle dispersions. Monte Carlo simulations of model platelet particles having a quadrupolar interaction, intended to model charged clay particles in solution, show a tendency of the dynamic clusters to form branched living polymer structures.³ Molecular-dynamics simulations of model dipolar particle fluids indicate a tendency of the particles to form linear living polymer chains.^{4,5} In each case, the fractal polymeric structures are *dynamic* in the sense mentioned above and we can see how the symmetry of the pair potential reflects itself in the geometry of the clusters. The “restricted primitive model” of idealized charged particle dispersions of finite-sized spherical anions and cations under the condition of solution charge neutrality has recently been generalized to include a short-range attractive interaction.⁶ This model indicates the existence of a segregation of the charged particles into domains whose symmetry is apparently dependent on the size and charge asymmetry of the ions.⁷ Local ordering of this kind accords qualitatively with Staudinger’s and Langmuir’s intuitive view of the clustering of charged particles into domains having a locally “salt-like” ordering.⁸ In the common physical situation in which there is a large size

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asymmetry between the size of the cation and anion we expect, based on the strong analogy of the generalized restricted primitive model⁶ to the theory of block copolymer microphase formation,⁹ that charged particles with spherical symmetry in a solution with small counterions will tend to form “compact” (i.e., somewhat irregular in shape, but non-fractal) domains coexisting with a disordered background fluid. Compact domains of this kind are in fact observed in colloidal dispersions of charged nearly spherical particles having a common charge if the charge density of the particles is sufficiently high.^{10–13} Charged compact particle clusters are notably observed in various charged protein solutions having important biological significance.¹⁴ There have also been reports of direct observation of micelle-like domains in aqueous polyelectrolyte solutions.¹⁵

In the present paper, we are concerned with the case of model synthetic polyelectrolyte solutions (sulfonated polystyrene with monovalent and divalent cations dissolved in water) in which there is likewise a large asymmetry between the average sizes of the cations and anions. The chain topology of the polyanion and charge valency asymmetry can then be expected to influence the resulting domain structure (we normally use the term “domain structure” or “domain” instead of “cluster” since it is not clear that the charged molecules or particles must physically touch to belong to a domain of particles exhibiting correlated motion). Prediction of the geometry of these transient domain structures is uncertain for this more complex charged particle geometry and we anticipate that the form of clustering will be dependent on the specific polymer chemistry.

Combined neutron and light scattering observations by Ermi and Amis¹⁶ on poly (N-methyl-2-vinylpyridinium chloride) in D₂O covering a large scattering wave vector \mathbf{q} range indicated that the polyelectrolyte domains had an approximately fractal structure at large scales ($d_f \approx 2.2 \pm 0.2$) and a peak was observed at high q that scaled with polymer concentration C_p to the exponent,¹⁷ 0.48 ± 0.02 ($q = |\mathbf{q}|$; see Sec. V below for further discussion). These observations are consistent with a domain structure, having an internal structure in which the high- q peak corresponds to an interchain correlation length ξ_d within the domains (ξ_d can be roughly identified as an average “mesh spacing” of the domain structures). A scaling $\xi_d \sim C_p^{-1/2}$ is consistent with a network-like domain structure having the topology of a two-dimensional surface,^{18–22} and this result is contrasted with domains having a three-dimensional network topology (“sponge random surfaces”) in which the ξ_d exponent should equal $-1/3$. (These concentration scaling relations assume a proportionality between the polymer concentration in the polyelectrolyte domains and the polymer solution.¹⁶ A reliable determination of the cluster d_f must be made by independent scattering measurements.) Equilibrium domain structures having a similar fractal dimension ($d_f \approx 2.0–2.1$) are commonly observed in particle dispersions^{23–28} and these exponents correspond to swollen “living” branched polymers^{1,2} having “sheet” or “sponge” topologies, respectively.²² These fractal dimensions are readily discriminated from linear living polymers where $d_f \approx 5/3$ and compact aggregates which are characterized by Porod-type scattering [corre-

sponding to a -4 power scaling of $I(q)$ due to the presence of sharp domain interfaces]. The scaling of $I(q)$ in relatively low- q light scattering measurements and the concentration dependence of the high- q peak accessible in x-ray and neutron scattering measurements thus provide important information about the geometry of the domain structures forming in polyelectrolyte solutions at equilibrium. Below we utilize scattering methods to investigate the influence of counterion charge valency and polymer charge density on the structure (size and form) of the polyelectrolyte domains.

Previous scattering measurements by our group utilized poly(N-methyl-2-vinylpyridinium chloride) in water and ethylene glycol solutions to investigate the importance of “solvent quality” effects and the polyelectrolyte backbone structure on the occurrence of polyelectrolyte domain formation.^{16,17,29} These measurements conclusively showed that a hydrophobic chain backbone is not required for the formation of polyelectrolyte domain structures in solution. In the present paper, we consider the more common sulfonated polystyrene (PSS) synthetic polymer, which has a rather hydrophobic chain backbone. The measurements below indicate that the geometrical form of the polyelectrolyte domains found for PSS are more compact than those found for poly (N-methyl-2-vinylpyridinium chloride), showing that the polyelectrolyte domain structures are indeed sensitive to the detailed chemistry of the polyelectrolyte and solvent.

Our original intent for the present investigation was to investigate a much wider range of counterion types—including alkali earth metals, transition metals, and especially counterions of high-charge valency, but we found that many of these polyelectrolyte-counterion combinations lead to precipitation of the polyelectrolyte solutions³⁰ (Narh and Keller³¹ have documented this phenomenon for PSS solutions, along with many other related interesting observations). Therefore, we restricted our attention to monovalent and divalent alkali earth metal counterions, apart from a couple of exceptions noted below.

II. EXPERIMENT

Polystyrene sulfonate samples (PSS) listed in Table I were used for the experiments. Sample NaPSS-h1 [$M_n = 1.24 \times 10^5$,³² degree of sulfonation (DS)=90%, $M_w/M_n = 1.23$, degree of polymerization (DP)=633] was obtained from Scientific Polymer Products, Inc.³³ Matched relative molecular mass deuterated sample NaPSS-d2 ($M_n = 5.88 \times 10^4$,³² DS=83%, $M_w/M_n = 1.06$, DP=300) and hydrogenated sample NaPSS-h2 ($M_n = 6.06 \times 10^4$,³² DS=90%, $M_w/M_n = 1.06$, DP=309) were purchased from Polymer Source Inc.³³ NaPSS samples with charge density (degree of sulfonation) of 84% (NaPSS-h3) and 50% (NaPSS-h4) were prepared by sulfonation of polystyrene $M_n = 1.81 \times 10^4$, $M_w/M_n = 1.03$, DP=174, obtained from Scientific Polymer Products, Inc.³³ according to the procedure of Makowski *et al.*³⁴ All samples were purified by mixed-bed ion exchange resin [Bio-Rad MSZ 501 (D)].³³ The acid form of polystyrene sulfonate was converted to a salt form by mixing with an equivalent hydroxide. The neutralized solution was further purified by dialysis against deionized water to a constant low conductivity. The CuPSS sample was prepared by

TABLE I. Characteristics of polystyrene sulfonate samples.

Samples	M_n^a	M_w/M_n	DP	DS	Origin
PSS-h1	1.24×10^5	1.23	633	90%	Scientific Polymer
PSS-h2	6.06×10^4	1.06	309	90%	Polymer Sources
PSS-d2	5.88×10^4	1.06	300	83%	Polymer Sources
PSS-h3	...	1.03 ^b	174	84% ^c	Prepared in this lab ^d
PSS-h4	...	1.03 ^b	174	50% ^c	Prepared in this lab ^d

^aRelative molecular mass of polystyrene sulfonate sodium salt.

^bPolydispersity of parent polystyrene.

^cDetermined by titration.

^dAccording to Ref. 34.

mixing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with the acidic form of PSS in a molar ratio at least 100 fold excess of Cu^{2+} to H^+ and by dialysis against deionized water until a permanent low conductivity of the exchanged water was achieved. The “salt-free” polyelectrolyte solutions were lyophilized and further dried in a vacuum oven to a constant weight. Deuterated water (D_2O , Cambridge Isotopes,³³ 99.9% D, low paramagnetic) was used as received. Other chemicals used such as NaOH, KOH, Mg (OH)₂, Ca(OH)₂ were all analytical grade and were used without further purification.

