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Structure and Applications of Ion-Containing Polymers

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Structure and Applications of Ion-Containing Polymers

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The interest in the subject of ion-containing polymers has continued unabated since the development of organic ion-exchange resins in the 1940's. This interest is due to the variety of properties and applications that result from the interactions of ions bound to organic macromolecules. These interactions affect the physical properties as well as the transport properties of the host material, and these polymers have found applications in areas as diverse as thermoplastic elastomers, permselective membranes, and microencapsulation membranes. The common thread in all these applications and the ion-containing polymers that are used is that the ionic moieties and their interactions dominate the behavior of the polymer. It is not surprising, therefore, that the great bulk of the scientific effort that has been devoted to ion-containing polymers for the past two decades has been directed at delineating and understanding the very complex nature of these ionic interactions and the microstructure of the polymers. This effort has spawned a number of scientific conferences devoted to ion-containing polymers, monographs(1-5), and review articles(6-9) in addition to hundreds of scientific papers and industrial patents.

The purpose of this paper is to provide an overview of the field of ion-containing polymers. This review is not intended to be exhaustive but is meant to provide a suitable introduction to the field as well as demonstrate the diversity of applications of ion-containing polymers. The main emphasis will be on ionomers-- that is, polymers composed of a hydrocarbon or fluorocarbon backbone containing a small amount of pendent acid groups (usually less than 10 mol%) that are neutralized partially or completely to form salts. This sub-field of ion-containing polymers is emphasized because it is the one that is currently experiencing the greatest activity, both from a scientific

standpoint of understanding the structure-property relationships and from the technological development of new materials and applications.

This is not to say that more highly ionized polymers, such as conventional polyelectrolytes, are not of technological importance and interest. In fact, just the opposite is true. Polyelectrolytes have historically been utilized as ion-exchange resins, but a number of novel applications such as cements, gels, and encapsulation membranes are under development. Several applications of these materials, such as polyelectrolyte complexes and ionic biopolymers, are also included in this review.

STRUCTURE OF IONOMERS

Theory

The first attempt to deduce the spatial arrangement of salt groups in ionomers was that of Eisenberg (10), in which he assumed that the fundamental structural entity is the contact ion-pair. On the basis of steric considerations, he showed that only a small number of ion-pairs, termed "multiplets", can associate without the presence of intervening hydrocarbon and that there is a tendency for multiplets to further associate into "clusters" that include hydrocarbon material. This association is favored by electro-static interactions between multiplets and opposed by forces arising from the elastic nature of the polymer chains. Eisenberg assumed that the chains on average would undergo no dimensional changes as a result of clustering of the ionic species. Forsman (11) later removed this restriction and showed that the chain dimensions must actually increase as a result of association, a result confirmed by neutron scattering experiments (12).

There is a considerable body of experimental and theoretical evidence that salt groups in ionomers exist in two different environments, i.e., multiplets and clusters. The multiplets are considered to consist of small numbers of ion dipoles, perhaps up to 6 or 8, associated together to form higher multipoles -- quadrapoles, hexapoles, octapoles, etc. These multiplets are dispersed in the hydrocarbon matrix and are not phase separated from it. This means that in addition to acting as ionic crosslinks, they affect the properties of the marix, such as the glass transition temperature, water sensitivity, etc. Clusters are considered to be small (< 5 nm) microphase separated regions rich in ion pairs but also containing considerable hydrocarbon. They possess at least some of the properties of a separate phase and have a minimal effect on the properties of the hydrocarbon matrix, though they may have some reinforcing effect.

The proportion of salt groups that resides in either of the two environments in a particular ionomer is determined by the nature of the backbone, the total concentration of salt groups, and their chemical nature. Despite considerable research by various groups the details of the local structure of these materials remains somewhat obscure, as does the question of how low molecular weight polar impurities such as water affect the local structure.

