
Poly- electrolytes

**Formation, Characterization
and Application**

H. Dautzenberg / W. Jaeger / J. Kötz
B. Philipp / Ch. Seidel / D. Stscherbina



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Polyelectrolytes

Formation, Characterization and Application



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Polyelectrolytes

Preface

Polyelectrolytes are a fascinating topic in polymers due to the broad variability of their molecular and supramolecular structure and the strong dependence of their properties in solution or dispersion on the surrounding medium. They are closely connected with processes of life, they play an indispensable part in many branches of modern technology, and they are a valuable tool in solving environmental water and soil problems.

In comparison to this scientific challenge and the practical relevance of polyelectrolytes the number of modern textbooks and monographs available is small and they are mainly concerned with physicochemical phenomena of polyelectrolytes in solution and their interpretation by theoretical models, while the peculiarities of polyelectrolyte synthesis are usually hidden in books or book-chapters on polymer synthesis in general, and recent developments in polyelectrolyte application are usually published in special journals or monographs of the industrial branch in question. On the other hand, further progress in research and development of polymers in general, and especially of polyelectrolytes, is closely related to a synoptic view covering chemistry supermolecular structure and comprising the whole route from synthesis via structure formation and characterization to application. Besides this, modern techniques of computer simulation established a good position to theoretical scientists to extend as well as to prove their models and to conduct an interactive research with experimentalists.

These trends outlined above encouraged the authors to write a textbook covering in a comprehensive manner synthesis, structure formation and application of polyelectrolytes as well as their electrochemical and macromolecular characterization, the physicochemical phenomena observed in polyelectrolyte solutions and the theoretical models for their interpretation. To keep the book within an acceptable frame regarding its volume, the subject matter was confined to water-soluble polyelectrolytes including polyelectrolyte dispersions, while products like ion-exchange resins and ionomeric materials are deliberately excluded.

The book is primarily intended as a textbook for graduate students and postgraduates of polymer chemistry and polymer physics, or in related areas within engineering and life sciences. Each of the chapters starts with the basic principles, but intends to guide the reader to the most recent developments and the present frontiers of knowledge. By this way, the book will be a useful source of information also for professional people with an academic background in science, active in manufacturing, processing, testing and application of polymers or in related areas.

The authors hope that the book will find a positive reception by the groups of readers addressed, and that it helps to promote knowledge and understanding of polyelectrolytes as an interesting class of polymers with a bright future.

List of Abbreviations

Latin letters

a	monomer length
a	radius of a sphere
a_i	activity of species i
A_2	second virial coefficient
A_3	third virial coefficient
b	average distance between two charged groups along the chain
c	mass concentration
c^*	critical concentration of coil overlapping
c^{**}	transition concentration to concentrated solutions
c_b	concentration of beginning bending of polyelectrolyte molecules
C	capacity
$C(t)$	time correlation function
D	diffusion coefficient
D_{app}	apparent diffusion coefficient
D_{coop}	cooperative diffusion constant
D_{CM}	self diffusion coefficient
D_{eff}	effective diffusion coefficient
e	elementary charge
E	electric field strength
f	friction coefficient
F	Faraday constant
$g^{(2)}(t)$	correlation function of the scattering intensity
$g^{(1)}(t)$	correlation function of the electric field
dG_{el}	free electrostatic energy
h	wave height
I	ionic strength in mol L ⁻¹
I	scattering intensity
k	Boltzmann constant
K	scattering contrast factor
K_a	acidity equilibrium constant
K_b	basicity equilibrium constant
l_K	Kuhn's segment length
L	contour length of a chain
L_p	persistence length
L_{po}, L_{pi}	intrinsic persistence length

L_{pe}	electrostatic persistence length
m	electrophoretic mobility
m_0	mass of a monomer unit
m_e	mass of electron
M	molecular mass of the polymer chain
M_0	molecular mass of a segment
M_n	number average molecular mass
M_w	weight average molecular mass
M_z	z-average molecular mass
n_i	molar concentration of species i
\tilde{n}	refractive index
N_A	Avogadro's number
N_i	number concentration of species i
N_K	number of Kuhn's segment of a Gaussian chain
pK_a	negative decadic logarithm of K_a
pK_b	negative decadic logarithm of K_b
pK_{app}	apparent pK_a -value
pK_a^0	intrinsic pK_a -value
P	degree of polymerization
$P(q)$	intraparticle scattering function
q	length of the scattering vector
q	linear charge density
Q	total charge
r	radius of a sphere
r_{ij}	distance between the units i and j in a particle
\vec{r}_i	bond vector
R	universal gas constant
R	end-to-end distance of a chain
R_F	Flory radius
R_G	radius of gyration
R_H	hydrodynamic radius
\vec{R}_i	vector of bead positions
\vec{R}_{CM}	center of mass vector
R_θ	Rayleigh ratio of scattered light
s	sedimentation coefficient
S	radius of gyration
$S(c, q)$	solution structure factor
t	time
T	absolute temperature
u	velocity

