Polymer 202 (2020) 122714

Contents lists available at ScienceDirect

Polymer

journal homepage: http://www.elsevier.com/locate/polymer

Polyelectrolytes: On the doorsteps of the second century

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ARTICLE INFO

Keywords:
Polyelectrolytes
Charged polymers
Polyelectrolyte solutions
Counterion condensation
Cell model

ABSTRACT

Polyelectrolytes are macromolecules with ionizable groups. In this perspective, I will present a brief history of polyelectrolytes starting from the seminal papers published in the first half of the 20th century followed by the current developments in the field and by the list of the standing problems. Particular emphasis will be on how static and dynamic properties of polyelectrolyte solutions depend on the fraction of dissociated ionic groups, solvent quality for the polymer backbone, and salt and polymer concentrations.

1. Introduction: a historical note

Charged polymers are macromolecules with ionic groups that could dissociate releasing counterions in a solution and leaving charged (ionized) groups on a polymer [1–12]. Polymers with either positive or negative charges are called polyelectrolytes. Commonly used polyelectrolytes are polyacids (poly(acrylic acid) and poly(methacrylic acid)), polysalts (poly(styrene sulfonate)), cellulose derivatives, and DNA (see Fig. 1). However, if after dissociation a polymer has both positively and negatively charged ionized groups such polymers are called polyampholytes [13,14]. The well-known examples of polyampholytes are proteins in their native state (bovine serum albumin), denatured/unstructured proteins (gelatin), and synthetic copolymers with both acidic and basic groups. In the case of large charge asymmetry (excess of charges of one type) properties of polyampholytes are similar to those of polyelectrolytes.

Unique features of charged polymers were recognized long ago. Natural charged polymers like gum arabic (mixture of polysaccharides and glycoproteins) were used over the centuries as glues, binders, thickeners, additives to ceramic glaze and as stabilizing agents in inks, photography, and lithographic processes. For example, in India ink finely ground soot suspended in water is stabilized by the gum arabic. The natural protein gelatin is widely used in the photographic industry for stabilization of the silver halide crystals [15,16].

At the beginning of the 20th century the studies of charged polymers were focused on protein solutions [17,18]. It was established that the properties of such solutions are governed by the balance of the basic and acidic groups, with solution viscosity observed to increase when acid or base is added to a solution of isoelectric proteins (proteins with balanced positively and negatively charged groups). Staudinger believed that a study of simpler high molecular weight synthetic polymers ("model" polymers) such as poly(acrylic acid) could help with uncovering the origin of solution properties of amphoteric natural polymers [19]. Trommsdorff [19] found that the reduced specific viscosity η_{sp}/c in solutions of ionized poly(acrylic acid) shows nonmonotonic dependence on polymer concentration. It first decreased with increasing polymer concentration then passing through the minimum began to increase again (see Fig. 2 below). At constant polymer concentrations, addition of sodium chloride salt resulted in a decrease of the solution viscosity. This was probably the first clear experimental evidence of the effect of interactions on macromolecular conformations. Discussing these results in "Polymers. The origins and growth of science" [20] Morawetz pointed out: "*It is remarkable that these dramatic changes of viscosity at constant polymer concentration did not shake Staudinger's conviction that the polymer chain molecules are unable to change their shape, that they behave as rigid rods.*"

Phase separation in solutions of oppositely charged polyions was reported by Bungenberg de Jong and Kruyt in 1930 [21]. This phenomenon was called complex coacervation due to solution clouding and formation of the dense precipitate. The dense phase was shown to dissolve as stoichiometry of the complexes was changed or salt was added to the mixture.

In the series of papers on solutions of poly(acrylic acid) [22–24], Kern showed that the properties of polyelectrolyte solutions are qualitatively different from their low molecular weight counterparts. One striking observation was that for some polymer concentrations the titration curves and the electrical conductance of polyacid solutions were independent of the chain degree of polymerization. Kern's

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https://doi.org/10.1016/j.polymer.2020.122714
Received 4 May 2020; Received in revised form 5 June 2020; Accepted 8 June 2020
Available online 28 June 2020

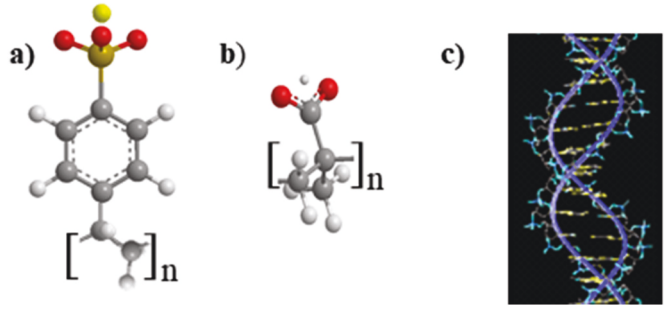

Fig. 1. Examples of polyelectrolytes poly(styrene sulfonate) **(a)**, poly(methacrylic acid) **(b)**, and DNA **(c)**. In panels a and b the following color scheme is used: carbon - grey, hydrogen – light grey, oxygen – red, sulfur – dark yellow and sodium – light yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

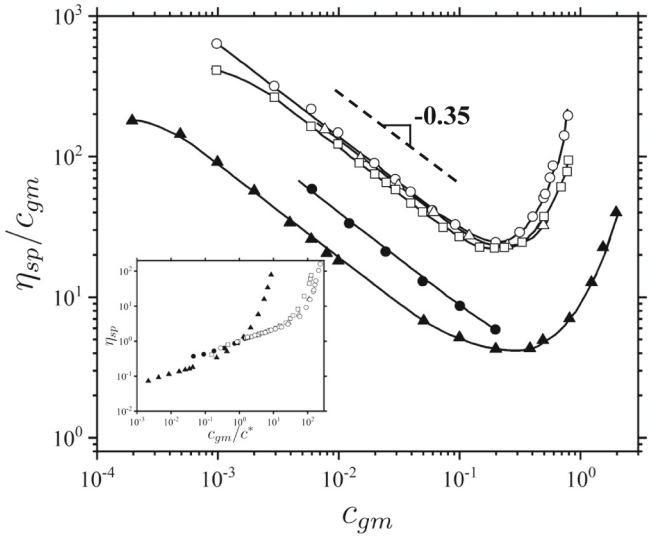

Fig. 2. Viscosity of polyelectrolyte solutions. Dependence of the reduced viscosity of polyelectrolyte solutions on polymer concentration in aqueous solutions of poly(acrylic acid) for different chain degrees of polymerizations: 200 (filled triangles), 350 (filled circle), 800 (open squares), 900 (open triangles), and 1000 (open circles). Inset shows dependence of the specific viscosity η_{sp} on the ratio of polymer concentration to overlap concentration c^* determined from intercept with $\eta_{sp} = 1.0$. Data from Kern, W. *Z. Phys. Chem. A* **1938**, *181*, 283.

explanation for this was that "*the high molecular acid ions form a wide mesh network which influences the macroviscosity but does not hinder the motion of hydrogen ions*" (see Fig. 2). This is exactly how we now describe structure of semidilute solutions of charged and neutral polymers [5, 25–27]. (In the inset of Fig. 2, viscosity data are replotted in terms of the normalized concentration to illustrate universality in semidilute solution regime as discussed in section 2.3 below.) Furthermore, the osmotic measurements pointed out that a solution of acidic polymers behaves as an "osmotic buffer".

Following on Kern's work, a decade later Fuoss [28,29] studied rheology of charged polymers (quaternized poly(vinyl pyridine)) and named them "polyelectrolytes" to reflect their polymeric nature and to separate them from ordinary electrolyte solutions. In particular, he has established that the solution viscosity of polyelectrolyte solutions increases with polymer concentration as $\eta_{sp} \sim c^{1/2}$. This concentration dependence of the solution viscosity is qualitatively different from that in solutions of ordinary salts.

The first theoretical description of polyelectrolytes was attempted by Kuhn, Kunze and Katchalsky in 1948 [30]. They studied the effect of evenly spaced charged groups on the expansion of flexible chains by accounting for change in the statistical weight of the end-to-end distribution function due to electrostatic interactions between ionized charged groups. Inclusion of electrostatic interactions resulted in a strong increase of the chain dimensions with increasing the charge density on the polymer backbone. This direct correlation between the chain size and its ionization explained a dramatic change in the solution viscosity with variation of the solution pH in solutions of poly(carboxylic) acid [31,32]. Note that, this tendency of chain expansion with increasing degree of ionization was later used by Katchalsky et al. [33] to demonstrate direct conversion of chemical energy into mechanical in polyelectrolyte gels, made by crosslinking polymer chains, as they were exposed to alkaline or acidic solutions (see Fig. 3).