Experimental Studies

1.   X-ray Scattering

Small angle x-ray scattering (SAXS) results have been of central importance in the interpretation of the structure of ionomers. Figure 1 compares the x-ray scattering observed for low-density polyethylene, ethylene-methacrylic acid copolymer, and its sodium salt over a range of scattering angles (2θ) from 2° to 40°. Polyethylene crystallinity is present in all three samples, though the acid copolymer and the ionomer exhibit less crystallinity than polyethylene. The ionomer scattering pattern contains a new feature, a peak centered at about 2θ = 4°. This "ionic peak" appears to be a common feature of all ionomers, regardless of the nature of the backbone or cation and regardless of the presence or absence of backbone crystallinity.

Both the magnitude and the location of the ionic peak are dependent on the nature of the cation. Thus the ionic peak occurs at lower angles for cesium cations of a given concentration than for corresponding lithium cations. In addition, the magnitude of the ionic peak is much greater for cesium than for lithium. The ionic peak persists at elevated temperatures but disappears when the ionomer is saturated with water. The scattering profile, however, in the vicinity of the ionic peak in the water-saturated ionomer is different from that of the parent acid copolymer.

A molecular interpretation of scattering data is model dependent, and several models for the distribution of salt groups in ionomers have been proposed to explain the ionic peak. They consist mainly of two approaches: (1) that the peak arises from structure within the scattering entity, i.e., from intraparticle interference, and (2) that the peak arises from interparticle interference.

The "shell-core" model(13) originally proposed in 1974 and later modified(14,15) is representative of the intraparticle interference models. It postulates that in the dry state a cluster of ca. 0.1 nm in radius is shielded from surrounding matrix ions not incorporated into clusters by a shell of hydrocarbon chains, Figure 2. The surrounding matrix ions that cannot approach the cluster more closely than the outside of the hydrocarbon shell are attracted to the cluster by dipole-dipole interactions. This mechanism establishes a preferred distance between the cluster and the matrix ions; a distance of the order of 2 nm accounts for the spacing of the SAXS ionic peak.

Yarusso and Cooper(16) proposed a different interpretaiton of the ionic peak that considers the liquid like scattering from hard spheres described originally by Fournet(17). With this interparticle interference model, Yarusso and Cooper were able to quantitatively model the ionic peak for lightly sulfonated polystyrene ionomers. They found that for the zinc salts about half of the ionic groups are aggregated in well-ordered domains, i.e., clusters, with the remainder dispersed in the matrix as multiplets. The clusters are about 2.0 nm in diameter and approach each other no more closely than 3.4 nm center to center. Although based on quite different physical principles,
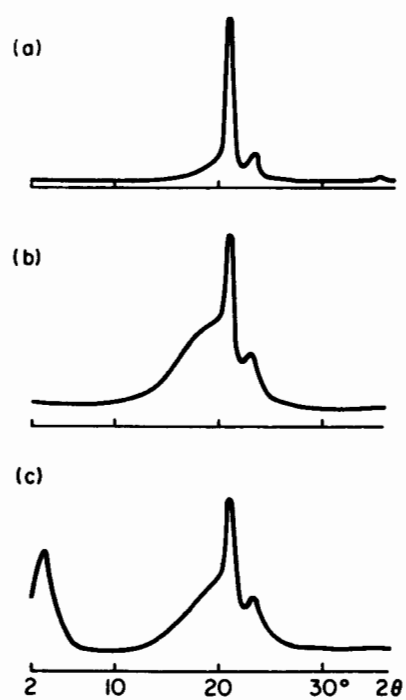
Fig. 1. X-ray diffraction from (a) branched polyethylene, (b) copolymer of 94% ethylene and 6% methacrylic acid, and (c) sodium salt of copolymer in (b), 90% neutralized. (reprinted with permission from ref 64)

this model yields structural parameters very similar to those obtained from the shell-core model.

2. Neutron Scattering

Small angle neutron scattering (SANS) has assumed great importance in the investigation of polymer morphology. One of its most impressive accomplishments is the measurement of single chain dimensions in bulk. This is generally achieved by selectively labeling a small percentage of the polymer chains by replacing hydrogen with dueterium in order to take advantage of the much higher coherent neutron scattering cross section of the deuteron compared to the proton.