U	electrostatic interaction energy	η_{sp}	specific viscosity
U	electrophoretic steady state velocity	η_r	reduced viscosity
U_{equ}	cell-voltage	$[\eta]$	intrinsic viscosity
v_0	velocity of light	θ	unperturbed state
\bar{v}_i	partial specific volume of species i	θ	scattering angle
V	volume	Θ	degree of condensation
\bar{V}_i	molar volume of species i	λ	wave length
w_i	weight fraction of species i	λ_B	Bjerrum length
x_i	molar fraction of species i	λ_D	Debye-Hückel screening length ($1/\kappa$)
z	excluded volume parameter	Λ	equivalent conductance
z_i	valency of the species i	Λ_∞	equivalent conductance of infinite dilution
Z	total number of charged groups of a chain	μ_i	chemical potential of species i
		ξ	correlation length (semidilute region)
<i>Greek Letters</i>		ξ_E	Edward's screening length
α	degree of dissociation	ξ_M	Manning parameter
α'	degree of neutralization	π	osmotic pressure
$\alpha(z)$	expansion coefficient of a coil	ρ	density
α_R	expansion coefficient of the end-to-end distance	ρ_c	electron density
α_S	expansion coefficient of the radius of gyration	$\rho(\vec{r})$	charge density
α_η	viscometric expansion coefficient	σ	parameter of polydispersity
β	excluded volume	τ	decay time, relaxation time
Γ	decay rate	τ_R	Rouse relaxation time
γ_i	activity coefficient of species i	v	excluded volume
ε	extinction coefficient	v_e	electrostatic excluded volume
$4\pi\epsilon_0\epsilon$	dielectric constant, relative permittivity	φ	specific resistance
ζ	zeta potential	Φ	volume fraction
η	viscosity	Φ	osmotic coefficient
η_0	viscosity of the solvent	Φ_0	viscosity constant
		$\Phi(\vec{r})$	electrostatic potential
		χ	specific conductance
		ψ	electrostatic potential
		ω	angular dependence

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1

General Introduction

1.1 Definition and General Description of Polyelectrolytes

The term “polyelectrolyte” is employed for polymer systems consisting of a “macroion,” i.e., a macromolecule carrying covalently bound anionic or cationic groups, and low-molecular “counterions” securing for electroneutrality. Examples of an anionic and a cationic polyelectrolyte (PEL) are presented in Figure 1.1.

Both Na-polystyrene sulfonate and poly(diallyldimethylammonium chloride) are dissociated into macroion and counterion in aqueous solution in the total pH range between 0 and 14. Also polymers like poly(acrylic acid) or poly(ethylene imine) are usually classified as polyelectrolytes, in spite of the fact that they form a polyion-counterion system only in a limited pH range, and remain as an undissociated polyacid in the acid range or an undissociated polybase in the alkaline range, respectively (Fig. 1.2), a behavior typical for weak polyelectrolytes and quite analogous to weak low molecular electrolytes.

On the other hand, a polymer like cellulose capable of dissociating partially into cellulosate anions and counteranions at extremely alkaline conditions ($\text{pH} > 14$) cannot be classified as a polyelectrolyte, as in the conventional pH range of dilute aqueous systems the OH groups of the polymer are not ionized.

A special case of polyelectrolytes, the “polyampholytes,” carrying both anionic and cationic groups covalently bound to the macromolecule, are represented in nature by an abundant number of proteins but can also be obtained by various

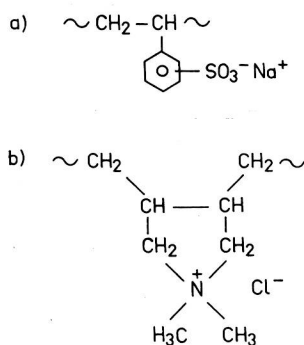


Figure 1.1 Chemical structure of (a) sodium polystyrene sulfonate and (b) poly(diallyldimethylammonium chloride) (poly-DADMAC).

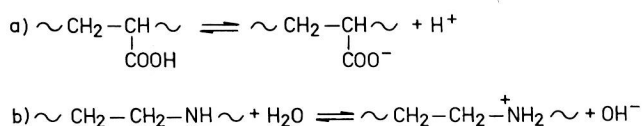


Figure 1.2 Dissociation equilibrium of the weak polyelectrolytes (a) poly(acrylic acid) and (b) poly(ethylene imine).