In the late 1940s and through 1950s the studies of polyelectrolyte solutions were focused on the effect of charged group ionization on solution properties. Arnold [34] has shown that the pK of poly(acrylic acid) increases monotonically with increasing ionization in agreement with expectation of pure electrostatic effects. However, the titration curve of poly(methacrylic acid) has a transition at a critical charge density. This transition is manifested in an abrupt change in solution viscosity with solution pH as was reported by Katchalsky and Eisenberg (see Fig. 4) [35]. Similar transition-like behavior was also observed by Ferry et al. [36] in copolymers of maleic acid with vinyl methyl ether and styrene. The main reason behind this unusual behavior of poly (methacrylic acid) was believed to be hydrophobicity of the methyl groups. This was further corroborated by similar trend observed by Strauss et al. [37] in solutions of polysoap macromolecules of poly(vinyl pyridine) quaternized with alkyl halide chains.

In 1951, a significant breakthrough in the theoretical understanding of the effect of counterions on properties of salt-free polyelectrolyte solutions was achieved by Alfrey, Morawetz and Berg [38] and by Fuoss, Lifson and Katchalsky [39]. By solving the nonlinear Poisson-Boltzmann equation describing counterion distribution around rod-like cylindrical polyions, they have shown that in the case of strongly charged polyions, a significant fraction of counterions will remain close to them, reducing counterion contribution to the solution osmotic pressure. It is worth pointing out that excess of counterions close to the polyion has served as a foundation for development of the theory of counterion condensation. This theory states that the counterions will effectively "condense" on the polyion when its linear charge density exceeds the critical value. This

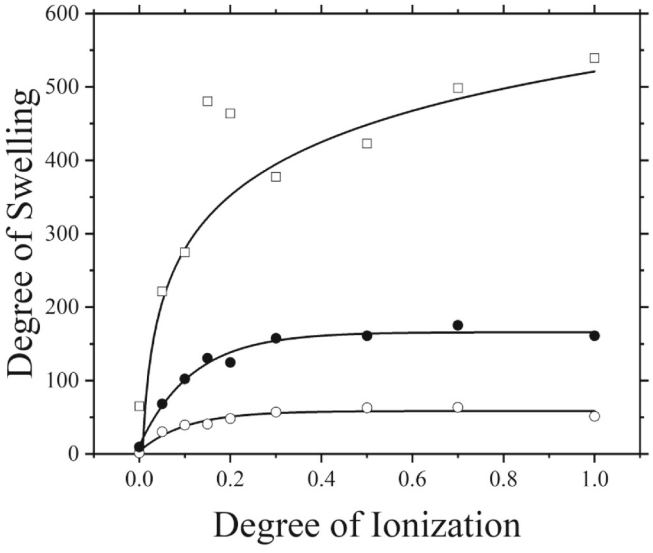

Fig. 3. Swelling of polyelectrolyte gels. Equilibrium swelling of poly(methacrylic) acid crosslinked with divinylbenzene in water as a function of the degree of ionization for different degrees of polymerization between crosslinks: 750 (open squares), 370 (filled circles), and 190 (open circles). Data from Kuhn, W., Hargitay, B., Katchalsky, A., Eisenberg, H. *Nature* **1950**, *165*, 514.

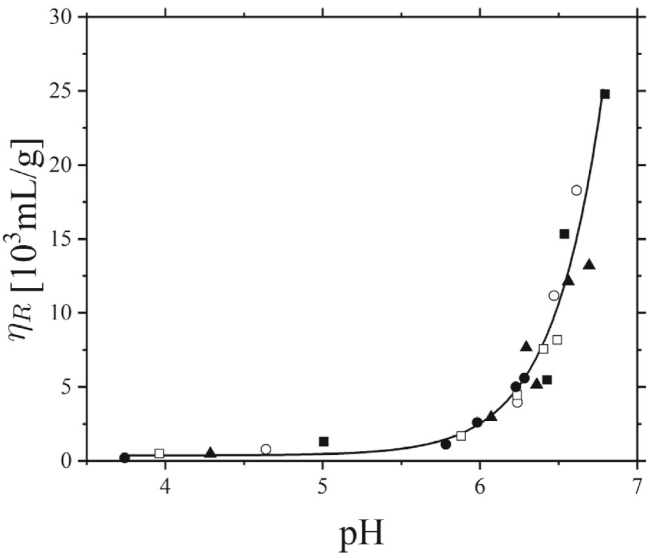

Fig. 4. Viscosity of aqueous solutions of poly(methacrylic acid). Dependence of the reduced viscosity, $\eta_R = \eta_{sp}/c$, of poly(methacrylic acid) on solution pH for different polymer concentrations: 0.11 mg/mL (filled squares), 0.22 mg/mL (open circles), 0.43 mg/mL (filled triangles), 0.86 mg/mL (open squares), and 1.72 mg/mL (filled circles). Data from Katchalsky, A., Eisenberg, H. *J. Polym. Sci.* **1951**, *6*, 145.

was demonstrated by Imai and Ohnishi [40] as an appearance of the special type of solution of the nonlinear Poisson-Boltzmann equation, described by Oosawa [41] in the framework of a simplified "two phase" model and was applied ten years later by Manning [42] to a case of rod-like polyion with ionized groups interacting through Debye-Huckel potential. From historical perspective it is important to mention Manning's acknowledgement of informal discussion with Onsager who observed that "*the statistical-mechanical phase integral for an infinite line-charge model diverges for all values of linear charge densities greater than a critical value*" [42]. A nice overview of the earlier development of the counterion condensation concept can be found in a book by Oosawa [4] and review by Manning [43].

Alexandrowicz and Katchalsky [44] modified the solution of the nonlinear Poisson-Boltzmann equation to describe polyelectrolytes at finite salt concentrations. They assumed that within a distance r_c from a rod-like polyion, where the strength of the electrostatic attraction of a counterion to a polyion is stronger than the thermal energy k_BT (k_B is the Boltzmann constant and T is the absolute temperature), the counterions or salt ions with similar charge dominate screening of the electrostatic potential similar to the salt-free case. Outside this zone the electrostatic potential is screened and one can use the Debye-Huckel approximation to solve the Poisson-Boltzmann equation. This solution was used to explain the potentiometric behavior, Donnan equilibrium of salt, and Donnan osmotic pressure.

The assumption of the rod-like polyion conformation was relaxed by Hermans and Overbeek [45] in 1948, by accounting for the chain-like character of a polyion and approximating it by a charged cloud in which charged groups interacted through the Debye-Huckel potential. Several years later, Flory [46] and Flory and Osterheld [47] applied the Donnan equilibrium concept to describe the swelling of a charged coil by assuming it to be surrounded by an imaginary membrane permeable to small ions only [48]. This approximation effectively reduces electrostatic interactions between ionized groups to the effective second virial coefficient which strength is inversely proportional to the salt concentration, c_s. Note that rod-like and coil-like approximations for configurations of the polyelectrolyte chains in a solution represent two limiting cases and do not cover the entire range of available chain conformations.

The first study of synthetic polyampholytes was reported by Alfrey, Morawetz, Fitzgerald, and Fuoss [49] in their 1950 article "Synthetic Electrical Analog of Proteins." Similar to proteins, these polymers demonstrate a nonmonotonic dependence of the solution viscosity on charge asymmetry with the minimum located at an isoelectric point (see Fig. 5) [50]. Katchalsky and Miller [51] studied the influence of oppositely charged groups on dissociation, and found that increasing the acid content of their copolymers caused a larger fraction of the basic monomers to dissociate at a given pH, and presented a simple theory for this observation. In particular, addition of salt diminishes this inductive influence of neighboring groups, through simple screening of electrostatic interactions. Based on these results Katchalsky and coworkers [52,53] formulated a full theory of dissociation in charged polymers.