A. Neutron scattering measurements

Small angle neutron scattering measurements were performed both on the 8 and 30 m SANS instruments at the Cold Neutron Research Facility at the National Institute of Standards and Technology to obtain scattering data over a wide range of observational scales. A fixed sample-to-detector distance of 3.5 m was used at the 8 m facility. The neutron beam was monochromated to a wavelength (λ) of 9 Å with a velocity selector having a spread of 0.25 ($\Delta\lambda/\lambda = 0.25$). This configuration corresponds to $q = (4\pi/\lambda_0)\sin(\theta/2)$ values in the range $0.0089 \text{ \AA}^{-1} < q < 0.0890 \text{ \AA}^{-1}$, where λ_0 is the neutron wavelength and θ is the scattering angle. Two sample-to-detector distances (8.1 and 1.5 m) were used at the 30 m facility. The wavelength $\lambda = 6 \text{ \AA}$ and $\Delta\lambda/\lambda = 0.22$. These configurations allowed us to perform measurements over a large wave vector range ($0.0075 \text{ \AA}^{-1} < q < 0.08 \text{ \AA}^{-1}$ and $0.0413 \text{ \AA}^{-1} < q < 0.535 \text{ \AA}^{-1}$, respectively). The resulting data were corrected for background electronic noise, detector inhomogeneity, empty cell scattering, and solvent scattering. The uncertainties are calculated as the estimated standard deviation of the mean. In case where the limits are smaller than the plotted symbols, the limits are left out for clarity. Fits of the scattering data are made by a least-square fit of the data giving an average and a standard deviation to the fit.

B. Light scattering measurements

Static and dynamic light scattering measurements were performed with a Brookhaven (BI-200SM) light scattering goniometer³³ using an Argon ion laser (Spectra Physics 2020-3)³³ operating at a wavelength of 488 nm. The static light scattering intensity was measured by photon counting over an angular range of 30° to 150° at 5° intervals and the scattering data were normalized by the scattering intensity of toluene as a reference. Background scattering due to water

was subtracted from the measured count rate. Light scattering autocorrelation functions $G(\tau)$ were acquired with a logarithmic digital correlator (ALV-5000) and the corresponding relaxation time distributions were obtained by CONTIN analysis.³⁵ The measurement temperature was controlled at $(25.00 \pm 0.05) \text{ }^\circ\text{C}$ using a circulating bath. All solutions utilized in the dynamic light scattering measurements were filtered through 0.20 μm Gelman PVDF filters.³³

III. SPECIFICATION OF CONCENTRATION REGIMES AND CHARGE INTERACTION STRENGTH

The clustering of particles at equilibrium characteristically depends on the concentration of the clustering particles, and on other parameters influencing the interparticle interaction leading to particle clustering (e.g., solution pH, dielectric constant, polymer charge density, salt concentration are potentially relevant parameters for polyelectrolyte solutions).^{1,2} The transition temperature at relatively low concentrations of the clustering species normally depends Arrheniusly on temperature and this behavior has been observed for thermally reversible gels, living polymer solutions, and micelle solutions.^{36–38}

The presence of clustering necessarily complicates the definition of concentration regimes in this type of particle dispersion. In solutions of neutral particles, we normally speak of “dilute,” “semidilute,” and “concentrated” regimes based on geometrical considerations of the absence of interchain contacts, chain interpenetration, and dense packing, respectively. This type of definition is not generally useful in predicting particle clustering. It is more natural to define concentration regimes in terms of a temperature-dependent concentration defining the onset of significant particle clustering (e.g., critical micelle concentration in surfactant solutions). It is also common for particle clusters to undergo further clustering at a larger scale or to change their cluster morphology with increased particle concentration or a change in the temperature (micelle solutions again provide a good illustration³⁹). The cluster reorganization at higher concentrations often involves multifunctional contacts leading to the formation of thermally reversible gels. The concentration regimes of solutions of clustering particles are then defined by a succession of clustering transitions and geometry based definitions of concentration regimes have little relevance.

Clustering transitions are commonly accompanied by sharp changes in the solution transport properties (for example, the Soret coefficient of micelle solutions exhibits a

maximum at micellization transition.⁴⁰) Variations in the equilibrium properties (specific heat, osmotic compressibility) are normally weak at clustering transitions.² Relative sharp changes in transport properties are helpful in locating the clustering transitions as a function of particle concentration.² Particle clustering near the critical point of fluid mixtures and colloid dispersions characteristically gives rise to a maximum in the solution viscosity as a function of composition^{41,42} and associating particle fluids can be expected to give rise to similar features.⁴³ The study of these clustering transitions as a function of temperature and other relevant parameters is necessary to define concentration regimes since clustering can initiate at very low concentrations.

Polyelectrolyte solutions exhibit characteristic maxima in the viscosity⁴⁴ at rather low-polymer concentrations on the order (10^{-6} to 10^{-5}) M and recent measurements have shown a nearly Arrhenius temperature dependence of this “transition” for sulfonated polystyrene in water. Unfortunately, it is very difficult to perform light or neutron scattering measurements in this very low-concentration regime so that our investigation must necessarily be restricted to a concentration regime where large polyelectrolyte domains already exist. (The mean dimensions of these domains are examined below). The size of the sulfonated polystyrene domains is insensitive to temperature [$22^\circ\text{C} \leq T \leq 95^\circ\text{C}$] in our measurements below. This is consistent with being far below the clustering temperature, but above the temperature of phase separation.^{1,2} The measurements of the present paper are also restricted to a concentration regime where the solutions remain fluid. Recent measurements on these polyelectrolyte solutions at high polymer concentrations ($C_p \geq 1$ M) indicate extremely long relaxation times for polymer composition fluctuations, as measured by dynamic light scattering (see Sec. VII). This observation is consistent with a phenomenon similar to thermally reversible gelation at these higher polyelectrolyte concentrations. (There are many interesting features of this “gelation regime,” but this phenomena will be discussed in a separate paper.) The current paper is restricted to the concentration regime (10^{-5} M $< C_p < 1$ M) where we expect to have relatively isolated polyelectrolyte clusters. (A monomer molar concentration of 1 M for NaPSS corresponds approximately to the mass concentration 200 g/L.)⁴⁵ An explanation of our estimate of the onset concentration $C_p \approx 10^{-5}$ M for polyelectrolyte clustering is given in Sec. VII.

Clustering transitions have been observed in lightly sulfonated PSS in nonpolar solvents (“ionomer” solutions) upon varying temperature and concentration by both static and dynamic light scattering.^{46,47} There have been many reports of a clustering in highly charged polyelectrolyte solutions upon lowering the salt concentration,⁴⁸ providing an accessible route to studying polyelectrolyte clustering by neutron scattering. There is also evidence for chain clustering in high molecular weight, uncharged polymer solutions.^{49,50} Douglas and Hubbard⁵¹ have developed a model of chain “entanglement” based on this phenomenon. Within this model, topologically induced particle clustering (entanglement) should be possible in spherical gel

particles,⁵² rodlike particles such as buckytubes,⁵³ and plate-like particles such as found in exfoliated clays.⁵⁴ This additional source of clustering leads one to expect clustering to persist in high-molecular weight polyelectrolyte solutions when the salt concentration is high.⁵⁵

The measurements discussed below are also restricted to relatively high-charge densities where charge condensation of the counterions onto the chain backbone makes an important contribution to the polyelectrolyte properties. The interaction strength is quantified through the Coulomb interaction coupling constant, $\Gamma = \lambda_B/a$, where λ_B is the Bjerrum length ($\lambda_B = 7.14 \text{ \AA}$ for water near room temperature and atmospheric pressure) and a is the average contour distance between charged groups along the chain backbone. Charge condensation occurs when Γ is on the order of unity [$\Gamma \sim O(1)$] since the Coulombic interaction energy becomes comparable to the thermal energy $k_B T$ under this condition.⁵⁶ All of our measurements are restricted to the charge condensation regime where a significant fraction of the counterions are “localized” to a region near the polyanion backbone. We denote the effective value of Γ in the regime of charge condensation by Γ^* . The idealized Manning model predicts that the effective charge density parameter Γ (sometimes denoted by ξ in the polyelectrolyte literature) sticks to a value inverse to the counterion valence Z_c , $\Gamma^* = 1/Z_c$ for $\Gamma > \Gamma^*$, so that the relative charge density between polyelectrolytes having divalent versus monovalent counterions is predicted to equal 1/2 in the regime of counterion condensation. A recent reformulation of the Manning model of charge condensation in terms of an association equilibrium process between the counterions and the polyelectrolyte chain indicates that the condensation transition should become more gradual with increasing polymer concentration.⁵⁷ Since our scattering measurements are restricted to a concentration range in which substantial domain formation occurs, we can expect the effective charge density Γ^* of the polymers to slowly increase with the bare charge density Γ rather than to plateau as in the infinite-dilution Manning model.

Existing theories of polyelectrolyte solution properties do not normally treat the strong Coulomb coupling regime corresponding to our measurements⁵⁸ and the investigation of the phenomenology of these solutions is thus basic for making progress in understanding polyelectrolyte solutions. Numerous theories and scaling arguments have been introduced based on the assumed picture of a homogeneous dispersion of polymer chains in solution and considerations of the ionic strength dependence of chain rigidity.⁵⁹ Applicability of these models to our measurements is not obvious since chain clustering is conspicuous at any concentration at which the scattering measurements are possible. Moreover, counterion condensation should significantly modify the chain rigidity and the intersegmental interactions. All these effects need to be incorporated in the modeling of polyelectrolyte solutions.