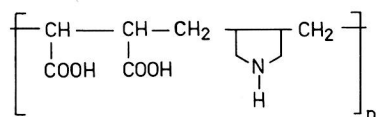


Figure 1.3 Chemical structure of a maleic acid–diallylamine copolymer.

synthetic routes. An example from the authors' work is presented in Figure 1.3. As a typical polyampholyte, this copolymer carries cationic charges in an acid and anionic charges in an alkaline medium, while at the so-called "isoelectric point," in the example at about pH 4, no free net charge exists at the macromolecule.

In principle, any macromolecular chemical structure can be transformed into a polyelectrolyte structure by covalently attaching a reasonable number of ionic groups to the polymer backbone, arriving with linear or branched macromolecules at a compound soluble in an aqueous medium of appropriate pH after introducing a sufficient number of ionic groups, while in the case of a crosslinked polymer its swellability in aqueous media is enhanced by transferring into a PEL. Limiting our further considerations to linear and branched structures, we arrive even then at a vast number of polyelectrolyte classes known today, a selection of which is listed in Table 1.1. Table 1.1 demonstrates the remarkable variability of the polyelectrolyte

Table 1.1 Selected Classes of Polyelectrolytes

Anionic and cationic polysaccharides and polysaccharidic derivatives
Nucleic acids
Gelatin
Lignosulfonic acids
Polyacrylic and polymethacrylic acid and its copolymers
Maleic acid anhydride copolymers
Polystyrene sulfonic acid
Polyethylene imine
Polyamines and polyamidamines
Ionenes
Poly(diallyldimethylammonium chloride)
Homo- and copolymers of cationic acrylic acid esters

Table 1.2 Structures of Ionic Sites of PEL

$-\text{COO}^-$	$-\text{NH}_3^+$
$-\text{CSS}^-$	$=\text{NH}_2^+$
$-\text{O}\cdot\text{SO}_3^-$	$\equiv\text{NH}^+$
$-\text{SO}_3^-$	$-\text{NR}_3^+$
$-\text{OPO}_3^{2-}$	

chemical structure, resulting from the tremendous number of polymer backbone structures. Today's commercial polyelectrolytes are predominantly obtained by a polymerization, polycondensation, or polyaddition process, but numerous important PEL also originate from nature, such as gelatin, as a representative of the widespread class of proteins or pectins belonging to the group of anionic polysaccharides. Furthermore, some PEL of practical importance result from a chemical modification of nonionic natural polymers such as cellulose or starch. In addition to the organic PEL, which are the topic of this book, two important classes of soluble inorganic PEL, i.e., the polyphosphates and water-soluble polysilicates, shall at least be mentioned here.

In contrast to the huge variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the peculiar behavior of PEL in solution is rather small (Table 1.2).

These ionic groups are usually classified as anionic and cationic; a further subdivision into weakly and strongly acid and basic groups is reasonable in analogy to "strong" and "weak" acids and bases of low molecular chemistry, with the sulfonate, the sulfate half-ester, and the tetraalkylammonium group being representative for the so-called "strong PEL."

Besides the acid or base strength of the ionic site, the average distance between adjacent anionic or cationic charges along the polymer chain is a decisive parameter determining PEL behavior, especially in the dissolved state. This charge carrier density or charge density is defined as the average distance between ionic sites, taking into account chain bond geometry, or as the average number of ionic sites per monomer unit in the case of copolymers, with the latter definition yielding comparable data only within the same class of copolymers with an ionic component. Besides this average charge density, the regularity of distribution of ionic sites along the chain can also influence PEL properties significantly, for example, with regard to solubility. As a rule, typical PEL behavior can be expected if more than 1 ionic site per 10 monomeric units is present in a copolymer.

In addition to acid or base strength and charge density a third important point determining PEL properties is the location of the charged sites within the molecular geometry of the macroion. According to Figure 1.4, we principally distinguish between an integral type of PEL with the ionic sites being part of the polymer backbone, and the pendant type with the ionic site being attached to the backbone as a side chain with a broad variability in spacer length. The geometric position of the charged sites is relevant especially in polyanion–polycation complex formation.