During the 1970s and 1980s there were two major developments that shaped our understanding of physical properties of solutions of charged polymers. First, a scaling model of polyelectrolyte solutions was developed by de Gennes, Pincus, Velasco and Brochard [54]. This approach introduced the concept of an electrostatic blob which separates length scales with dominant roles of the chain's conformational entropy and electrostatic interactions. Application of the scaling approach to the chains' dynamics in the semidilute solution regime of overlapping polyelectrolyte chains has reproduced the classical Fuoss law [28,29] for solution viscosity, $\eta \sim c^{1/2}$ and explained the peak in the scattering function by suppression of the polymer density fluctuations on the length scales larger than the solution correlation length. In 1977 Skolnick and Fixman [55] and independently Odijk [56] showed that the electrostatic interactions between ionized groups on worm-like (semiflexible) polymers like DNA could stiffen the polymer chain beyond the Debye screening length, r_D. For such polyelectrolytes, the chain's effective persistence length is proportional to the square of the screening length, $l_p \sim r_D^2$. The concept of electrostatic persistent length was adapted by Khokhlov and Khachaturian [57] to intrinsically flexible polyelectrolytes in the framework of the scaling approach. This formulation of the electrostatic persistence length for intrinsically flexible polyelectrolyte chains is the source of debates that continue to this day (see for review [9,10,58]).

In the last thirty years the number of papers dealing with properties of charged polymers have exploded as shown by the chart in Fig. 6. This is a manifestation of the important role that charged polymers play in colloidal and surface science, biophysics and biochemistry, rheology of

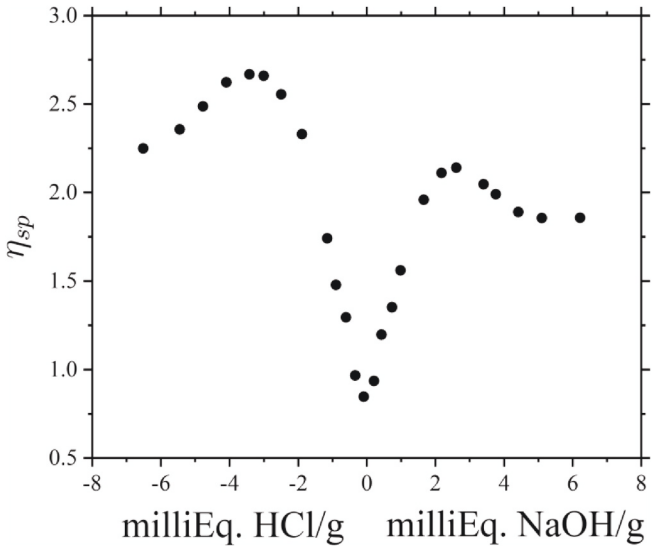

Fig. 5. Viscosity of dilute polyampholyte solutions. Dependence of the specific viscosity on added acid or base in dilute (1 g/dL) solution of a synthetic random copolymer of 68% 2-vinyl pyridine and 38% methacrylic acid in 90% methanol and 10% water at 30 °C. Data from Alfrey, T., Jr.,Morawetz, H. *J. Amer. Chem. Soc.* **1952**, *74*, 436.

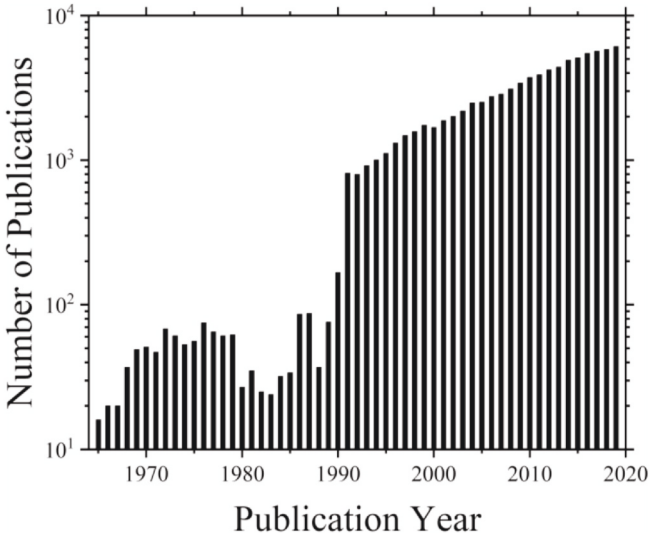

Fig. 6. Evolution of the number of publications in scientific journals on topics related to polyelectrolytes and charged polymers.

complex fluids, polymers, and soft matter. In addition to conventional experimental and theoretical techniques exponential growth of the computational power during this period made Monte Carlo and Molecular Dynamics (MD) simulations of charged polymers an important force in solving the puzzles of these systems [59–61]. The modeling of charged macromolecules in solutions has evolved from simple bead-spring chains in dielectric continuum to full atomistic representation of macromolecules and solvents. New experimental techniques such as atomic force microscopy, particle tracking and force microscopy have allowed probing molecular conformations and force response of individual macromolecules. Adaptation of the random phase approximation techniques [62–64], PRISM [65] and self-consistent field and field theoretical methods [66–69] to charged macromolecules have provided a more robust and in some cases quantitative comparison with experimental data.

In the short introduction it is impossible to give full credit to all the scientists who contributed to the progress in understanding of charged polymers. Good places to look for a more detailed overview of the research on physical properties and structure of charged polymers with extensive bibliography are the books [3,4,7,8,70] and reviews [1,2,8–10,58,71,72].

In this perspective I will briefly overview current understanding of polyelectrolyte solutions and will highlight remaining unanswered questions.

2. Polyelectrolyte solutions

2.1. Dilute salt-free solutions

In dilute solutions, the distance between chains is larger than their size. Therefore, in such a concentration range the intrachain electrostatic interactions dominate over the interchain ones which are also effectively screened by counterions filling the space between the chains. To describe the general features of polyelectrolytes I will use a scaling approach. Note that one can also use the Flory-like method [10] or other advanced theoretical techniques [65,68,69,73,74] for calculations of the chain size and its dependence on the chain degree of ionization.

Consider a polyelectrolyte chain with the degree of polymerization N, bond projection length l, and Kuhn length b having fraction f of the charged groups on the polymer backbone in a medium with the dielectric permittivity ε. In a dilute solution the majority of counterions is outside the volume occupied by a chain. At these polymer concentrations the electrostatic interactions between charged groups and the chain's elasticity control chain dimensions.

In the framework of the scaling approach [54,75] there is a separation of length scales. At short length scales the strength of the electrostatic interactions is insufficient to perturb local chain conformations. At the large length scales the electrostatic interactions play a dominant role resulting in the elongation of the polyelectrolyte chain (Fig. 7a). The crossover length scale between two chain deformation regimes is called the *electrostatic blob*. The statistics of the chain at length scales smaller than the electrostatic blob depends on the solvent quality for uncharged polymer backbone. In the case of the Θ-solvent, the number of monomers in the electrostatic blob g_e and its size D_e are related as $D_e \approx \sqrt{lbg_e}$. The electrostatic energy of the electrostatic blob is on the order of the thermal energy k_BT

$$\frac{l_B(fg_e)^2}{D_e} \approx uf^2(g_e)^{3/2} \approx 1 \tag{1}$$

where the Bjerrum length $l_B = e^2/4\pi\varepsilon\varepsilon_0 k_BT$ is the length scale at which the energy of electrostatic interaction between two elementary charges e in the medium with the dielectric constant ε is equal to the thermal energy k_BT ($\varepsilon_0 = 8.85 \times 10^{-12} C^2/m^2N$ is dielectric permittivity of the vacuum), and $u = l_B/\sqrt{lb}$ is dimensionless parameter. Solving for the number of monomers in the electrostatic blob and using its relationship with the electrostatic blob size one has

$$g_e \approx (uf^2)^{-2/3};\ D_e \approx (lb)^{1/2}(uf^2)^{-1/3} \tag{2}$$

At length scales larger than the blob size, electrostatic interactions between charged monomers result in the elongation of the polyelectrolyte chain into an array of blobs. The size of the polyelectrolyte chain is estimated as the number of blobs per chain N/g_e times the blob size D_e

$$R_e \approx \frac{N}{g_e} D_e \approx (bl)^{1/2}(uf^2)^{1/3} N \tag{3}$$

It follows from eq (3) that the chain size is a monotonic function of the fraction of ionized groups f. This is in agreement with classical results regarding the monotonic increase of viscosity in solutions of poly (acrylic acid) with increasing neutralization reflecting the smooth expansion of the chain. A polyelectrolyte chain shrinks with decreasing fraction of ionized groups and reaches the size of an ideal polymer chain $R_e \approx \sqrt{lbN}$ when the number of charged monomers on the chain fN is on the order of $u^{-1/2}N^{1/4}$.