IV. INTERCHAIN CORRELATION LENGTH ξ_d

The maximum in the scattering intensity as a function of q is perhaps the best known feature of the scattering proper-

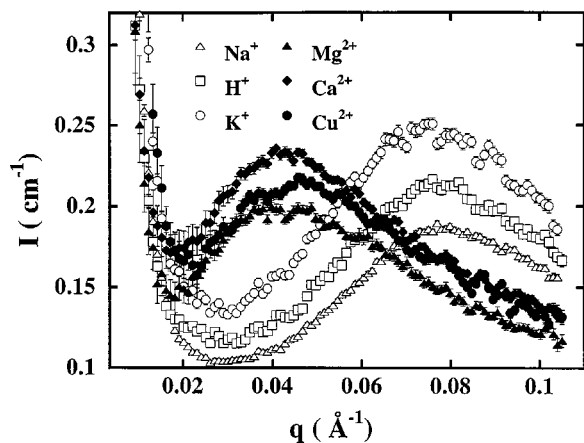


FIG. 1. SANS scattering intensity data for PSS with monovalent and divalent counterions, showing the shift of divalent ion peaks to smaller q , where the polyanion concentration is 0.20 M and the degree of sulfonation (Ref. 34) (charge density) is 90% ($\Gamma=2.57$) (sample PSS-h1). The absolute intensities shown in the figure have not been calibrated so that comparison of relative intensities cannot be reliably made in this figure.

ties of polyelectrolyte solutions. This scattering intensity maximum has been observed in many previous x-ray and neutron scattering studies, and the scaling of this peak position q^* with particle concentration C_p has provoked much theoretical speculation. A crossover between a $q^* \sim C_p^{1/3}$ and a $q^* \sim C_p^{1/2}$ concentration scaling has frequently been noted for polyelectrolyte solutions. This crossover has been observed both for relatively flexible and rodlike polyelectrolytes^{60,61} so the effect seems to have little to do with polymer chain conformation.

Figure 1 shows our SANS scattering data for salt-free PSS solutions with a range monovalent and divalent counterions where the polymer concentration is fixed at $C_p=0.20$ M. (Sample specification is given in figure captions.) The SANS data falls into two distinct groups, the peak positions q^* corresponding to monovalent ion (H^+ , Na^+ , K^+) scattering data occur near 0.08 \AA^{-1} while the peak positions q^* for the divalent ions (Mg^{2+} , Ca^{2+} , Cu^{2+}) cluster near 0.04 \AA^{-1} . This corresponds to an interchain correlation length $\xi_d \approx 2\pi/q^*$, having a size $\xi_d \approx 8$ and 16 nm for monovalent and divalent ions, respectively.

In an extensive set of measurements that we plan to publish elsewhere, we investigated q^* for Na^+ and Mg^{2+} counterions at higher polymer concentrations where the size of the polyelectrolyte domains and the relaxation times from dynamic light scattering measurements become very large, a phenomenon similar to thermally reversible gelation.⁶² These measurements indicate that q^* for monovalent and divalent counterions approach each other as C_p approaches a characteristic concentration on the order of 1.0 M where the slow mode relaxation time also becomes very large. This indicates a significant change in the interchain correlations with counterion valency at these relatively high-polymer concentrations, and suggests a change in the character of the counterion condensation phenomenon at high polymer concentrations. This ‘‘gel-regime’’ is avoided in the present paper.

Observations of q^* as a function of C_p , counterion type (or charge density⁶³) and polymer molecular weight show

that the counterion valency is a primary determinant of the fine structure of PSS polyelectrolyte domains. This conclusion is further supported by SANS studies of PSS solutions having more complex counterions such as K^+ caged by a (18-crown-6) crown ether.⁶⁴ Complexed counterions were prepared by stoichiometrically adding the crown ether to a KPSS salt-free solution. The crown ether is a very strong ligand for K^+ so that adding this molecular to a KPSS solution traps the K^+ ions into the crown ether cages stoichiometrically.⁶⁴ Surprisingly, we observed the peak position for the crown ether complexed KPSS and the uncomplexed KPSS solutions to be nearly the *same* (data not shown). Similar results were found for Cu^{2+} stoichiometrically converted to a $Cu(NH_3)_4^{2+}$ complex ion in a CuPSS salt-free solution (data not shown). All these observations indicate that the counterion size has remarkably little influence on the internal structure of the polyelectrolyte domains.

The qualitative difference between the peak positions for the monovalent and divalent counterions can be understood from the Manning model of charge condensation. As mentioned before, the Manning model⁵⁶ predicts that the relative charge density of a polymer having divalent counterions is 1/2 the charge density of a chain with monovalent counterions in the regime of counterion condensation. (In the present measurements we have³⁴ $\Gamma=1.43-2.57$, so that the polymers are highly charged.) Essafi *et al.*⁶³ have shown that q^* of salt-free PSS solutions is nearly proportional to the polyanion charge density. [We have independently confirmed that our PSS solutions follow the trend for $q^*(\Gamma)$ indicated by Essafi *et al.*] The presence of the divalent counterion reduces the effective charge density near the chain surface because of their more effective compensation of the bare cation charge when the multivalent ions are condensed.⁵⁶ This relative charge density reduction makes ξ_d of the PSS domains larger for the divalent ions. The degree of agreement between the Manning model and our scattering observations is probably fortuitous, but we are confident in the qualitative correctness of the Manning model explanation of the effect. Some of the limitations of Manning model in treating multivalent charge condensation are discussed by Ludwig and Loebel.⁶⁵

The Manning model of a sharp counterion condensation at a critical charge density is restricted to low-polymer concentrations, $C_p \rightarrow 0^+$. Levin has indicated that the *effective charge density* Γ^* should increase smoothly, albeit somewhat slowly, at higher polymer concentrations (i.e., the transition is ‘‘rounded’’) so that counterion condensation corresponds to a broad crossover regime in Γ , rather than a sharply defined transition point. We interpret the dependence of q^* on Γ to arise from transition rounding at nonvanishing polymer concentrations. This argument would suggest that q^* should saturate to a constant value at high-charge density Γ where the saturation value of Γ should depend on the polymer concentration. However, recent simulations⁶⁶ of flexible polyelectrolytes at nonvanishing concentrations do not indicate a tendency for Γ^* to saturate to a constant value for large values of Γ so that it is possible that the effective charge density Γ^* can increase well-above the Manning critical value. (Charge condensation effects still reduce Γ^* relative to the bare charge density Γ so that the Manning

model should still be qualitatively applicable in describing *relative* changes in Γ^* with charge valence.) Further studies of q^* over a wide range of polymer concentrations and charge densities are needed to better understand this phenomenon.

While the charge density is clearly a relevant parameter for determining the structure of polyelectrolyte domains in solution, we must warn about the extension of our finding of a direct relation between charge density and ξ_d to polyelectrolyte solutions generally. There are observations that indicating q^* can be independent of charge density for certain polyelectrolytes.⁶⁷ We tentatively interpret this effect as arising from strong interchain (e.g., hydrogen bonding) interactions.⁶⁸ In this view, the chemical nature of the chain backbone should then be relevant to determining the internal structure of the polyelectrolyte domains. We next consider the influence of charge density and Z_c on the average radius of gyration $R_{g,d}$ of the polyelectrolyte domain structures.

V. RADIUS OF GYRATION $R_{g,d}$ OF POLYELECTROLYTE DOMAIN STRUCTURES

Although previous papers have emphasized the importance of the charge density for the qualitative observation of domain structures in aqueous solutions, especially in the case of colloidal particle dispersions,^{69–71} there have been relatively few quantitative investigations of how the size of the domain structures depends on the charge density and other system parameters. This situation is particularly surprising in the case of the colloidal measurements where the particle “domains” or “clusters” are perhaps the most conspicuous feature observed in optical images. There have been previous studies in which measurements of the average domain size have been noted for polyelectrolyte solutions. From the angular dependence of total scattered light intensity (static light scattering) and the angular dependence of the diffusion coefficient of the slow mode (dynamic light scattering), Sedlak and Amis⁷² have estimated the polyelectrolyte domain dimensions for NaPSS for a range of molecular weights and a fixed charge density. Both static and dynamic light scattering measurements indicated that a domain radius of gyration $R_{g,d}$ lies in the range 50 to 100 nm with only a weak dependence of $R_{g,d}$ on chain molecular mass. (We note that R_g of chain clusters forming in aqueous methylcellulose solutions undergoing thermally reversible gelation are likewise insensitive to both temperature and concentration, provided that the temperature is restricted to the one-phase region.⁷³ The insensitivity of the cluster size to polymer concentration, molecular mass, temperature, and other parameters seems to be a common characteristic of equilibrium associating polymers.) Somewhat later, Sedlak⁷⁴ noted that the $R_{g,d}$ of polyacrylic acid (PAA) polyelectrolyte domains in water and methanol had a similar order of magnitude to the PSS domains in water. He further noted a decrease of $R_{g,d}$ with a decrease of the solvent dielectric constant. From the angular dependence of scattering intensity of poly(N-benzyl-2-vinylpyridinium bromide) aqueous solutions, Förster *et al.*⁷⁵ reported an increase in $R_{g,d}$ with molar mass and charge