Several SANS studies of ionomers have appeared on both deuterium labeled and unlabeled systems(8,12,18-20). The earlier work(14) showed that an ionic peak, similar to that observed by x-rays, could be discerned in some cases, especially when the sample was "decorated" by the incorporation of D_2O. It was also tentatively concluded(19) that the radius of gyration, R_g, of the individual chains is not altered when the acid is converted to the salt in the case of poly-styrene-methacrylic acid copolymers. Subsequent SANS experiments were performed on sulfonated polystyrene ionomers with up to 8.5% sul-fonation(12). The results of this study indicated that aggregation of the ionic groups is accompanied by considerable chain expansion, which is consistent with the theory of Forsman(11).

In a separate investigation, a series of polypentenamer sulfonate ionomers was studied(20). In this case, contrast was achieved by adding measured amounts of D_2O to the samples. Figure 3 shows the results for a 17 mol% cesium sulfonate ionomer. For the dry film there is no evidence of a scattering maximum. As small amonts of D_2O are added, however, the SANS peak becomes detectable. The Bragg spacing of the SAXS ionic peak observed for the same sample in the dry state is essentially the same as the SANS peak at low D_2O concen-trations. Above a D_2O/SO_3 ratio of about 6, the SANS ionfc peak moves markedly to lower angles.[3] These results are consistent with a phase separated model where absorbed water is incorporated into the ionic clusters, remaining separate from the matrix even at saturation.

3. Electron Microscopy

Reference 7 reviews a number of electron microscopy studies of ionomer morphology in the period up to 1979. None of these studies makes a convincing case for the direct imaging of ionic clusters. This is because of the small size of the clusters (less than 5 nm based on scattering studies) and difficulties encountered in sample prepara-tion. The entire problem was reexamined in 1980(21). In this study ionomers based on ethylene-methacrylic acid copolymers, sulfonated polypentenamer, sulfonated polystyrene and sulfonated ethylene-propylene-diene rubber (EPDM) were examined. The transfer theory of imaging was used to interpret the results. Solvent casting was found to produce no useful information about ionic clusters, and microtomed sections showed no distinct domain structure even in ionomers neutra-lized with cesium. Microtomed sections of sulfonated EPDM, however,
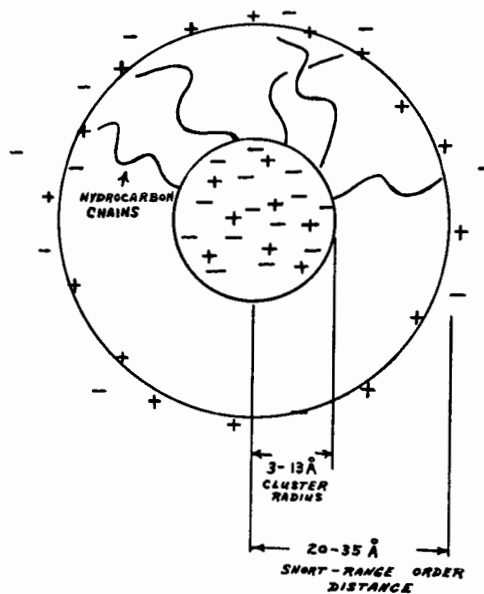
Fig. 2. Model of the ionomer sructure. (reprinted with permission from ref 65. Copyright 1974 John Wiley and Sons).
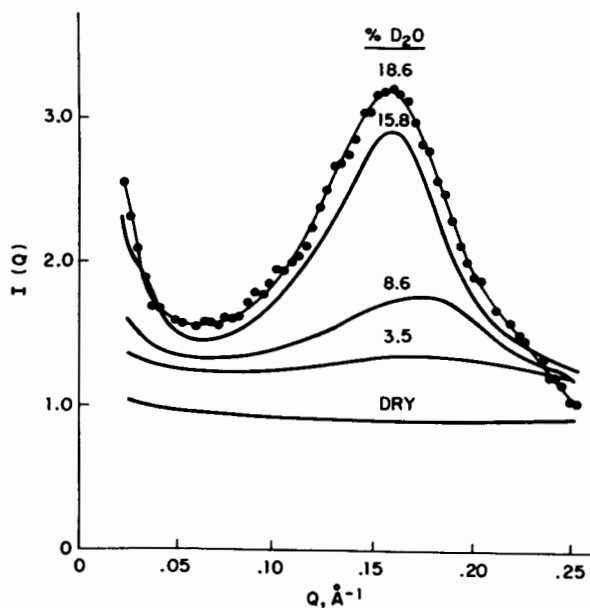