It is important to point out that the blob model of a polyelectrolyte chain is only valid if the number of monomers per electrostatic blob is larger than unity, $g_e >> 1$. This condition is satisfied when the value of the parameter uf^2 is smaller than unity. Polyelectrolytes for which $uf^2 << 1$ are called *weakly charged polyelectrolytes*. A polyelectrolyte chain approaches a fully extended chain conformation when the number of

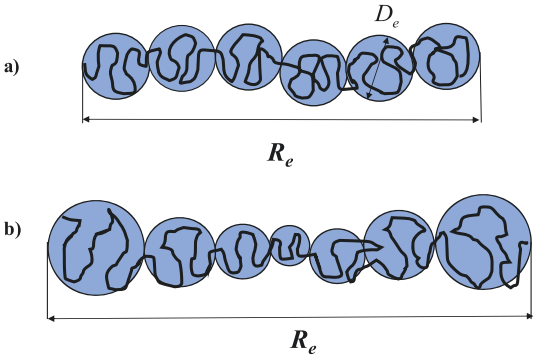

Fig. 7. Scaling model of polyelectrolyte chain. a) Polyelectrolyte chain as a chain of electrostatic blobs. b) Nonuniform chain stretching and corresponding blob size distribution.

monomers per electrostatic blob g_e becomes on the order of the number of monomers per Kuhn length b/l. This takes place for the fraction of charged monomers $f \approx l/\sqrt{bl_B}$. For stronger charged chains $f > l/\sqrt{bl_B}$ the blob picture breaks down and one has to take into account nonlinear effects in chain deformation [26,27]. In this range of fractions of charged monomers the chain size is on the order of its contour length $R_e \approx lN$. Such polyelectrolytes are referred to as *strongly charged polyelectrolytes*.

This formulation of the scaling model does not account for nonuniform chain stretching. In reality due to the long-range nature of the electrostatic interactions, the blobs in the middle of the chain interact with the rest of the chain stronger than ones located at the chain's ends (see Fig. 7b). This additional contribution from longer length scales results in nonuniform chain stretching with blobs increasing in size towards chain ends and chain size growing faster than linear with the degree of polymerization N such that [76,77]

$$R_e \approx \frac{N}{g_e} D_e [\ln(N/g_e)]^{1/3} \propto N[\ln N]^{1/3} \tag{4}$$

Contrary to the scaling approach, the Flory approach, based on the balance of conformational and electrostatic parts of the chain free energy, considers deformation of the chain on the longest length scales. This analysis results in the expression similar to eq (4) with a logarithmic correction for the chain end-to-end distance (see for review [10]).

In a poor solvent for the polymer backbone polyelectrolytes demonstrate qualitatively different behavior with increasing ionization degree or fraction of the charged monomers. A neutral polymer chain in a poor solvent collapses forming a dense globule to minimize the number of unfavorable polymer-solvent contacts. The size of the globule scales with the chain degree of polymerization as $R_{glob} \propto N^{1/3}$ [26]. The problem of the shape instability of a charged globule bears similarity with the classical problem of the instability of a charged droplet, considered by Lord Rayleigh [78]. The charged globule is unstable and can undergo shape transformations when the globule charge exceeds a critical value $Q_{glob} > Q_{crit}$. The value of the critical charge is determined by the electrostatic energy, $Q_{glob}^2/\varepsilon_0\varepsilon R_{glob}$, of the globule with size R_{glob} and carrying charge Q_{glob}, and its surface energy γR_{glob}^2 where γ is the surface tension of the polymer-solvent interface. Balancing these two energies, one finds that the critical charge Q_{crit} scales with the size of the globule as $R_{glob}^{3/2}$. Rewriting this relationship in terms of the fraction of charged monomers one arrives at

$$f_{crit} \propto N^{-1/2} \tag{5}$$

Thus, for a fraction of charged monomers $f > f_{crit}$, the electrostatic energy of the charged globule becomes larger than its surface energy and the globule abruptly changes its shape forming a necklace globule of beads connected by strings (see Fig. 8) [79–81].

This phenomenon was first observed by Katchalsky and Eisenberg in their study of the viscosity of aqueous solutions of poly(methacrylic acid) (PMA) (see Fig. 4) [35]. The viscosity of dilute PMA solution stayed almost constant at a low pH and then abruptly increased as solution pH reached some critical value, indicating a dramatic change in the chain dimensions. This dramatic change in the solution viscosity is due to the fact that water is a poor solvent for PMA which contains hydrophobic methyl groups.

2.2. Semidilute salt-free solutions

In a dilute solution regime, as polymer concentration increases, the distance between polyelectrolyte chains decreases. Eventually, when the distance between chains becomes comparable with their size, polyelectrolyte chains start to overlap. Note that at the overlap concentration the concentration of monomers within a volume occupied by a chain is on the order of the average monomer concentration in a solution

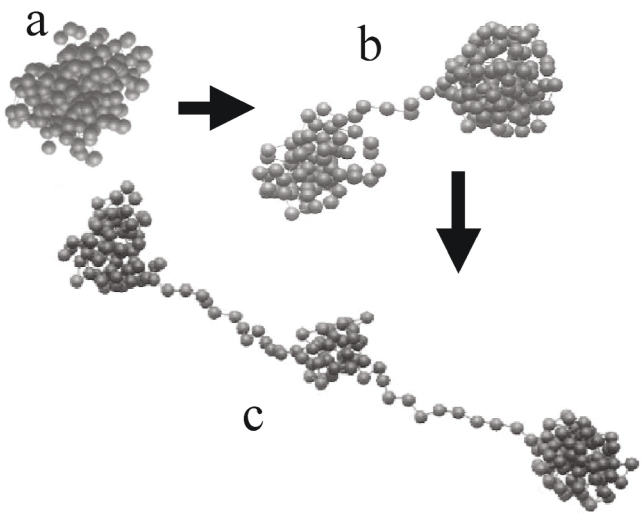

Fig. 8. Typical configurations of freely-jointed uniformly charged chains in poor solvent conditions for three different charge fractions: (a) a spherical globule for f=*0*; (b) a dumbbell for f=*0.125* and (c) a necklace with three beads for f=*0.15*. Reproduced with permission from Dobrynin, A.V., Rubinstein, M., Obukhov, S.P. *Macromolecules* **1996**, *29*, 2974. Copyright 1996, American Chemical Society.

$$c^* \approx \frac{N}{R_e^3} \tag{6}$$

For strongly charged chains in salt-free solutions, the chain size is close to that of a fully extended chain $R_e \approx lN$ resulting in the chain's overlap concentration to be inversely proportional to the square of the degree of polymerization, $c^* \approx N/R_e^3 \propto N^{-2}$. It is important to point out that this dependence of the solution overlap concentration on the chain's degree of polymerization is much stronger than that in a solution of neutral chains in a Θ-solvent, $c^* \propto N^{-1/2}$. Thus, crossover to semidilute solution regime takes place at much lower polymer concentrations in polyelectrolyte solutions than in solutions of neutral polymers [9,54,75,82]. This is illustrated in Fig. 9 which confirms the expected scaling dependence $c^* \propto N^{-2}$ obtained from X-ray scattering [83] and viscosity [84–89] data in salt-free solutions of NaPSS.

As in the case of semidilute solutions of neutral polymers, $c > c^*$, correlation length ξ - the average mesh size of the solution (see Fig. 10) – plays an important role in determining polyelectrolyte solution properties. The average charge of the correlation volume ξ^3 is equal to zero since the polymer charge of the section of the chain with g_ξ monomers within the correlation length (blob) ξ is compensated by counterions on average. Note that a counterion distribution in a correlation volume can be estimated in the framework of the cell model [2,9,38,39,90] by considering a section of polyelectrolyte chain to be aligned along the axis of the cylindrical cell with radius $\xi/2$ as illustrated in Fig. 11.