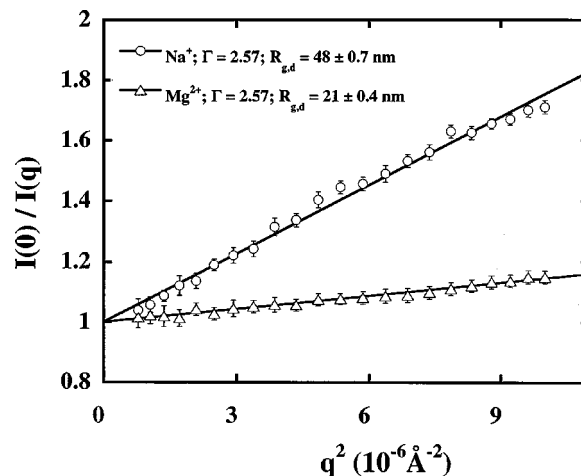


FIG. 2. Angular dependence of the normalized reciprocal excess scattering intensity $I(0)/I(q)$ for PSS with Na^+ and Mg^{2+} counterions at a fixed polyanion charge density (Ref. 34) of 90%, $\Gamma = 2.57$ (sample PSS-h2), where the polyanion concentration is 0.20 M. The solid lines are Lorentzian fits [$I(0)/I(q) = 1 + \frac{1}{3}(R_{g,d})^2 q^2$]. Note that the polyelectrolyte domain structures become smaller for divalent counterions than for monovalent counterions. Similar apparent $R_{g,d}$ values were determined from Debye-function fits to the data shown in figure.

density, which is relevant to our current investigation of charge density effects on the domain structures of polyelectrolyte solutions.

Figures 2 and 3 show the angular dependence of the total scattering intensity of PSS solutions where the counterion charge valence and the polyanion charge density are varied, respectively. The polymer chains in Fig. 2 have a $M_n = 6.06 \times 10^4$ and $\Gamma = 2.57$. The data in Figs. 2 and 3 were fit to a Lorentzian (lines in figures) according to the formula, $I(0)/I(q) = 1 + \frac{1}{3}(R_{g,d})^2 q^2$, where $I(q)$ is the excess scattering intensity obtained by subtracting the solvent background (H_2O) scattering intensity. The resulting apparent $R_{g,d}$ of the

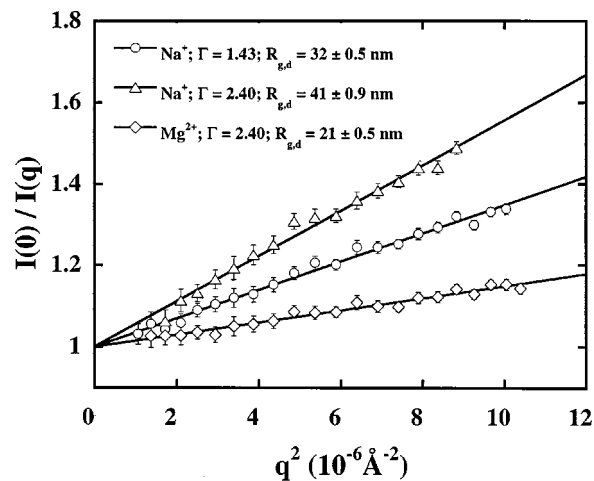


FIG. 3. Angular dependence of the normalized reciprocal excess scattering intensity $I(0)/I(q)$ for NaPSS with variable charge density (Ref. 34), 84%, ($\Gamma = 2.40$, sample PSS-h3), and 50% ($\Gamma = 1.43$, sample NaPSS-h4), where the polyanion concentration is 0.20 M. The solid lines are Lorentzian fits [$I(0)/I(q) = 1 + \frac{1}{3}(R_{g,d})^2 q^2$]. Note that the polyelectrolyte domain structures become smaller with a decrease in the charge density. Divalent counterion data is also included for comparison of the magnitude of the effect.

polyelectrolyte domains for the monovalent counterion (Na^+) is found to be 48 nm while $R_{g,d}$ for the divalent ion (Mg^{2+}) is 21 nm. (We use the term “apparent radius of gyration” since interdomain interactions are neglected in our Lorentzian fits of $R_{g,d}$.) Thus, we find roughly a factor of 2 reduction in the polyelectrolyte domain size in the case of the divalent (Mg^{2+}) relative to the monovalent counterion (Na^+). Our measurements of the domain dimensions for NaPSS agree qualitatively with previous observations by Sedlak⁷² and Matsouka and Ise⁷⁶ under comparable solvent conditions (molecular mass, polyanion charge density, polymer concentration). The lowering of the polyelectrolyte domain size in the case of the divalent counterion is apparently another consequence of the lowering of the polyanion charge density by the presence of divalent counterions. Notably, the rough factor of 2 change in the polyelectrolyte domain dimensions between the divalent and monovalent counterion cases acts in the *opposite direction* to the change found for ξ_d . This trend is natural since a lowering of the charge density should diminish the tendency of polyelectrolyte domain formation, as found for colloid dispersions.⁷⁷

Ray and Manning⁷⁸ have recently developed a model of chain domain formation in highly charged polyelectrolyte solutions that has relevance to our measurements. They account for charge condensation effects in polyelectrolyte solutions and their arguments indicate the presence of an attractive interaction between highly charged polyelectrolyte chains at an intermediate length scale set by the Debye screening parameter, κ . This predicted interaction between polyelectrolyte chains is mediated by the counterions and has the property that the well depth *decreases* with charge valence. Moreover, the range of the interaction is predicted to be *independent* of charge valence for a fixed ionic strength. The decreased attraction with increased charge valence is consistent with our observations, but the insensitivity of the potential range to charge valence is hard to reconcile with our observed charge valence dependence of ξ_d . The modeling of Ray and Manning makes several assumptions (e.g., chains are long rods) that may not be appropriate to semiflexible polyelectrolyte chains so that the cluster morphology is unrealistic in comparison to our measurements (e.g., formation of bundles of rods). In our view, this model makes interesting qualitative predictions and incorporates essential physical features of polyelectrolyte solutions. A quantitative comparison of our measurements to this model will require further theoretical developments, however.

To further check our physical intuition relating the domain size $R_{g,d}$ to the charge density we can consider the direct influence of the charge density on $R_{g,d}$. Figure 3 shows light scattering intensity data for NaPSS data having 84% and 50% degrees of sulfonation³⁴ ($\Gamma = 2.40$ and 1.43, respectively) and a common degree of polymerization ($\text{DP} = 174$) and polymer concentration ($C_p = 0.20$ M). Decreasing the charge density causes $R_{g,d}$ to decrease from 41 to 32 nm. This observation supports the qualitative idea that the overall chain dimensions of the polyelectrolyte domains increases with the charge density and our suggestion that the reduction of $R_{g,d}$ arises from the reduction of the polymer charge den-

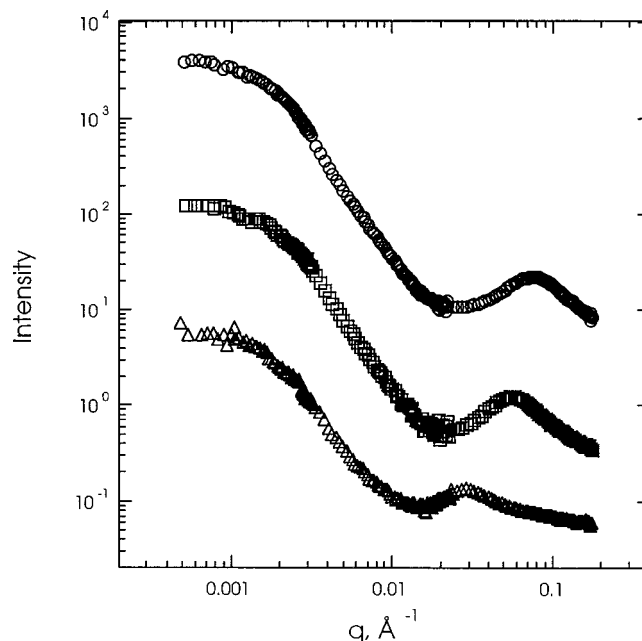


FIG. 4. Combined static light scattering and SANS intensity data $I(q)$ over large wave vector range for poly(N-methyl-2-vinylpyridinium chloride) in D_2O (Ermi and Amis, Ref. 16, Fig. 4). The polymer concentrations are equal: (Δ) 3.0 g/L, (\square) 15 g/L, and (\circ) 30 g/L. The sharp decrease in scattering intensity with increasing q follows an apparent power law, $I(q) \propto q^{-2.2 \pm 0.2}$, for each sample.

sity by the divalent counterion through its more efficient compensation of the bare polyanion charge.