Fig. 3. Neutron scattered intensity vs. scattering vector for a 17 mol% cesium sulfonated polypetenamer. Numbers above each curve indicate weight percent D_2O. (reprinted with permission from ref 20. Copyright 1982 American Chemical Society)

appeared to contain 300nm phase separated regions. Osmium tetroxide staining of these EPDM sections revealed domains averaging less than 3 nm in size primarily inside those regions. Unfortunately, the section thickness prohibited an accurate determination of the size distribution or the detailed shape of these domains.

APPLICATIONS

Ionomers of practical interest have been prepared by two synthetic routes: (a) copolymerization of a low level of functionalized monomer with an olefinically unsaturated monomer or (b) direct functionalization of a preformed polymer. Typically, carboxyl containing ionomers are obtained by direct copolymerization of acrylic or methacrylic acid with ethylene, styrene and similar comonomers by free radical copolymerization. Rees (22) has described the preparation of a number of such copolymers. The resulting copolymer is generally available as the free acid which can be neutralized to the degree desired with metal hydroxides, acetates and similar salts. Recently, Weiss et al.(23-26) have described the preparation of sulfonated ionomers by copolymerization of sodium styrene sulfonate with butadiene or styrene.

The second route to ionomers involves modification of a preformed polymer. Sulfonation of EPDM, for example, permits the preparation of sulfonated-EPDM with a level of sulfonate groups in proportion to the amount of sulfonating agent(27). These reactions are conducted in homogeneous solutions permitting the direct neutralization of the acid functionality to the desired level. Isolation of the neutralized ionomer is effected by conventional polymer isolation techniques, such as coagulation in a nonsolvent or solvent flashing. These procedures are detailed in several patents and publications(28-31).

Ionic Elastomers and Plastics

Over the past 30 years a number of ionic elastomers and plastics have been developed that possess a wide variety of properties leading to different applications. A list of some representative ionomers is given in Table I.

In the early 1950's, B.F. Goodrich introduced the first commercial elastomer based on ionic interactions, a poly(butadiene-co-acrylonitrile-co-acrylic acid). Typically less than 6% of carboxylic monomer is employed in order to preserve the elastomeric properties inherent in these systems. When neutralized to the zinc salt, these elastomers display enhanced tensile properties and improved adhesion compared to conventional copolymers. This enhancement of properties can be directly attributed to ionic associations between the metal carboxylate groups.

A second family of ionic elastomers based on the sulfonation of chlorinated polyethylene was also introduced in the early 1950's by E. I. du Pont de Nemours & Co., Inc. Curing these materials with various metal oxides gives rise to a combination of ionic and covalent crosslinks, and these elastomers are commercially available under the trade name Hypalon.

Table 1 - Representative Ionomers

Polymer System	Trade name, if Commercial	Manufacturer	Uses
Commercial			
Poly(ethylene-co-methacrylic acid)	Surlyn	DuPont	Flexible thermoplastic
Poly(butadiene-co-acrylic acid)	Hycar	BF Goodrich	High green strength[a] elastomer
Telechelic carboxylate elastomers	Hycar	BF Goodrich	Specialty uses
Chlorosulfonated polyethylene	Hypalon	DuPont	Elastomeric Sheeting
Sulfonated ethylene-propylene terpolymer	Ionic Elastomer[b]	Uniroyal	Thermoplastic elastomer
Perfluorosulfonate Ionomers	Nafion	Dupont	Multiple membrane uses
Perfluorocarboxylate Ionomers	Flexion	Asahi Glass	Chloralkali Membrane
Experimental			
Sulfonated butyl elastomer			High green strength[a] elastomer
Thermal reversible SBR[c]			Modified SBR
Sulfonated polypentenamer			Model ionomer
Telechelic polyisobutylene sulfonate ionomers			Model ionomer
Sulfonated polystyrene			Model ionomer
Poly(styrene-co-acrylic acid)			Model ionomer

[a] Green strength = gum tensile strength (prior to vulcanization)
[b] Development stage
[c] (styrene/butadiene/N-isobutoxy methyacrylamide terpolymer ionomers)

In the mid-1960's Dupont introduced poly(ethylene-co-methacrylic acid)
under the trade name Surlyn; these were partially neutralized with
sodium or zinc cations. These modified polyethylenes possess re-
markable clarity and tensile properties superior to those of con-
ventional polyethylene. The high melt viscosity that results from
ionic interactions that persist even at elevated temperatures offers
advantages in heat sealing and extrusion operations. Other properties
attributable to ionic aggregation include toughness, outstanding
abrasion resistance, and oil resistance in packaging applications.