The correlation blobs are space filling such that the average polymer concentration c is equal to that within the correlation volume g_ξ/ξ^3. On the length scales smaller than the correlation length ξ the intrachain electrostatic interactions dominate resulting in elongation of the chain section with g_ξ monomers. Thus, the correlation length and number of monomers per correlation length can be determined from the following conditions

$$\xi \approx g_\xi D_e \Big/ g_e \approx (bl)^{1/2} g_\xi \left(uf^2\right)^{1/3} \text{ and } c \approx g_\xi \Big/ \xi^3 \tag{7}$$

Solving these two equations for the correlation length as a function of polymer concentration, one finds

$$\xi \approx (cD_e/g_e)^{-1/2} \propto c^{-1/2} \tag{8}$$

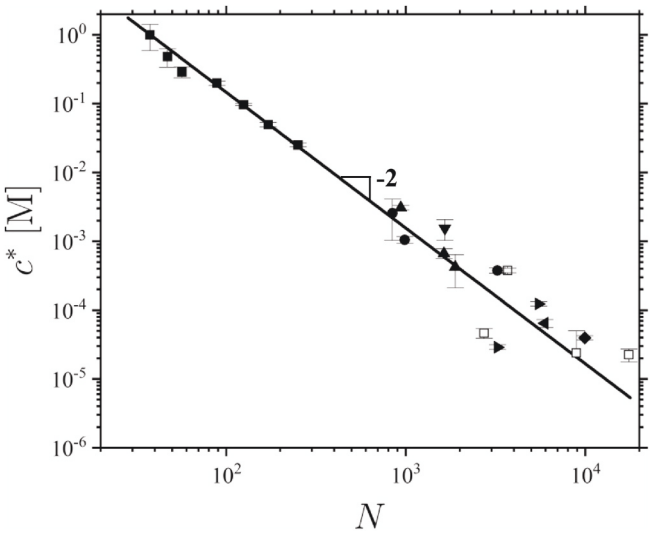

Fig. 9. Overlap concentration of salt-free polyelectrolyte solutions. Dependence of the overlap concentration, c^*, on chain degree of polymerization, N, in salt-free polyelectrolyte solutions of NaPSS. Data sets from Kaji et al. (filled squares), Vink (open squares), Cohen et al. (filled circles), Oostwal (filled triangles), Prini and Lagos (inverted triangles), Butler et al. (filled right triangles), Boris and Colby (filled left triangles) and Ganter et al. (filled rhombs). Data assembled by Boris and Colby.

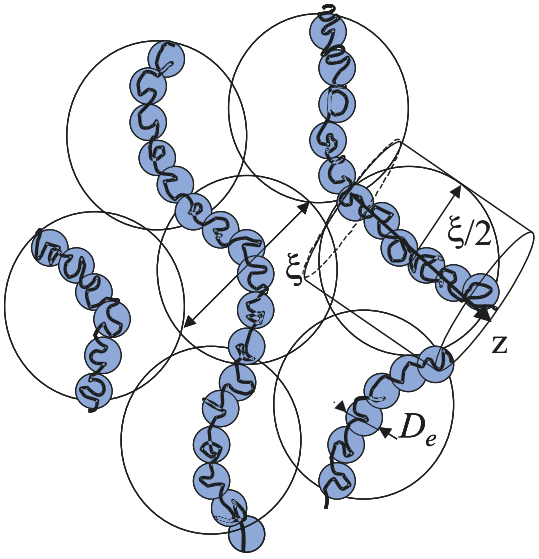

Fig. 10. Schematic representation of semidilute polyelectrolyte solution. Each polyelectrolyte chain can be viewed as being made of effective monomers (electrostatic blobs) shown in blue. Cell model approximation is illustrated by a cylindrical cell surrounding section of the chain within correlation length.

Fig. 11 displays the results of molecular dynamics simulations for concentration dependence of the correlation length ξ for several chain lengths (open symbols) [77] and results of scattering experiments (filled symbols) [91,92] in semidilute salt-free polyelectrolyte solutions. Light scattering [91] and neutron scattering [92] data were combined to cover 4 orders of magnitude in concentration of salt-free solutions of polystyrene sulfonate sodium salt: $5 \times 10^{-5} < c < 5 \times 10^{-1}$ *M*. All data sets confirm that the correlation length varies reciprocally with the square root of polymer concentration, $\xi \propto c^{-1/2}$.

The scaling model of a polyelectrolyte chain in semidilute solutions is based on the assumption of the existence of a characteristic length scale — the correlation length ξ. At the length scales larger than the

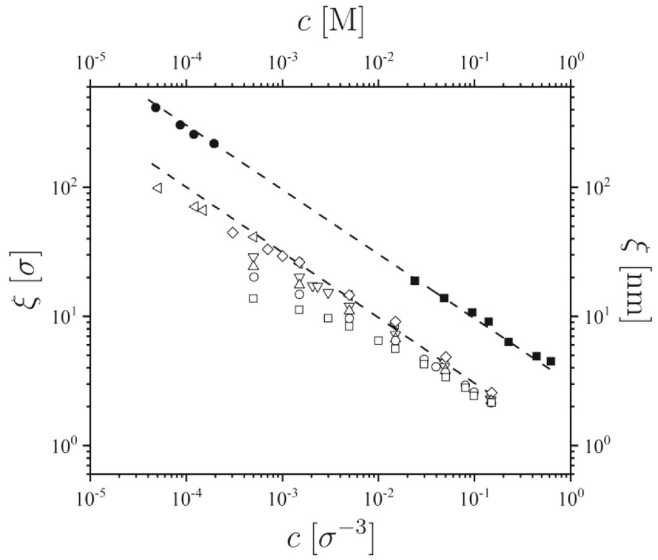

Fig. 11. Solution correlation length. Concentration dependence of the correlation length ξ in salt-free polyelectrolyte solutions. Filled symbols corresponds to SANS data (circles) (Nierlich, M. et al. J. Phys. (Paris) **1979**, *40*, 701) and light scattering data (squares) (Drifford, M.; Dalbiez, J. P. *J. Phys. Chem.* **1984**, *88*, 5368) in solutions of NaPSS. Open symbols represent results of the molecular dynamics simulations Liao, Q. et al. *Macromolecules* **2003,** *36*, 3386. The dashed lines with slope −1/2 are shown to guide the eye. Reproduced from Dobrynin A.V., Rubinstein M. *Prog. Polym. Sci.*, **2005**, *30*, 1049. Copyright 2005 ELSEVIER.

solution correlation length ξ, other chains and counterions screen electrostatic interactions and the conformations of the chains are those of Gaussian chains with the effective persistence length on the order of the correlation length ξ. Under this assumption a polyelectrolyte chain is considered to be flexible at the length scales on the order of the correlation length ξ and its statistics is a random walk of a chain of correlation blobs with size

$$R_e(c) \approx \xi (N/g_\xi)^{1/2} \propto N^{1/2} c^{-1/4} \tag{9}$$

This scaling model assumption was confirmed in molecular dynamics simulations as shown in Fig. 12, displaying dependence of the normalized chain size R_e/ξ as a function of the number of correlation blobs per chain N/g_ξ [77]. As expected for Gaussian chains with N/g_ξ correlation blobs all simulation data for chains with different degrees of polymerization, different fractions of charged monomers, and different polymer concentrations collapse onto one universal line, with the slope 1/2.

With increasing polymer concentration, the correlation length ξ decreases and reaches the size of the electrostatic blob D_e at polymer concentration, $c_b \approx g_e/D_e^3$. For larger polymer concentrations, $c > c_b$, the properties of polyelectrolyte solutions are similar to those of the solutions of neutral polymers [25–27]. The corrections to the neutral solution behavior can be obtained in the framework of the RPA method [62,64,93–95].

Polyelectrolytes in poor solvent conditions for the polymer backbone phase separate [96–99] and could form mesophases – alternating regions with high and low polymer densities. These mesophases appear as a result of optimization of the electrostatic and short-range interactions. The possibility of this type of instability of the homogeneous phase in solutions of weakly charged polyelectrolytes was first discovered by Borue and Erukhimovich [62] and then studied in a series of papers by Joanny and Leibler [63], and by Khokhlov et al. [100,101] This instability was confirmed for polyelectrolyte gels [102,103] and solutions [104]. One can also think of the necklace structure of a polyelectrolyte chain in a dilute solution as a precursor to mesophase formation on the length scales of individual macromolecules [79,99,105,106].

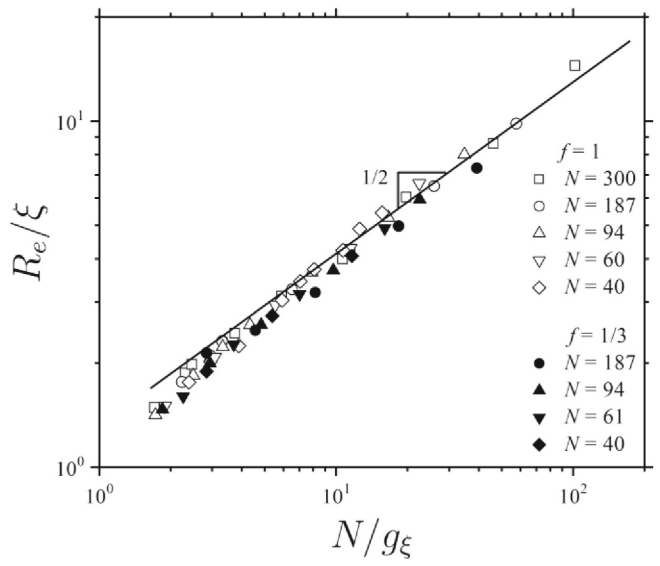

Fig. 12. Scaling model of polyelectrolyte chain in semidilute salt-free solution. Dependence of the reduced chain size R_e/ξ on the number of correlation blobs N/g_ξ for chains with different degrees of polymerization, fraction of charged monomers, and at different polymer concentrations. Thin solid line has slope 1/2. Reproduced with permission from Liao, Q., Dobrynin, A.V., Rubinstein, M., *Macromolecules* **2003**, *36*, 3386. Copyright 2003, American Chemical Society.