A more complete view of the scattering properties of polyelectrolyte solutions which simultaneously emphasizes the large scale chain domain structure and the local inter-chain correlations within the polymer domains requires a combination of light and neutron (or x-ray) scattering measurements to cover the wide range of scales required. Ermi and Amis¹⁶ recently made a pioneering study of this kind for poly(N-methyl-2-vinylpyridinium chloride) in D_2O with combination of light and neutron scattering intensity data. We reproduce some of this data in Fig. 4 for salt-free solution having a range of polymer concentrations, (3.0, 15, 30) g/L, to illustrate this “broader view” of the scattering properties of a polyelectrolyte solution. The average polyelectrolyte domain size in these measurements was ≈ 90 nm, independent of the polymer concentrations. This is a typical dimension for polyelectrolyte or colloidal charged particle domains. We also observe that the scattering intensity data in Fig. 4 has a strong resemblance to the structure factor of tethered random surfaces,^{17–21} suggesting that the polyelectrolyte domains have a geometry similar to a cobweb. (Polymer networks similar to tethered random surfaces form the “skeleton” of eukaryotic cell membranes and are found in a variety of other cell types.⁷⁹)

A closer look at the wavevector dependence of the scattering intensity data for the PSS solutions reveals an important difference between the PSS solution data and the observations of Ermi and Amis.¹⁶ The poly(N-methyl-2-vinylpyridinium chloride) data (Fig. 4) shows a convincing power law scaling at low q that is representative of a fractal structure having a dimension, $d_f \approx 2.1 \pm 0.2$. In contrast, the

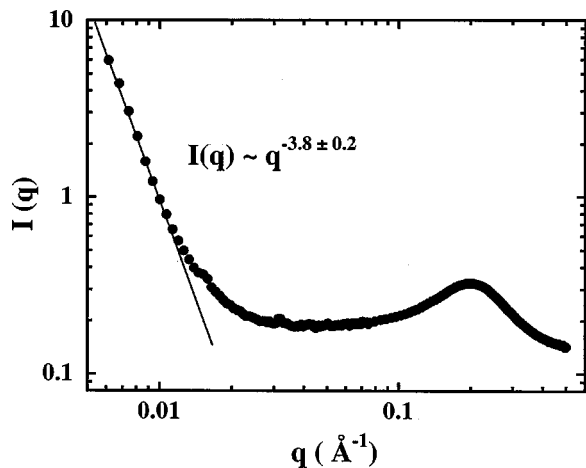


FIG. 5. SANS scattering intensity $I(q)$ data for representative NaPSS polyelectrolyte solution at intermediate wave vector q scales (sample PSS-h2). The data are shown in a log-log representation and the fitted apparent power scaling exponent is indicated in the figure. Γ and C_p are 2.57 and 1.6 M, respectively. (This is notably a rather high polymer concentration relative to the solutions considered elsewhere in the paper.) Optimally, the data should cover a larger q range to assign scaling exponents for $I(q)$ with confidence, but the apparent scaling is clearly distinct from former measurements on poly(N-methyl-2-vinylpyridinium chloride) solutions (Fig. 4). The current measurements are consistent with earlier measurements on NaPSS by Ise and co-workers (Ref. 77).

magnitude of the corresponding apparent power law for the PSS data was generally found to lie in the range 2.5–4, consistent with a more compact network structure or a domain structure having a sharp interface. Representative scattering intensity data for PSS solutions with monovalent (Na^+) counterions are given in Fig. 5. The data emphasize the intermediate q range where a power law scaling for $I(q)$ should be a reasonable approximation. These measurements (Light scattering data as in Fig. 4 would allow for a more complete analysis) indicate that the polyelectrolyte domains formed in the case of Na^+ counterions are “globular” (non-fractal; $d_f \approx 3$) domains. This change in cluster geometry from the previous poly(N-methyl-2-vinylpyridinium chloride) observations (Fig. 4) might be related to the strong hydrophobic backbone structure of PSS chains, which is also a notable feature of many biologically significant polyelectrolytes. Ise and co-workers have previously made observations of a similar wave vector scaling at intermediate scales for NaPSS and they found a similar scattering intensity scaling as in our Fig. 5.⁸⁰ Taken together, these observations indicate that while the formation of polyelectrolyte domain structures may be a general feature of polyelectrolyte solutions for strong Coulomb coupling, the geometrical form of the polyelectrolyte domains appears to be *nonuniversal*. The chain and solvent structure influences the domain geometry. A similar situation has been observed in the aggregation of uncharged fullerene C_{60} particles in various solvents where both fractal ($d_f \approx 2.1$) and globular ($d_f \approx 3$) dynamical clusters are found depending on the solvent.^{81–83} Future studies of polyelectrolyte solutions in the strong coupling regime should focus on how counterion valence, short-range interactions, chain stiffness, monomer structure, polymer concen-

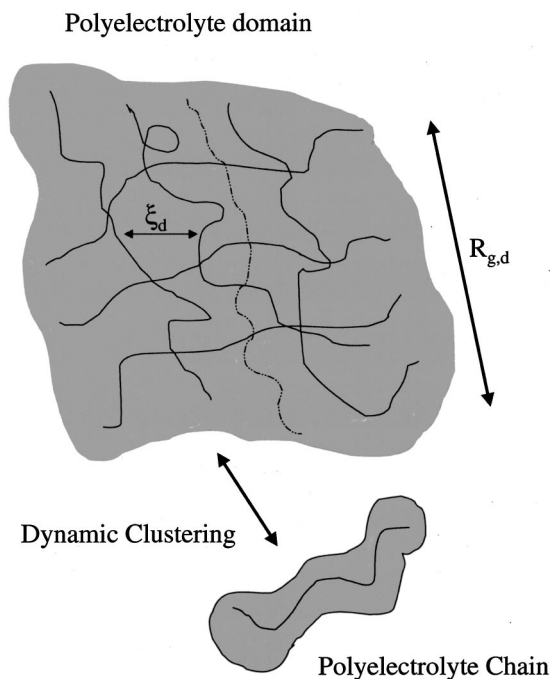


FIG. 6. Conceptual two-dimensional representation of polyelectrolyte domain, showing a domain composed of many chains and surrounded by a counterion cloud in equilibrium with unassociated polyelectrolyte chains. Our cartoon naively indicates that the counterion cloud is entirely enclosing the polymer chains with the polyelectrolyte domains, but the real situation probably involves a diffuse counterion enrichment layer about chains within the domains. The dashed chain is an individual chain.

tration, salt concentration, etc., influence the polyelectrolyte domain morphology.

The combination of light and neutron scattering data indicates that highly charged polyelectrolyte chains form domain structures at moderate polymer concentrations and that the internal structure of these transient chain clusters normally depends on the polymer concentration and charge density. We indicate a cartoon of the physical situation in Fig. 6, which shows a polyelectrolyte domain, composed of many chains and surrounded by a counterion cloud, and in equilibrium with unassociated polyelectrolyte chains. Our measurements indicate that the size of these domains $R_{g,d}$ increases with the polymer charge density while the interchain correlation length ξ_d within the cluster decreases with the polymer charge density. Our cartoon naively indicates that the counterion cloud entirely encloses the polymer chains within the polyelectrolyte domains, but the real situation probably involves a diffuse counterion enrichment layer about chains within the domains. We then expect the counterion cloud structure within the domains to have “sponge-like” morphology. Further neutron scattering measurements are needed to establish the geometry of the counterion cloud.

VI. RADIUS OF GYRATION $R_{g,c}$ OF INDIVIDUAL POLYMER CHAINS

The problem of calculating the mean dimensions of polyelectrolyte chains has attracted much theoretical attention, but the measurement of this property is complicated by the general tendency of polyelectrolyte chains to form do-

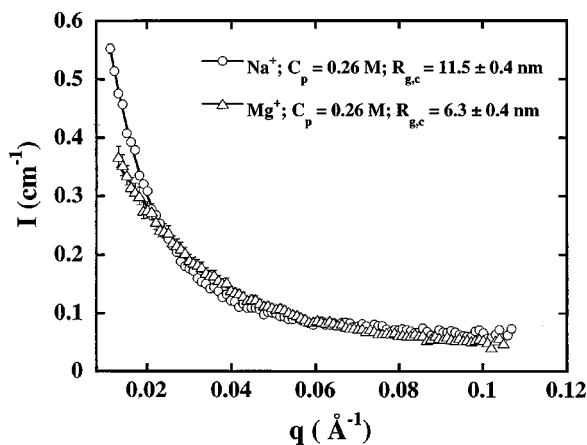


FIG. 7. SANS measurement of PSS polymer radius of gyration for Na^+ and Mg^{2+} counterions using the zero average contrast (ZAC) method to compensate intermolecular scattering. Lines denote Debye function fits to data and fitted $R_{g,c}$ of PSS chains (equimolar mixture of sample PSS-h2 and sample PSS-d2). We also fitted data to a wormlike chain model using the function from Sharp and Bloomfield (Ref. 128) which, however, gives almost identical fits.

main structures beyond even very low-polymer concentrations under salt-free conditions. Existing theory has little to say about the present measurements where counterion condensation must have a large influence on the local chain rigidity as well as dispersion of chains in solution. It is then interesting to estimate the individual polyelectrolyte chain dimensions for polyelectrolyte solutions in the strong coupling regime by combining SANS measurements with isotopic labeling techniques to separate intrachain from interchain correlations. Notably, this method can be employed even for the salt-free conditions of our measurements. We next examine how the chain dimensions depend on the counterion charge valency and compare these changes to those found for the polyelectrolyte domain $R_{g,d}$ and polyelectrolyte inter-chain correlation length, ξ_d .