A specialty class of carboxyl containing elastomers are the telechelic
ionomers. In these systems the carboxyl functionality terminates both
ends of the polymer chain. Such polymers range in molecular weight
from 1500 to about 6000. These materials can be prepared via several
synthetic routes involving anionic or free radical initiated polymeri-
zation(32-34). Recently, telechelic sulfonate ionomers of poly-
isobutylene have been synthesized(35). These systems offer an unusual
opportunity to assess the influence of chain length, chain archi-
tecture, cation type, and the influence of polar additives on ionomer
properties.

Thermally reversible ionomers based on styrene-butadiene rubber, SBR,
were prepared by Gunisin(36). The incorporation of functional monomers
containing acid, amide, or amine side groups is achieved by emulsion
terpolymerization techniques. Usually the amount of the functional
monomer is kept low, about 1-3%. Metal or halogen ions are incorpo-
rated either by coagulation or bulk mixing. The tensile properties of
these polymers are enhanced by ionic associations, and this technique
may be used to enhance green strength in elastomers where this charac-
teristic is deficient. Gunisin also reports that blends of an SBR
containing small amount of N-(isobutoxymethyl)acrylamide, IBM, salts
with plastics such as polystyrene or styrene-acrylonitrile copolymers
result in impact strength substantially higher than with systems
without IBMA.

A thermopolastic elastomer based on sulfonated-EPDM, S-EPDM, was
developed in the 1970's by Exxon and more recently by Uniroyal.
Unlike the synthesis of the carboxylate ionomers described above,
S-EPDM is prepared by a post-polymerization sulfonation reaction(28).
Compared to the metal neutralized S-EPDM, the sulfonic acid derivative
is not highly associated. The free acid materials possess low
strengths and are less thermally stable. The metal salts of S-EPDM
have properties comparable to crosslinked elastomers, but they do
exhibit viscous flow at elevated temperatures. In the absence of a
polar cosolvent, such as methanol, hydrocarbon solutions of the metal
salts of S-EPDM are solid gels at polymer concentrations above several
percent(31). With the addition of 1 to 5% alcohol the polymer solution
becomes fluid with solution viscosities of the order of 10 to 100
poise.

Most of the published work on ionomers has been concerned with dif-
ferent approaches to incorporation of ionic groups and the resulting
influence of these associations on bulk or solution properties.
Studies by Makowski et al.(37), Agarwal et al.(38), Weiss(39) and

Duvdevani(40) have been directed at modification of ionomer properties
by employing polar additives to specifically interact or plasticize
the ionic interactions. This plasticization process is necessary to
achieve the processability of thermoplastic elastomers based on
S-EPDM. Crystalline polar plasticizers such as zinc stearate can
markedly affect ionic associations in S-EPDM. For example, low levels
of metal stearate can enhance the melt flow of S-EPDM at elevated
temperatures and yet improve the tensile properties of this ionomer at
ambient temperatures. Above its crystalline melting point, ca. 120°C,
zinc stearate is effective at solvating the ionic groups, thus lower-
ing the melt viscosity of the ionomer. At ambient temperatures the
crystalline additive acts as a reinforcing filler.

Weiss, et al.(41) have studied the effect of the counterion on the
physical properties of sulfonated polystyrenes with degrees of sub-
stitution up to 21 mol%. They neutralized these materials with mono-,
di-, and tri-substituted alkyl amines with alkyl chain lengths up to
C_{20}. They demonstrated that the ionic interactions significantly
weakened as the size of the cation increased. In fact, for extremely
bulky substituents such as in tri-stearyl or tri-lauryl amine salts
the glass transition temperature and the melt viscosity were much
lower than for the unionized polystyrene. This work represents the
first case where ionic substituents were used to internally plasticize
a polymer. It also demonstrates the extreme flexibility one has to
vary the properties of an ionomer by selection of the counterion.