Besides these three parameters characterizing the macroion, the species of low molecular counterions has a strong influence on the properties of the whole system

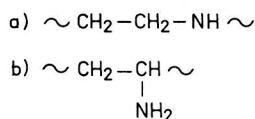


Figure 1.4 PEL of the integral and pendant type: (a) linear poly(ethylene imine) as an example of the integral type and (b) poly(vinylamine) as an example of the pendant type.

in solution, especially on solubility and structure formation. Two examples may illustrate this and demonstrate that the counterion is not just an anonymous particle securing electroneutrality: The chloride of the poly(diallyldimethylammonium) polycation is easily soluble in water, while the corresponding iodide is rather insoluble. The K^+ salt of some water-soluble high molecular cellulose sulfates forms a stiff, cuttable thermoreversible gel at a polymer concentration between 1 and 2%, while the Na^+ salt of the same sample at the same concentration gives quite a normal polymer solution of the expected viscosity.

1.2 Some Peculiarities of PEL in Solution

The most striking feature of polyanion or polycation systems, i.e., the solubility in aqueous media even in the case of a hydrophobic polymer backbone such as polystyrene, has already been mentioned. In consequence, the physical chemistry of PEL is predominantly concerned with the phenomena observed in aqueous solutions and with their interpretation. Processing and application of PEL in most cases also take place after dissolving the PEL in water. Both these points will be the main topics of this book and will be treated in detail in chapters on characterization and on theory of polyelectrolytes.

But, nevertheless, some of these phenomena resulting from a superposition of the typical behavior of macromolecules in solution and the well-known behavior of ionic species shall be considered briefly in this introduction.

First, properties of PEL solutions such as viscosity are strongly dependent on the ionic strength of the aqueous medium. Changes in the course of viscosity with increasing ionic strength are mainly caused by an electrostatic shielding of the electric charges at the macroion with the latter increasingly approaching the behavior of a “normal” uncharged macromolecule, as demonstrated in Figure 1.5 for the dependence of η_{spec}/c of Na-carboxymethylcellulose on the polymer concentration c .

Besides the ionic strength, the pH of the medium affects strongly the properties of a weak polyelectrolyte in solution, as this pH determines the degree of dissociation of a given ionic group and thus the actual charge density of the PEL in question. This effect is very clearly demonstrated by the η_{spec} vs pH plot of a polyampholyte containing a weakly acid and a weakly basic group; the plot indicates a viscosity minimum in the pH range of the isoelectric point (Fig. 1.6).

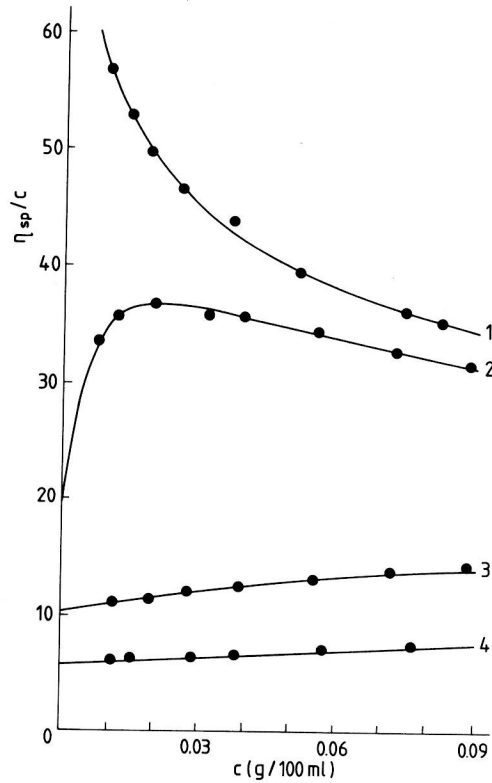


Figure 1.5 Dependency of η_{spec}/c on polymer concentration c for aqueous solutions of Na-carboxymethylcellulose at different ionic strengths: (1) no NaCl added, (2) 2.5×10^{-4} mol NaCl/liter, (3) 5×10^{-3} mol NaCl/liter, and (4) 5×10^{-2} mol NaCl/liter.

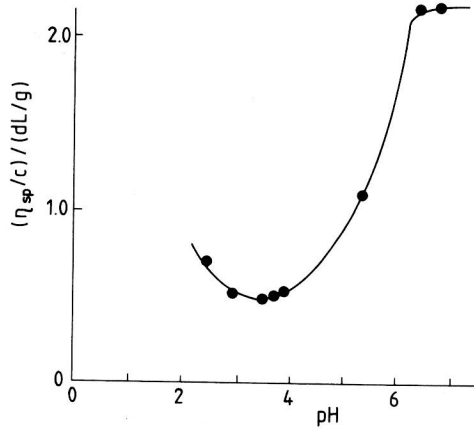


Figure 1.6 Plot of η_{spec}/c vs pH of an aqueous solution of an alternating copolymer of maleic acid anhydride and N-methylallylamine.