The zero average contrast (ZAC) method is used to separate the intramolecular scattering function from the overall scattering and this method was described in detail in previous works.^{84,85} In brief, we prepared equimolar mixtures of equivalent DP deuterated and hydrogenated PSS in a mixture of H_2O and D_2O . The fraction of D_2O in the solution is set to the ‘‘optical theta condition’’ where the scattering length density of the hydrogenated and deuterated monomers are equal and opposite so that the interchain correlations are compensated. Figure 7 shows SANS scattering data utilizing ZAC matching for NaPSS and MgPSS solutions ($C_p = 0.26$ M, equimolar mixture of samples PSS-h2 and PSS-d2). The absence of a peak in Fig. 7 (compare to Fig. 1) gives direct evidence for the compensation of interchain correlations. (The molecular mass for the data shown in Fig. 7 is lower than for measurements shown in Fig. 1 and this difference should be accounted for in comparing the dimensions of the polymer chain and the interchain correlation length ξ_d .) We observe that the divalent counterion gives rise to a relative decrease of the chain radius of gyration, $R_{g,c}$. The fits to the data in the figure correspond to a Debye function. It is found

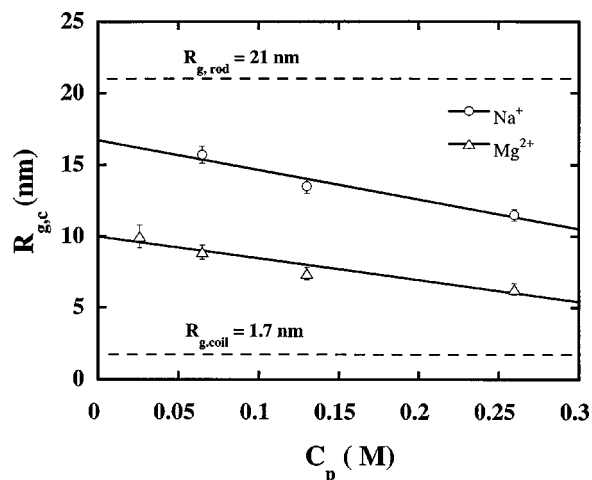


FIG. 8. SANS measurements of the C_p dependence of radius of gyration of PSS chains with Na^+ and Mg^{2+} counterions obtained by the zero average contrast method (using an equimolar mixture of sample PSS-h2 and sample PSS-d2). Note that chain dimensions are intermediate between rodlike and random coil dimensions (limits denoted by dashed lines) and that the chains become smaller in the presence of divalent counterions. The change of the polyelectrolyte dimensions for divalent counterions relative to monovalent counterions is comparable to the change in the polyelectrolyte domain size with counterion valency (see Fig. 2).

that a fit to a wormlike chain model gives almost identical fits in the q range studied.

We can obtain some further insights into this chain contraction caused by the divalent counterions by comparing the polyelectrolyte chain dimensions to an idealized rod configuration for our polymer and an ideal random flight coil having a statistical segment length assumed to equal 2.5 \AA . Since the normal experience with uncharged polymer solutions gives rise to some dependence of the chain dimensions on the polymer concentration, we also performed our measurements over a range of polymer concentrations. Figure 8 shows the results of these extensive ZAC measurements for NaPSS and MgPSS solutions having the same molecular mass and degree of sulfonation as the data shown in Fig. 7. We made further ZAC measurements on new NaPSS and MgPSS samples prepared by ourselves. The average DP^{34} of the new samples was $\text{DP} = 291$ which is close to value for commercial sample data shown in Figs. 7 and 8, average $\text{DP} = 305$. These new measurements give $R_{g,c}$ which agree with the data in Fig. 8 to within experimental uncertainty over the concentration regime indicated.

The magnitude of the relative chain contraction caused by the divalent counterions is generally in the range 1.5–2, a change similar in magnitude to the change in scale observed for the overall dimensions ($R_{g,d}$) of the polyelectrolyte domains. The chain dimensions within the polyelectrolyte domains $R_{g,c}$ seem to be consistent with a semiflexible polymer. The increase of the polymer concentration apparently leads to increased screening of the charge and excluded volume interactions, leading to a contraction of the chain dimensions to a value closer to the value for an ideal ‘‘random coil’’ polymer. This trend is accentuated in the case of the divalent counterions and we suggest that this effect has its origin in the change in the polyanion charge density as in the

previous $R_{g,d}$ and ξ_d observations on polyelectrolyte domains. We also varied the molecular mass over a wide range [$58 \leq DP \leq 553$] at a fixed polymer concentration and high-charge density ($C_p = 0.26$ M; $\Gamma = 2.17-2.57$) and we found a reasonably good fit of our data to the Kratky–Porod worm-like chain model.

We note that the change in the rigidity (i.e., the persistence length) of polyelectrolytes with Z_c has many biological implications and this effect has been observed previously in the biological literature. A change of l_p with Z_c has recently been observed in optical tweezers measurements on DNA solutions.⁸⁶ Electro-optical⁸⁷ and other techniques⁸⁸ provided earlier, but indirect estimates of the change in l_p with charge valency. These changes in the rigidity of polyelectrolytes with Z_c have important implications for the extent of DNA knotting,⁸⁹ DNA supercoiling⁹⁰ and are potentially important for DNA packaging in cells and viruses, and DNA molecular recognition and function.⁸⁸ It is notable from our observations that the change of l_p with charge valency in highly charged polyelectrolytes is not restricted to molecules having a double helix structure.

These observations on synthetic and biological polyelectrolytes raise questions about the electrostatic origin of chain rigidity in strong-coupling polyelectrolyte polymer solutions. The existence of counterion condensation suggests that the ion concentration near the polymer should become somewhat insensitive to salt concentrations, at least at low-salt concentrations. Thus, we might expect the ionic strength dependence of l_p to be secondary in its dependence on the counterion valency under the conditions of strong Coulomb coupling. A change of the extent of the counterion cloud with salt concentration should make l_p dependent on salt concentration, as in the case of weak coupling polyelectrolyte solutions⁴⁸ (“weak polyelectrolytes”) where a dependence of chain rigidity on ionic strength can be theoretically investigated with greater confidence.⁴⁸ The condensation of counterions onto the backbone of the polyelectrolyte chain can naturally be expected to modify the effective rigidity of the chain-counterion “complex” and it is important to understand how charge valency influences this rigidification. In the case of neutral polymers there is good correlation between relative chain rigidity and the cross-sectional radius of the polymer, as measured by scattering measurements.⁹¹ This correlation for neutral polymers extends reasonably to polyelectrolytes whose bare charge is largely compensated by condensed counterions (“strong-coupling”). Recent simulations and density functional theory calculations indicate that the counterion cloud extent for highly charged rod polymers is significantly reduced in the case of a low-concentration (16 mM) of divalent (Mg^{2+}) counterion salt relative to a salt with a monovalent (Na^+) counterion.⁹² If we identify the sum of the hard-core polyelectrolyte cross-sectional dimension with the spatial extent of the counterion cloud we then obtain a larger cross-sectional radius in the case of a monovalent counterions (relative to divalent counterions). This leads to the expectation that polyelectrolyte chains with monovalent counterions should be more rigid (other chain parameters being equal), in accord with our present measurements.

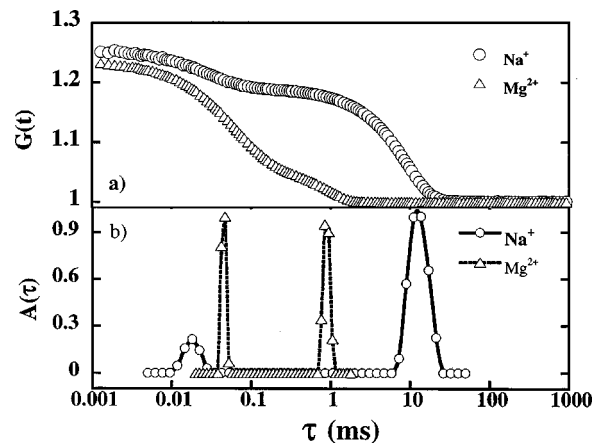


FIG. 9. Representative light scattering autocorrelation functions $G(\tau)$ for NaPSS and MgPSS solutions showing the effect of counterion valence on polyelectrolyte solution relaxation (sample PSS-h2). (a) Upper half of figure shows raw dynamic light scattering data. (b) Bottom half of figure shows the spectrum of relaxation times obtained by CONTIN analysis: $\theta = 45^\circ$, $C_p = 0.20$ M. The relaxation time for the fast mode becomes *slower* for the divalent counterions (Mg^{2+}) while the slow mode becomes *faster*.