2.3. Dynamics of salt-free polyelectrolyte solutions

Unentangled regime ($c^* < c < c_e$). In semidilute solutions, similar to electrostatic interactions, the hydrodynamic interactions between sections of polyelectrolyte chains are screened on the length scales larger than the solution correlation length ξ [5,25–27,82,89,107,108]. On the length scales smaller than the solution correlation length the motion of the chain sections are hydrodynamically coupled resulting in Zimm-like chain dynamics. The relaxation of the sections of the chain with g_ξ monomers is proportional to the volume pervaded by the section (Zimm relaxation time) [25–27].

$$\tau_\xi \approx \eta_s \xi^3 / k_B T \tag{10}$$

where η_s is the solvent viscosity. Screening of the hydrodynamic interactions on the length scales larger than the correlation length results in dynamics of the chain to be that of the Rouse chain consisting of N/g_ξ correlation blobs [25,27].

$$\tau_{Rouse} \approx \tau_\xi (N/g_\xi)^2 \propto c^{-1/2} N^2 \qquad c^* < c < c_e \tag{11}$$

The chain relaxation time in this concentration range decreases with increasing polymer concentration as $\tau_{Rouse} \sim c^{-1/2}$ [75,89,109,110]. This behavior of solution relaxation time with polymer concentration is a unique feature of unentangled polyelectrolyte solutions and is qualitatively different from that in solutions of neutral polymers for which relaxation time increases with increasing polymer concentration [25].

The terminal modulus G of a solution in the framework of the Rouse model for unentangled polymers is k_BT per chain [25,27] and solution viscosity is estimated as

$$\eta \approx G \tau_{Rouse} \propto c^{1/2} N \qquad c^* < c < c_e \tag{12}$$

In the salt-free solution, the viscosity grows as the square root of concentration $\eta \sim c^{1/2}$. Thus, the scaling model of polyelectrolyte solutions recovers the well-known phenomenological Fuoss law [28].

Entanglement concentration, c_e. According to the Kavassalis-Noolandi conjecture [111–113], there should be a universal number n of the overlapping chains to form an entanglement. This requires a significant chain overlap in the semidilute solution regime such that each chain has to overlap with $5 < n < 10$ other chains (see for discussion [27, 111–113]). The number of chains at concentration c_e within a volume $R_e^3(c_e)$ occupied by a chain is estimated as

$$n \approx c_e R_e^3(c_e) \Big/ N \approx (c_e/c^*)^{1/4} \Rightarrow c_e \approx n^4 c^* \tag{13}$$

where the following relation between the chain size at entanglement concentration c_e and that at overlap concentration c^* was used $R(c_e) \approx R(c^*)(c^*/c_e)^{1/4}$. Eq (13) indicates that the unentangled semidilute regime in salt-free solutions could be three to four decades wide ($10^3 < c_e/c^* < 10^4$) [75,89,110]. Note that this concentration interval could even be wider if one uses $n \approx 15 \div 20$ that are typical values for neutral polymer solutions and melts [27]. The physical reason for this unusually wide unentangled regime is the strong concentration dependence of the chain size ($R_e \sim c^{-1/4}$) which is only slightly weaker than the concentration dependence of the distance between centers of mass of the neighboring chains ($R_{cm} \sim c^{-1/3}$).

Entangled regime ($c_e < c$). Entanglements are characterized by the tube diameter d_T (the mesh size of the temporary entanglement network) as shown in Fig. 13. The polymer strand between entanglements containing N_e monomers is a random walk of $N_e/g_\xi \approx (d_T/\xi)^2$ correlation blobs. There are n such strands inside the volume d_T^3, so that $(d_T/\xi)^3 \approx nN_e/g_\xi$ leading to the tube diameter to be proportional to the correlation length, $d_T \approx n\xi$. The longest relaxation time of a polymer chain is calculated by assuming that the dynamics of the chain at the length scales smaller than a correlation blob size is Zimm-like, and the relaxation of a polymer strand between entanglements is Rouse-like [75, 110]. This results in the longest relaxation time of the chain to be concentration-independent

$$\tau_{rep} \approx \tau_\xi \left(\frac{N_e}{g_\xi}\right)^2 \left(\frac{N}{N_e}\right)^3 \propto n^{-2} N^3. \tag{14}$$

The plateau shear modulus in this regime is proportional to the number density ν_e of the entanglement strands times thermal energy k_BT, $G \approx \nu_e k_B T$. Taking into account the volume per entanglement strand $\xi^3 N_e/g_\xi \approx \xi d_T^2$, one obtains the following expressions for the plateau modulus

$$G \approx \frac{k_B T}{\xi d_T^2} \propto n^{-2} c^{3/2} \tag{15}$$

and the solution viscosity [54,75]

$$\eta \approx \tau_{rep} G \propto n^{-4} c^{3/2} N^3 \tag{16}$$

Fig. 14 shows the dependence of the specific viscosity of salt-free solutions of 2-vinyl pyridinium chloride and N-methyl-2-vinyl pyridinium chloride random copolymers on the ratio of polymer

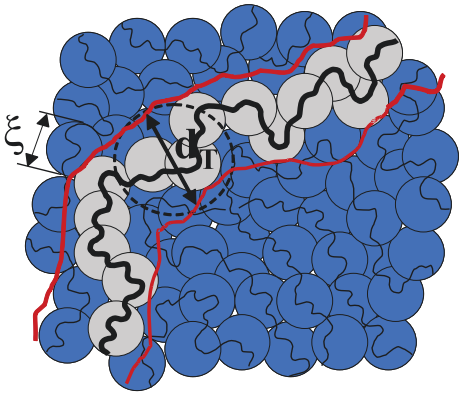

Fig. 13. Schematic representation of an entangled polyelectrolyte solution.

concentration c to the overlap concentration c^*. These data clearly indicate linear concentration dependence of specific viscosity in dilute solutions ($\eta_{sp} \approx c/c^*$ for $c < c^*$). There is a wide range of polymer concentrations where solution viscosity follows the Rouse dynamics manifested by the Fuoss law, $\eta_{sp} \sim c^{1/2}$ [28]. This regime of unentangled semidilute polyelectrolyte solutions has a much wider concentration range than the similar regime in solutions of neutral polymers. This concentration dependence of specific viscosity is general for salt-free polyelectrolyte solutions [82,89]. There is as well a concentration regime corresponding to entangled solutions with $\eta_{sp} \sim c^{3/2}$. Finally, at high polymer concentrations, $c > c_b$, one observes a crossover to solutions of neutral polymers, $\eta_{sp} \sim c^{15/4}$ [27,82]. Note that one can see qualitatively similar viscosity increase by replotting Kern's data as a function of c/c^* (see inset in Fig. 2).

2.4. Counterion condensation and ionization equilibrium

Increasing the polymer concentration decreases the entropic penalty for counterion localization in the vicinity of the polyelectrolyte chain. Two groups of models are used to describe counterion distribution in polyelectrolyte solutions as a function of the polymer concentration [2,4,8,38,39,42,90,114–121]. The first group of models decouples the counterion and polymeric degrees of freedom and is based on the solution of the nonlinear Poisson–Boltzmann equation describing distribution of the electrostatic potential around a rod-like macroion [2,8,38,39,90,114,122]. The second group of models (Oosawa-Manning condensation theory) approximates the counterion distribution profile by a step-like function separating counterions into "free" and "condensed" [4,42,115–121]. In the case of flexible polyelectrolytes, chain conformations are directly coupled with the intrachain electrostatic interactions between uncompensated charges which fraction is controlled by the amount of condensed counterions [9,58,59,118–121,123–129]. Independent of the approach, however, the main result of counterion condensation is a reduction of the linear charge density of a polyelectrolyte to about one charge per Bjerrum length which corresponds to electrostatic repulsion between neighboring ionized groups to be on the order of thermal energy k_BT with logarithmic accuracy.