Membranes

Crosslinked polyelectrolyte resins in the form of beads, powders,
membranes and coatings are useful in a variety of separations appli-
cations, e.g., ion-exchange and electrodialysis(42,43). Over the past
40 years there has developed an extensive literature dealing with the
swelling, ion-exchange and transport properties of these materials.
The relationship between these properties and factors such as cross-
link density, pK and number density of ionogenic groups, nature of
counterion, and external solution concentration have been established
through exhaustive experimental studies. These developments have been
accompanied by molecular or semi-molecular theoretical models of the
thermodynamic states of crosslinked polyelectrolyte gels and by
continuum mechanical models of the steady-state transport of electro-
lytes through such gels.

In the last 1960's ionomer membranes became available. In contrast
with the traditional ion-exchange resins, ionomers are rendered
insoluble by the presence of crystalline domains and ionic clusters.
A good measure of past and continuing interest in ionomer membranes
issued from the development of perfluorinated ionomers, the first-
announced being Nafion(44). These materials are characterized by
remarkable chemical resistance, thermal stability and mechanical
strength, and they have a very strong acid strength, even in the
carboxylic acid form. The functionalities that have been considered
include carboxylate, sulfonate, and sulfonamide, the latter resulting
from the reactions of amines with the sulfonyl fluoride precursor.

Although perfluorinated ionomers have been evaluated as membranes in a number of applications, such as water electrolysis, fuel cells, air-driers, Donnan dialysis in waste metal recovery, and acid catalysis, the primary system of practical interest is the production of chlorine and caustic by electrolysis. The major advantage of a membrane process is the ability to produce high concentration caustic soda directly without requiring the energy intensive evaporation step. Use of the perfluorinated membrane results in long separator lifetimes, product purity, and high efficiency with low power consumption. The significance of these membranes within the context of chlor-alkali electrochemical cells is discussed by Dotson later in this book.

The economic advantge of chlor-alkali processes based on ionomer membrane technology over more traditional separation processes has spawned considerable research in an effort to develop relationships between the microstructure of the ionomer and the selective transport of ions acorss these membranes. These studies have been directed at the chemistry and physics of ionomer membranes as well as the engineering aspects of their performance. For example, a direct investigation of the operating parameters on the performance of a chlor-alkali cell as been described by Yeager and Malinsky(45). Using a laboratory-scale cell designed for automated operation, they characterized membrane permselectivity and resistance as a function of solution concentration, temperature, and current density.

On the other hand, the nature of the microstructure and the physics of concentrated electrolytes in the context of these systems have also been considered. Hsu(46) has formulated a theoretical percolation model of ion transport that considers ionic clusters that conduct water but which cannot contribute to long-range transport at low water contents where no connectivity of clusters is expected. As the water content increases, an insulator-to-conductor transition occurs at a cluster volume-fraction percolation threshold.

Infrared studies of ionomers have provided information on the cluster and microstructure and the nature of ion-ion, ion-water, and water-backbone interactions(47,48). Risen(49) has extended thee studies into the far-infrared spectral region that is characterized by ion motion vibrational bands that reflect the force constants of cation-anion sidechain interactions. In a later chapter of this book Risen discusses results for Nafion and several other ionomers, and he relates his findings to the energetics of macromolecular organization and the glass transition. From the standpoint of industrial applications of ionic separations using ionomer membranes, these studies may ultimately prove to be important in the understanding the relaxation behavior of ionomers.

Until recently, perfluorinated ionomrs with high equivalent weights were believed to be insoluble. Covitch(50), however, has identified a number of solvents and dissolution procedures for the sulfonyl fluoride precursor and sulfonate and carboxylate Nafion ionomers with 1100 to 1200 equivalent weight. This development has great potential for the preparation of sulfonate and carboxylate ionomer blends, the

application of very thin films to electrodes or other substrates, and the production of porous membranes that may be useful in chlor-alkali diaphram cells and solid polymer electrolyte electrodes.