There have been other interpretations of increased flexibility of polyelectrolytes induced by multivalent counterions. A prevalent idea, introduced in discussions of DNA rigidity, is that the high charge of multivalent counterions causes the polyelectrolyte to “kink”⁸⁸ so that the polyelectrolyte chain becomes more “coiled.” This picture of the change of change of polymer rigidity with charge valency is very sensitive to model assumptions such as assumed variations in the dielectric constant of the solvent about the polymer chain⁹³ so that this interpretation remains uncertain. It seems likely to us that a combination of effects arising from the counterion “dressing” about the chain and local chain polarization effects are responsible for the large changes of chain rigidity with counterion valency. The origin of chain rigidity for highly charged polyelectrolytes in the regime of counterion condensation deserves further experimental and theoretical investigation.

VII. INFLUENCE OF COUNTERION VALENCE Z_c ON DYNAMIC LIGHT SCATTERING PROPERTIES

There have been numerous dynamic light scattering measurements on polyelectrolyte solutions in the strong coupling regime. Dynamic light scattering measurements first suggested the existence of polyelectrolyte domain structures and some authors tried to estimate the size of these structures by assuming that the Stokes–Einstein relation can be applied to the slow diffusive mode that is a characteristic feature of “strong coupling” polyelectrolyte solutions.⁹⁴ Of course, these estimates of the polyelectrolyte domain size are complicated by the fact that osmotic interparticle interactions can give an appreciable contribution to the magnitude of the collective diffusion coefficient and, moreover, there is a viscous contribution arising from the change in the solution viscosity that must be accounted for before this type of model could be used to reliably estimate the dimensions of the polyelectrolyte domains. However, dynamic light scattering data can provide valuable information about the lifetime of counterion

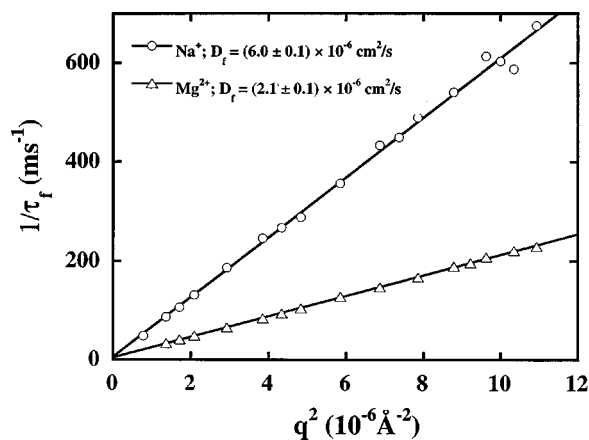


FIG. 10. Wave vector q dependence of the "fast" mode relaxation times τ_f for PSS with Na^+ and Mg^{2+} counterions (sample PSS-h2). Fitted fast mode diffusion coefficients D_f are indicated in figure.

and polymer concentration fluctuations occurring at equilibrium in polyelectrolyte solutions. We next consider the influence of counterion valency on the nature of dynamic light scattering data for PSS solutions.

Figure 9(a) shows typical light intensity-intensity correlation function $G(\tau)$ for NaPSS and MgPSS polyelectrolyte solutions. The concentration for these measurements equals $C_p = 0.20$ M and $\Gamma = 2.57$, so these measurements correspond to strong coupling. First, we observed that the long time relaxation of the solution with divalent ions is significantly "faster." We quantify this effect by a standard CONTIN³⁵ analysis of the relaxation time τ spectrum and the result of this analysis is indicated in Fig. 9(b). These measurements show the typical well-defined double-exponential relaxation of salt-free polyelectrolyte and colloidal particle solutions in the strong-coupling Coulomb interaction regime. A plot of the wavevector dependence of the fast and slow relaxation times is shown in Figs. 10 and 11. These modes are clearly diffusive and we introduced fast and slow diffusion coefficients through the definitions, $D_f = 1/(\tau_f q^2)$ and $D_s = 1/(\tau_s q^2)$, respectively.

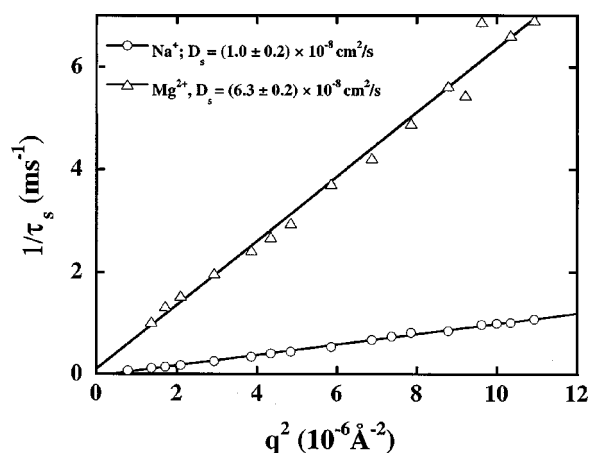


FIG. 11. Wave vector q dependence of "slow mode" relaxation times τ_s for PSS with Na^+ and Mg^{2+} counterions (sample PSS-h2). Fitted slow mode diffusion coefficient D_s are indicated in figure.

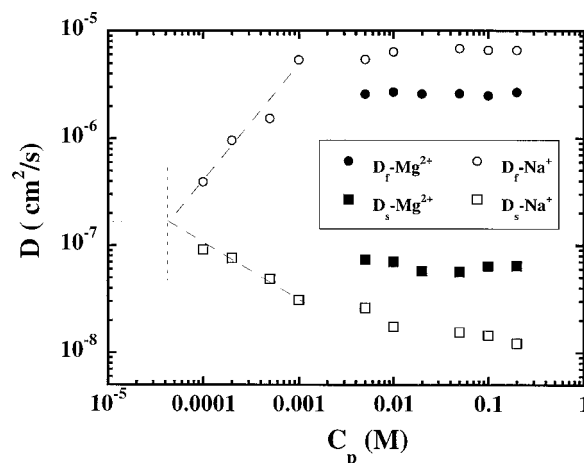


FIG. 12. Concentration dependence of diffusion coefficients for NaPSS and MgPSS salt-free solutions. We obtain a rough estimate of the onset of clustering in the case of the NaPSS data by extrapolating the D_f and D_s data to low concentrations (dotted lines) to find a crossing point (sample PSS-h2).

Figures 9–11 show that the overall shape of $G(\tau)$ is not dependent on the counterion type, but there are significant changes in the diffusion constants. D_f and D_s of the NaPSS solution are estimated to equal $(6.0 \pm 0.1) \times 10^{-6}$ cm²/s and $(1.0 \pm 0.2) \times 10^{-8}$ cm²/s, respectively, while we find $(2.1 \pm 0.1) \times 10^{-6}$ cm²/s and $(6.3 \pm 0.2) \times 10^{-8}$ cm²/s for the MgPSS solution. Figure 12 shows the concentration dependence of the diffusion coefficients D_f and D_s for Na PSS and MgPSS solutions (sample PSS-h2) over a range of polymer concentrations. The concentration dependence of D_f and D_s is weak at concentrations greater than 5×10^{-3} M, so that the changes in the diffusion coefficients with Z_c indicated in Figs. 9–11 apply to a good approximation over a wide concentration range. An extrapolation of the D_f and D_s for the NaPSS solutions to low concentrations leads to a "merging point" concentration $C_p^* \sim O(10^{-5}$ M or 10^{-5} g/mL). If D_f is taken to be comparable to the chain self-diffusion coefficient at low-polymer concentrations, then we expect this concentration to correspond to the onset of polyelectrolyte domain formation. Notably, reduced viscosity data for NaPSS solutions commonly exhibit maxima⁴⁴ for concentrations on the order of our rough estimate of the critical concentration for polyelectrolyte domain formation, C_p^* . Data for divalent counterion solutions at low-polymer concentrations are not included in Fig. 12 because of the difficulty in determining the diffusion coefficients. There was no difficulty in measuring $G(\tau)$ in these low-polymer concentrations, but the relaxations in $G(\tau)$ become significantly non-exponential so that D determinations became unreliable. We tentatively attribute the nonexponentiality in the slow mode contribution to $G(\tau)$ in the case of the divalent counterion (Mg^{2+}) to polydispersity in the domain size distribution.

A. Fast mode

There have been many interpretations proposed for D_f and D_s for polyelectrolyte solutions. The fast-diffusive mode has been interpreted as a coupled diffusion between the polyelectrolyte and its counterions^{72,95–97} or as a gel mode of the transient network.⁷⁵ The gel mode was claimed to be invalid

because D_f shows no dependence on polymer concentration.⁷² Moreover, the diffusive nature of the fast mode indicated in Fig. 10 is inconsistent with the gel mode interpretation of the fast mode. The idealized Nernst–Hartley (NH) model predicts that $D_f \approx D_{\text{NH}} = (1 + Z_p) D_p D_c / (Z_p D_p + D_c)$ where D_p is the diffusion coefficient of the polymer without the charges, D_c is the counterion diffusion coefficient, and Z_p is the effective polyanion charge.^{72,95–98} If $Z_p D_p \gg D_c$, then $D_f \sim D_{\text{NH}} \sim D_c$, i.e., the coupled diffusion is dominated by D_c . The Nernst–Hartley theory does not address itself to polyelectrolyte domain formation at nonvanishing polymer concentrations, but we still expect the fast mode in our measurements to be dominated by the mobility of the counterions (in the absence of interchain “cross-linking” phenomena mediated by counterions). Consistent with this reasoning, Matsuoka *et al.*⁹⁹ have shown that the D_f of PSS varies as $\text{LiPSS} \leq \text{NaPSS} < \text{CsPSS} \ll \text{HPSS}$, which is in accord with the inequalities in the magnitudes of counterion diffusion coefficients. Since the diffusion coefficient of Mg^{2+} ($0.706 \times 10^{-5} \text{ cm}^2/\text{s}$) is smaller than D_c of Na^+ ($1.33 \times 10^{-5} \text{ cm}^2/\text{s}$)⁹⁸ by a factor of 2, the observed reduction of D_f for MgPSS by a factor near 2 in Fig. 12 is understandable based on a counterion–polyion coupling type model of the fast mode. A similar influence of counterion valence has also been found in the study of the dynamics of DNA solution¹⁰⁰ where D_f of CaDNA is found to be smaller than D_f for NaDNA. Although the strong dependence of D_f on counterion valence supports the qualitative picture of a coupled polyelectrolyte–counterion transport, further theory is required to describe polyelectrolyte solutions exhibiting domain clustering.