Solvent quality plays an important role in counterion condensation. In a poor solvent, where polyelectrolyte chain forms a necklace globule as shown in Fig. 8 [79,81,99,105,106,130–140], the counterion condensation can occur in avalanche-like fashion [9,99,118,123]. By increasing polymer concentration or decreasing temperature one can induce a spontaneous condensation of counterions inside beads of the necklace globule. This reduces the bead's charge and results in increase of the bead mass (size), which initiates further increase of the number of condensed counterions inside beads starting the avalanche-like counterion condensation process (see for review [9]).

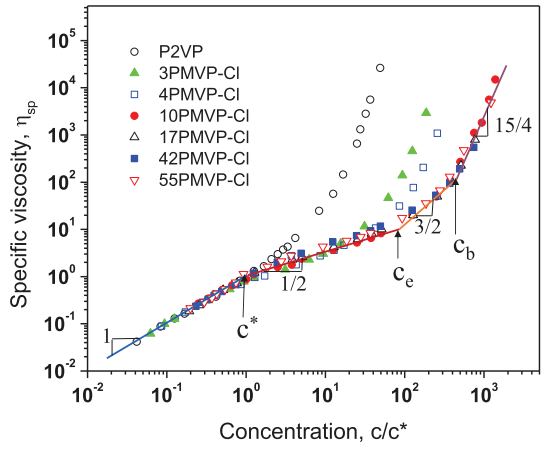

Fig. 14. Viscosity of salt-free polyelectrolyte solutions. Reduced concentration, c/c^*, dependence of the specific viscosity, η_{sp}, at 25^0C in ethylene glycol solvent of the random copolymer 2-vinyl pyridine and N-methyl-2-vinyl pyridinium chloride (PMVP-Cl) with various charge densities [numbers in the legend correspond to the extent (mole %) of quaternization] and the uncharged neutral parent poly (2-vinyl pyridine) (P2VP) of M_w=*364* 000 Da (open circles). Data provided by Dou, S. and Colby, R. H.

The condensed counterions can also induce effective attractive interactions between charged monomers [120,124–126,129–131]. In particular, condensed counterions could form ionic pairs with oppositely charged ions on the polymer backbone [120,121,124,125,141]. The formation of the ionic pairs leads to additional dipole-dipole and charge-dipole attractive interactions which decreases the value of the effective second virial coefficient for monomer-monomer interactions shifting the position of the Θ-point.

In the case of weak polyelectrolytes, the ionic equilibrium between dissociated and undissociated ionic groups is controlled by the solution pH [3,4]. By varying solution pH one directly couples the change in fraction of charged monomers on the polymer backbone with chain's conformations (see Fig. 4) [142–148].

2.5. Polyelectrolytes in salt solutions

At high salt concentrations, electrostatic interactions between univalent charged groups on the polymer backbone separated by a distance r are exponentially screened at the length scales larger than the Debye screening length

$$\frac{U_{DH}(r)}{k_BT} = \frac{l_B}{r}\exp(-r/r_D) \tag{17}$$

where $r_D = (8\pi l_B c_s)^{-1/2}$ is the Debye screening length in a solution with monovalent salt concentration c_s. This results in the contraction of the polyelectrolyte chain with increasing salt concentration [9,30,45,58,66,149–153]. Over sixty years ago Kuhn, Kunzle and Katchalsky [30,149] Hermans and Overbeek [45] accounted for this effect by representing the total chain's free energy as a sum of configurational (elastic) and interaction parts.

$$\frac{F}{k_BT} \approx \frac{R_e^2}{blN} + B_{DH}f^2\frac{N^2}{R_e^3} \tag{18}$$

The interaction part of the chain free energy was estimated by calculating the second virial coefficient for the Debye-Huckel potential, $B_{DH} \approx 4\pi l_B r_D^2$. Minimization of the total chain free energy (eq (18)) with respect to the chain size R_e gives the following expression for chain size

$$R_e \propto c_s^{-1/5} N^{3/5} \tag{19}$$

Thus, in salt solutions conformations of a polyelectrolyte chain are those of a self-avoiding chain with the excluded volume determined by the electrostatic repulsion between charged monomers.

This result was unchallenged until Skolnick and Fixman [55] and Odijk [56] showed that the electrostatic interactions between charged monomers can also induce additional local chain stiffening, $l_p \propto r_D^2$. The combined effect of the electrostatic interactions on the local chain stiffening and swelling was taken into account by Odijk and Houwaart [154]. Their analysis leads to a chain size,

$$R_e \propto r_D^{3/5} N^{3/5} \propto c_s^{-3/10} N^{3/5} \tag{20}$$

which has a stronger salt concentration dependence than the chain size given by eq (19). Note, that eq (19) can also be derived by assuming a linear scaling of a chain's persistence length l_p with the Debye screening length r_D. Thus, the discrepancy between the two results is due to different dependence of the chain's persistence length on the Debye radius. While issue of the dual effect of electrostatic interactions in dilute solutions of the semiflexible polyelectrolytes like DNA appears to be resolved, the discussions of how electrostatic persistence length

depends on the Debye screening length in the case of flexible polymers still continue. Analysis of the experimental data on flexible polyelectrolytes shows that their properties are better described by assuming that effective chain persistence length scales linearly with the Debye screening length, $l_p \sim r_D$. This is one of the unresolved issues in the field of polyelectrolytes (see for review [9,10]).

The problem of the electrostatic induced chain stiffening becomes even more complex in semidilute polyelectrolyte solutions where counterions, salt ions and sections of the chains contribute to the screening of electrostatic interactions [10,75]. This combined screening of the electrostatic interactions results in the screening length to be proportional to the correlation length up to relatively high salt concentrations. Due to this relationship a solution property X in semidilute polyelectrolyte solutions with salt concentration c_s can be expressed in terms of the same property X_0 in a salt-free solution as [75,155].

$$X = X_0\left(1+\frac{2c_s}{fc}\right)^{\alpha} \tag{21}$$

The observed exponents are consistent with the assumption of the linear relationship between electrostatic induced persistence length and solution screening length [10,75,156].

Addition of multivalent salts containing divalent and trivalent ions magnifies electrostatic screening effect and could induce complexation [157–162], gelation [84,143,144] and phase separation. The multivalent ions play the role of physical crosslinks bridging together polyelectrolyte chains [95,163,164]. The behavior of such polyelectrolyte systems is similar to those of associating polymers which thermodynamics and dynamics are controlled by properties of the physical crosslinks [165]. Multivalent counterions are also responsible for the packing of bacteriophage DNA into compact and ordered forms [166]. Stiff polyelectrolytes such as F-actin and tobacco mosaic virus are capable of forming laterally ordered aggregates (bundles) in the presence of multivalent counterions.

The condensation of multivalent counterions on polyelectrolytes is qualitatively different from condensation of monovalent counterions [167–171]. The multivalent ions position themselves along the polymer backbone in the correlated fashion in such a way that equilibrium distance between them is determined by a balance between attraction to the oppositely charged monomers of the polymer and by the repulsion from other multivalent ions. Due to strong correlations between multivalent ions [167–171] these ions could invert the charge of the polyelectrolyte (overcharge it) leading to an effective attraction between originally similarly charged species promoting an aggregate formation and growth.

2.6. Osmotic pressure

In ionic systems the charge neutrality is required on both sides of the membrane across which the osmotic pressure π is measured. This condition is known as the Donnan equilibrium [4]. The electroneutrality condition leads to the partitioning of salt ions between the reservoir and the polyelectrolyte solution

$$c_s^- = c_s^+ + fc \tag{22}$$

where c_s^+ and c_s^- are the average concentrations of positively and negatively charged salt ions in the polyelectrolyte solution. The chemical equilibrium on both sides of the membrane requires that the product

$$c_s^+ c_s^- = c_{s,s}^2 \tag{23}$$

stays constant in the reservoir with the average salt concentration $c_{s,s}$. In the broad salt concentration range, the ionic contribution to the osmotic pressure is equal to the difference between the ideal gas pressure of salt ions in the polyelectrolyte solution and in the reservoir [4].

$$\frac{\pi_{ion}}{k_BT} = c_s^+ + c_s^- - 2c_{s,s} = \sqrt{(fc)^2 + 4c_{s,s}^2} - 2c_{s,s} \tag{24}$$

In addition to the ionic contribution, polyelectrolyte solutions have the polymeric contribution to their osmotic pressure which is estimated to be on the order of thermal energy k_BT per correlation volume ξ [3]. [26,27] The total osmotic pressure of polyelectrolyte solutions is a sum of the ionic and polymeric contributions

$$\frac{\pi}{k_BT} = \frac{\pi_{ion}}{k_BT} + \frac{\pi_{pol}}{k_BT} \approx \sqrt{(fc)^2 + 4c_s^2} - 2c_s + \xi^{-3} \tag{25}$$

It is important to point out that for the vast majority of the systems studied so far [172–180], the ionic contribution dominates the osmotic pressure of polyelectrolyte solutions. This is illustrated in Fig. 15 showing together simulation results [156] and experimental data on sodium poly(styrene sulfonate) (NaPSS) [179,180], DNA [175], sodium polyacrylate (NaPAA) [181], poly(acrylic acid) (PA) [174], poly(vinyl benzoic acid) (PVB) [174], sodium poly(anethole sulfonic acid) (NaPASA) [181] and poly(diallyl dimethyl ammonium chloride) (PDADMA-Cl) [181] (see for details ref [156]).