Polyelectrolyte Complexes

Mixtures of oppositely charged polyelectrolytes dissolved in water can interact to form a variety of precipitates, gels, or phase-separated solutions. What is formed depends on the mixing conditions and the density of ionic charges carried by the polymer chains. Polyelectrolytes with high charge densities usually interact to form precipitates. As the charge density decreases, liquid-liquid phase separation, called complex coacervation, occurs.

Complex coacervation was extensively studied between 1930 and 1945 by Bungenberg de Jong and coworkers(51). Although this group focused its studies on the bheavior of gelatin and gum arabic, many mixtures are capable of forming complex coacervates. For example, complex coacervates have been formed from gelatin and pectin, serum albumin and gum arabic, haemoglobin and gum arabic, dupin and gum arabic and histon and DNA. These biopolymers will also form complex coacervates with various synthetic polyelectrolytes.

Complex coacervation is affected by pH, polyelectrolyte concentration, polyelectrolyte mixing ratio, and the neutral salt concentration. It normally occurs over a limited pH range and is suppressed by neutral salts. The optimum polyelectrolyte mixing ratio is that which neutralizes the ionic charges carried by the polyelectrolytes. The coacervation intensity is increased by dilution, which has led some researchers to suggest that complex coacervation is the mechanism by which various polymeric species are selectively isolated and concentrated in biological systems.

Although complex coacervation has been known since the 1930's, the phenomenon was not commercially exploited until 1957. At that time, Green and Schleicher(52) developed a process for fabricating microcapsulates by coacervating gelatin with gum arabic. This process played a key role in the development of carbonless copy paper and led to other studies of the gelatin-gum arabic encapsulation process. As a result, a wide range of hydrophobic materials, such as liquid crystals, flavors, fragrances, vitamins, and organic solvents, can now be microencapsulated with gelatin-gum arabic coacervates.

Because of the success of gelatin-gum arabic microcapsules, encapsulation processes based on other complex coacervation reactions are receiving considerable attention. The driving force for this activity is to reduce the materials costs and to alter the capsule properties by using different polyelectrolytes. Two reactions that have been used successfully are the coacervation of gelatin with polyphosphate(53) and the coavervation of pI 5 gelatin with pI 9 gelatin(54). The gelatin-polyphosphate interactions are more intense than the gelatin-gum arabic interactions, while the gelatin pI5-gelatin pI9 interactions are less intense.

The formation of microcapsules is only one example of the use of polyelectrolyte complexes. Another example is the formation of a permselective membrane around live cells by a complex formed between alginate and poly(L-lysine)(55). This complex is formed under mild conditions so as not to harm the cells, and the membrane can be tailored so that it is permeable to cell nutrients, but impermeable to the cellular products. This process is of interest to those concerned with large-scale cell cultures.

Biopolymers

With the exception of natural polyisoprene, all the important biological macromolecules are polyelectrolytes. Proteins contain weakly acidic and weakly basic groups and their net charge is affected by the pH of the surrounding medium. The nucleic acid backbone incorporates the relatively more acidic phosphate diester linkage in strict alternation with D-ribose or 2-deoxy-D-ribose to yield a chain with a large negative linear charge density over most of the biologically significant pH range. Many naturally occurring polysaccharides are non-ionic. The majority are, however, polyelectrolytes with charges arising either from weakly acidic uronate carboxyl groups or from strongly acidic sugar sulfate derivatives; the linear charge densities at neutral pH vary widely depending on the chemical structure. Ionic derivatives of certain neutral polysaccharides, most notably, carboxymethyl cellulose, are of considerable commercial importance.

The ionic character of biopolymers is important in guaranteeing that they are well solvated in the predominantly aqueous media in which they function. Most biological macromolecules are not dissolved (i.e., molecularly dispersed) in vivo. Their cellular structures, however, are usually in intimate contact with the ambient aqueous solution of the cytoplasm or intercellular fluid and must be able to readily interact with it.