B. Slow mode

The slow diffusive mode in Fig. 11 has previously been interpreted in terms of the diffusion of polyelectrolyte domains.^{97,101–102} We observe that D_s becomes much larger in the case of the divalent counterions (contrast this result with the decrease of D_f discussed above). This result is expected qualitatively based on our previous observation of a reduction of the polyelectrolyte domain size for the divalent counterions relative to the monovalent ions. The effect is much too large to be accounted for by the naïve application of the Stokes–Einstein relation, however. We have already mentioned that the neglect of interparticle interaction makes this kind of domain size estimation uncertain, and we note that a substantial change in the viscosity between the cases of monovalent and divalent counterion can be expected and this must have an effect on D_s . Cohen and Patel^{103,104} show that a change from monovalent to divalent cations in PSS solutions can lead to a substantial reduction of the polyelectrolyte solution viscosity. This effect is apparent in our samples which are much more fluid in the case of divalent counterions, other solution parameters being equal and we ascribe the main increase of D_s with charge valence to this viscosity effect rather than a direct change in domain size.

A reasonable estimate of domain size from D_s measurements requires both a measure of the osmotic interparticle interaction and the solution viscosity. Measurement of the zero-shear solution viscosity of strong coupling polyelectro-

lyte solution is necessarily complicated by the breakdown of the polymer domain structures under shear, which leads to substantial shear thinning.¹⁰⁵ Very significant slowing down of the slow mode can be anticipated at higher polyelectrolyte concentrations where the domain structures should percolate and we are currently investigating these more concentrated polymer solutions.

The measured τ_s (or D_s) is perhaps more usefully considered to represent the lifetime of the compositional fluctuations represented by the polyelectrolyte domains. This property should be very important for characterizing many other properties of polyelectrolyte solutions such as the Soret coefficient,¹⁰⁶ electrical conductivity, shear relaxation etc. The change from a monovalent to a divalent counterion can be expected to enhance compositional transport in strong coupling polyelectrolyte solutions.

Further dynamic light scattering properties of PSS solutions have been systematically investigated by Sedlak and Amis^{72,97} where dynamic light scattering properties of polyelectrolyte solutions are summarized as a function of polymer concentrations, salt concentration, chain molecular mass, etc. The qualitative findings are unchanged by a change of charge valency so we do not repeat this discussion here.

VIII. DISCUSSIONS

The effect of multivalent counterions on the structure and properties of polyelectrolyte solutions has recently attracted attention because of the recognition of the importance of ionic interactions in many biological processes such as DNA condensation,¹⁰⁷ salt-bridges stabilizing numerous biological structures,¹⁰⁸ nerve excitation,¹⁰⁹ and protein folding.¹¹⁰ Interest has also been stimulated by recent theory and simulation studies that have indicated substantial changes in polyelectrolyte interaction when monovalent counterions are replaced by multivalent counterions.^{30,78,111–115} Many measurements on synthetic polyelectrolyte show that the addition of salts containing multivalent cations tend to cause gelation and phase separation for a sufficient quantity of salt,^{30,31,104,116–120} suggesting the stabilizing effect of the polyanion charge against large scale phase segregation is diminished by the condensation of multivalent counterions. Multivalent contacts can also be expected to participate in multifunctional chain contact association interactions for certain temperature ranges so that many new effects and polyelectrolyte solution morphologies arise when the cations are multivalent.

Neutron scattering and static and dynamic light scattering measurements were performed on aqueous solutions of sulfonated polystyrene having a range of multivalent counterions, charge densities, molecular weight, and polymer concentrations. The measurements were performed in the strong coupling regime where counterion condensation has a strong influence on the polyelectrolyte solution properties. Neutron scattering measurements of the high- q peak position q^* in the scattering intensity $I(q)$ data (defining the interchain correlation length $\xi_d = 2\pi/q^*$ of the polyelectrolyte domain structures) increases by a factor of 1.5–2 for divalent counterions, relative to the monovalent counterion case. This

finding is a natural consequence of the reduction of the polymer charge density by divalent counterions in the strong-coupling regime, qualitatively consistent with Manning's model of charge condensation. Light scattering measurements of the overall dimensions of the polyelectrolyte domains indicate that the size of these domains becomes reduced for divalent relative to monovalent counterions. A reduction of the polyelectrolyte charge density is also found to lead to a reduction in the size of the polyelectrolyte domains. These findings suggest that the particle charge density is the primary parameter governing the polyelectrolyte domain formation and future work should consider whether a critical charge density Γ_c is required for the occurrence of the polyelectrolyte domains in low molecular mass polymers.

To gain insight into the single chain properties of the polymer chains within the polyelectrolyte domains we performed contrast matching neutron scattering measurements of the chain radius of gyration. The change of the chain size $R_{g,c}$ was found to be reduced in the case of divalent ions to an extent that was similar in magnitude to the change in the polyelectrolyte domain size, $R_{g,d}$. We also observe that the chains are not extended into a rodlike configuration in these relatively low-concentration polyelectrolyte solutions. The chains have an extension intermediate between extended and random coil chains and the chain swelling due to electrostatic and excluded volume interactions becomes diminished with increasing polymer concentrations, an effect reminiscent of solutions of uncharged polymer solutions.¹²¹ These observations raise questions about the role of charge density in influencing the rigidity of polyelectrolyte in the strong coupling regime.

Finally, we performed dynamic light scattering measurements to determine the influence of counterion charge valency on collective diffusion processes in strong coupling polyelectrolyte solutions. The collective diffusion coefficient D_s associated with the "slow mode" in the dynamic light scattering is significantly increased in the case of divalent counterions and this effect is argued to be general because of the decrease of the polyelectrolyte domain size $R_{g,d}$ for multivalent ions and the tendency of multivalent ions to reduce the solution viscosity.¹⁰² This enhancement of mass diffusion and solution relaxation has many implications for transport properties in polyelectrolyte solutions. The "fast diffusion coefficient" D_f changes seems to be dominated by the counterion diffusion rather than by the polyion diffusion.

One of the topics neglected in the present paper is the influence of multivalent ions on osmotic properties and phase stability of strong coupling polyelectrolyte solutions. Horkay *et al.*¹²² have recently made preliminary measurements exploring charge multivalency effects in highly charged polyacrylic acid gels. These measurements indicate the *absence* of a change of the gel elasticity with alkaline earth metal divalent cations that might be associated with a "bridging interaction" mediated by the counterions. (For certain transition metal cations, however, a change in elasticity with charge valency was observed, presumably associated with the formation of "salt-bridge" like counterion chain complexes.¹²²) These observations are consistent with

our observations indicating an increased flexibility of highly charged polyelectrolyte chains with the condensation of divalent counterions.

The increased flexibility and reduced chain repulsion caused by multivalent counterions is a general effect that can be expected to have many ramifications in material science and biology. These effects are known to facilitate the "condensation" of DNA into compact toroidal or rodlike forms^{123–125} and to influence the stiffness, knotting and supercoiling properties of DNA.^{86,89,90} We can also anticipate that multivalent counterions will have a large influence on the stability of charged lipid vesicles used in drug delivery and many other biological applications and on the fusion of membrane in living cells. In particular, an increase in the flexibility should facilitate membrane fusion and lead to a destabilization of vesicle dispersions. It is well known that Ca^{2+} counterions play a central role in membrane fusion phenomena in biological systems¹²⁶ and Ca^{2+} counterions have also been shown to cause the aggregation of phosphatidylserine vesicles in aqueous salt solutions.¹²⁶ These observations suggest that we should expand our studies of charge valency effects to "polyelectrolytes" having a two-dimensional topology (i.e., membranes).²² Changes in membrane transport induced by changes in the concentration of multivalent counterions deserve special attention because of the many potential biological applications.¹²⁷ We can also anticipate that multivalent counterion effects should be important in the area of tissue and drug preservation since changes in the polymer rigidity should also lead to changes in the glass transition of biological materials. Further systematic studies of charge valence effects on polymer rigidity and interaction should be very fruitful.

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