Note that in salt-free polyelectrolyte solutions the osmotic coefficient, $\phi = \pi/k_BTc$, changes nonmonotonically with increasing polymer concentration [11,122,182,183]. First it decreases in dilute solutions then begins to increase in semidilute solutions.

The osmotic pressure of polyelectrolyte solutions is a driving force behind the swelling of polyelectrolyte networks made by crosslinking polyelectrolyte chains [184–193]. Such polymeric networks could absorb up to hundred times their dry weight of water. At low salt concentrations the high osmotic pressure created by dissociated counterions drives swelling of polyelectrolyte gels. With the addition of salt, excess of the salt ions reduces the osmotic imbalance decreasing the gel swelling ability. In solutions with high salt concentrations, the properties of polyelectrolyte gels are similar to those of neutral gels. This strong response of polyelectrolyte gels to the ionic environment made them perfect for use as superabsorbent materials in medical, chemical and agricultural applications, as ion-exchange resins, as drug delivery

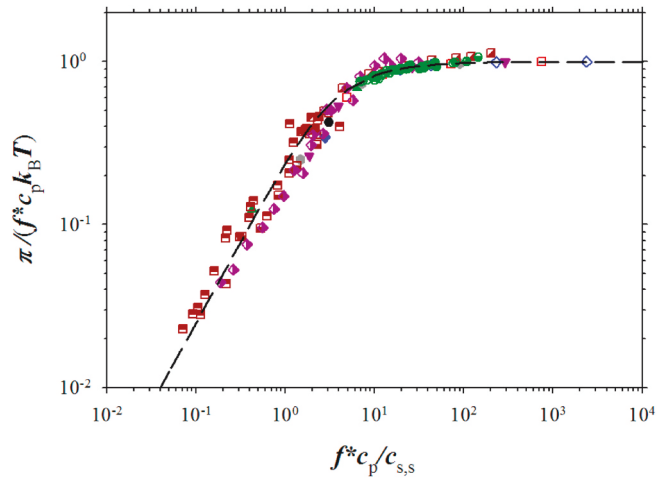

Fig. 15. Dependence of the reduced osmotic coefficient on the ratio of concentration of osmotically active counterions f^*c_p and salt ions $c_{s,s}$. NaPSS data are from Takahashi et al. (brown squares with filled right bottom corner), and Koene et al. for $M_w = 4 \times 10^5$ g/mol (brown squares with filled left top corner), $M_w = 6.5 \times 10^5$ g/mol (brown squares with filled top), and $M_w = 1.2 \times 10^6$ g/mol (brown squares with filled bottom). DNA data (purple rhomb with filled right side) are from Raspaud et al., NaPAA data (green circle with filled right side) and PDADMA-Cl data (green circles with filled bottom) are from Zhang et al., and polyacrylate (PAA) data (green circle with filled left side) and PVB (green circle with cross) are from Kakehashi et al.. Simulation data are from Carrillo and Dobrynin. Dashed line corresponds to eq (24). f^* is the effective fraction of ionized groups and c_p is polymer concentration.

carriers targeting specific organs [191,192], and as sensors and actuators [187,194].

The counterion contribution to the osmotic pressure of salt-free polyelectrolyte solutions has important consequences for the scattering function $S(q)$. The osmotic compressibility is related to the scattering at zero wavelength such that the scattering function $S(0)$ is inversely proportional to the fraction of ionized groups [54,75,155].

$$S(0) = k_B T \partial c/\partial \pi \approx 1/f \quad (26)$$

Therefore, the high osmotic compressibility suppresses density fluctuations on length scales larger than the solution correlation length ξ maintaining system electroneutrality. For wave numbers $q > 2\pi/\xi$, the scattering function $S(q)$ decreases with q as in the case of neutral polymers. This leads to a maximum in the scattering function $S(q)$ of salt-free polyelectrolyte solutions at the wave number q on the order of $2\pi/\xi$. The maximum in the scattering function $S(q)$ disappears at high salt concentrations. This was demonstrated in molecular dynamics simulations of polyelectrolyte solutions with added salt [155]. It is important to point out that scattering data from polyelectrolyte solutions have an upturn in function $S(q)$ at small q [104,195–197]. This behavior is ascribed to existence of slow modes [195–200] and is still debated.

3. Conclusions and outlook

Electrostatic interactions between ionized groups, counterions and salt ions are responsible for the rich behavior of polyelectrolyte solutions and the significant improvement of polymer solubility [10,12]. The main features that distinguish polyelectrolyte solutions from solutions of neutral polymers are now well documented [9,10,12,82]. In particular, semidilute polyelectrolyte solutions occupy a significant region of the concentration space due to the strong dependence of the overlap concentration on the chains' degree of polymerization $c^* \propto N^{-2}$in salt-free and low salt concentration regimes. This dependence could even be stronger because of nonuniform chain stretching resulting in additional logarithmic correction to the chain size. The osmotic pressure of polyelectrolytes is dominated by counterions and salt ions. It is also independent of the chain molecular weight in a wide range of polymer concentrations in salt-free solutions and exceeds the osmotic pressure of neutral polymers at similar polymer concentrations by several orders in magnitude. This dominant role of the ionic component of the osmotic pressure of polyelectrolyte solutions manifests itself in the appearance of a peak in the scattering function $S(q)$ which position scales with polymer concentration as $c^{1/2}$. This peak gradually disappears with increasing salt concentration. There is no such peak in solutions of neutral polymers. The viscosity of polyelectrolyte solutions is proportional to the square root of polymer concentration $\eta_{sp} \sim c^{1/2}$ (Fuoss' law [28]) resulting in reduced viscosity $\eta_{sp}/c \sim c^{-1/2}$ to decrease with polymer concentration. The characteristic feature of this regime is the decrease of chain relaxation time with increasing polymer concentration, $\tau_{Rouse} \propto c^{-1/2}$. In the same polymer concentration range the solution viscosity of neutral polymers demonstrates linear increase of the specific viscosity with polymer concentration. There is a wide concentration regime in semidilute solutions with unentangled polyelectrolyte chains. Viscosity of polyelectrolyte solutions monotonically decreases with increasing salt concentration.

The progress made in understanding properties of polyelectrolyte solutions was successfully applied to a more complex ionic systems such as polyelectrolyte gels [184,188,201], polyelectrolyte brushes [202], polyelectrolyte-protein complexes [70,203], coacervates [204–208], ionomers [6], charged polymers at surfaces and interfaces [9,209] and multilayer formation by charged macromolecules [210–212].

However, there are still important issues that require answers. It is still unclear if one can simply transfer the notion of topological constraints to describe entanglements in polyelectrolyte solutions. There are experimental indications that this hypothesis is violated leading to a weaker than theoretically expected N-dependence of the entanglement concentration [82,89,213]. Another interesting issue that awaits an explanation is the origin of the so-called slow modes in polyelectrolyte solutions [195–200]. The effects of ions and backbone solvation, of ion specific interactions (known as the Hofmeister series effect [214,215]) on polyelectrolyte solubility and ionization equilibrium pose important questions addressing which would require going beyond classical description of the charge polarization and continuum dielectric constant approximation [216,217].

Declaration of competing interest

The author declares no competing financial interests.

CRediT authorship contribution statement

Andrey V. Dobrynin: Conceptualization, Data curation, Writing - review & editing.

Acknowledgements

I would like to express my gratitude to M. Rubinstein, R. Colby, R. Weiss, M. O. de la Cruz, M. Muthukumar, A. Grosberg, B. Shklovskii, J-F Joanny, L. Leibler, S. Kumar, T. Seery, D. Hoagland and P. Dubin for numerous discussions during the last quarter of a century on the topics of charged polymers. This work was supported by the National Science Foundation under the Grants DMR1535412 and DMR1921923.

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