These interactions are frequently ionic in character. The coulombic forces of interaction between macroions and lower molecular weight ionic species are central to the life processes of the cell. For example, intermolecular interactions of nucleic acids with proteins and small ions, of proteins with anionic lipids and surfactants and with the ionic substrates of enzyme catalyzed reactions, and of ionic polysaccharides with a variety of inorganic cations are all improtant natural processes. Intramolecular coulombic interactions are also important for determining the shape and stability of biopolymer structures, the biological function of which frequently depends intimately on the conformational features of the molecule.

Theoretical considerations of the coulombic interactions of dissolved biopolymers have produced a complete picture of the distributions of counter and coions under the influence of the electrostatic charge on the macroion(56,57). The counterion condensation theory of Manning(56) has stimulated a great deal of activity in the study of dissolved macroions, especially because it provides a group of limiting laws describing the contribution of electrostatic effects to the thermodynamic and transport properties of polyelectrolyte solutions. Data

gathered over the past decade confirm the general validity of the
limiting laws of counterion condensation theory. An alternative
approach, complementary to the counterion condensation theory, has
been to solve the classical Poisson-Boltzmann equation(57). When the
macroion is modeled as an infinite cylinder, an idealization also
employed in counterion condensation theory, limiting laws in agreement
with those from the Manning theory are obtained(57). In addition,
more direct information about the distribution of small ions in the
vicinity of the macroion becomes available.

Several chapters of this book discuss applications and extensions of
the theory of polyelectrolyte solutions. Counterion condensation
theory postulates that for a cylindrical macroion, if the linear
charge density exceeds a well-defined critical value, a sufficient
fraction of the counterions will "condense" into the immediate domain
of the macroion so as to reduce the net charge density due to the
macroion and its condensed counterions to the critical value. No
condensation is predicted for macroions with less than the critical
charge density.

Counterion condensation theory, however, does not provide a detailed
picture of the distribution of the condensed ions. Recent research
using the Poisson-Boltzmann approach has shown that for cylindrical
macroions exceeding the critical linear charge density the fraction of
the counterions described by Manning theory to be condensed remain
within a finite radius of the macroion even at infinite polyion
dilution, whereas the remaining counterions will be infinitely dis-
persed in the same limit. This approach also shows that the con-
centration of counterions near the surface of the macroion is re-
markably high, one molar or more, even at infinite dilution of the
macromolecule. In this concentrated ionic milieu specific chemical
effects related to the chemical identities of the counterions and the
charged sites of the macroion may occur.

An important application of polyelectrolyte theory has been to eluci-
date the role of the tightly held counterions in those conformational
changes of biopolymers that may alter the liner charge density of the
macroion and thus the numbers of bound counterions(58,59). Because
substantial changes in the numbers of bound counterions may accompany
a given conformational change, the equilibrium distribution of the
system among the several conformational forms of a macroion may be
quite sensitive to the added salt concentration. Significant small
ion redistribution may also occur upon interaction of two biopolymer
molecules. The influence of low molecular weight electrolyte concen-
tration on the equilibria and kinetics of the interactions between
nucleic acids and proteins suggests that salts may play an important
regulatory role in the protein-nucleic acid interactions involved in
gene expression(60). Similarly, the stabilities of ordered structures
in ionic polypeptide chains are markedly affected by interactions with
small molecules of opposite electrical charge(61). This has implica-
tions for the conformational changes induced in certain peptide
hormones as a consequence of interactions with anionic lipids of the
sort that might occur at or near receptor sites on the cell surface.

The electrostatic potential generated by a dissolved biological macroion is clearly important for determining the equilibrium macromolecular conformation and the distribution of counterions or other ionic ligands in its immediate environment. Recently it has been recognized that the electrostatic field in the vicinity of a biological macroion may influence the dynamics of its biologically important interactions. In particular, analysis of the electrostatic field vectors in the vicinity of the active site of the enzyme Cu, Zn-superoxide dismutase (SOD) suggests that the electrostatic field is instrumental in guiding the negatively charged substrate, the superoxide ion, into the catalytic center(62). Computer graphics techniques have been employed to resolve the contributions to the electrostatic potential gradient of SOD from individual charged residues(63). Similar methods have been used to illustrate the electrostatic potential surfaces of a variety of biological macromolecules and to emphasize electrostatic and steric complementarity in biologically important macromolecule-ligand interactions.

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