SOLUBLE INTERPOLYMERIC COMPLEXES AS A NEW CLASS OF SYNTHETIC POLYELECTROLYTES

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Abstract - Some routes of preparation of water-soluble nonstoichiometric complexes (N-PEC) are considered. The structure of water-soluble N-PEC is examined and it is shown that in certain aspects they behave like individual macromolecular compounds and represent a new class of complex water-soluble polyelectrolytes. The behavior of N-PEC in aqueous salt solutions is considered and reasons and a mechanism of conformational transformations of the N-PEC macromolecules in these media are discussed. Disproportionation phenomena observed in N-PEC solutions are described in connection with the peculiarities of a phase separation in these systems, possible reasons and a mechanism of these phenomena are suggested. Data on the kinetics of the macromolecular exchange reactions in N-PEC solutions are presented. It is shown that the rate of interchange is dramatically controlled by simple electrolytes present in the reaction media.

The increasing interest in the chemistry and physical chemistry of synthetic polyelectrolytes is due to the continuous expansion of the areas of their practical application as highly effective flocculants, cross-linking agents and stabilizers of colloidal dispersions, ion-exchange materials specific sorbents, biologically active compounds etc. Therefore the problem of production of diphilic water-soluble macromolecules, which chains contain both hydrophilic and hydrophobic units, is of special importance. In this paper one of the new approaches to the synthesis of these systems is considered, it is based on the use of interpolymer chemical reactions.

Interpolymer reactions became a special area of research during last 25 years. Today quite a large number of original papers and reviews devoted to this problem has been published (see, for example, (1-5)).

In this paper reactions between oppositely charged polyelectrolytes are considered. These reactions have a distinct cooperative character and result in formation of interpolymeric salts usually defined as polyelectrolyte complexes (PEC).

Early studies of PEC formation were related to stoichiometric PEC (S-PEC) in which the ratio between the oppositely charged groups was 1:1. S-PEC are insoluble in any of the known solvents, but are capable of limited swelling in water. The interest in S-PEC is primarily caused by the possibility of their use as membranes for desalinization of water (1,6), for hemodialysis (7-9) etc. A large number of publications involving reviews (1-6) has been devoted to synthesis, properties and applications of S-PEC. However, a detailed analysis of these works does not fall within the scope of the present paper.

The paper is devoted to a new area of research which has arisen due to the discovery of nonstoichiometric PEC (N-PEC). These interpolymeric compounds are also the products of reactions between electrostatically complementary chains. However, in contrast to S-PEC they are soluble in aqueous solution if specific conditions are maintained. As a result they can be used as ordinary soluble polyelectrolytes. At the same time in contrast to ordinary polyelectrolytes, N-PEC also show a number of unique properties, which, as we shall see later on permit us to place them into a special class of water-soluble polymeric compounds.

Today it is known that water-soluble N-PEC can be obtained from oppositely charged polyelectrolytes of various chemical structure when specific

conditions are met (10-15). They can be formed by pairs of strong poly-electrolytes, pairs of weak polyelectrolytes, or by mixed pairs. A polyelectrolyte included in N-PEC in excess can be charged both negatively and positively. The routes of N-PEC preparation are very simple. These macromolecular compounds can be obtained by a simple mixing of aqueous solutions of completely ionized oppositely charged polyelectrolytes taken in non-equivalent ratios. However, a number of specific conditions must be met for the preparation of water-soluble N-PEC. Data permitting the formulation of one of the necessary conditions for the formation of N-PEC were presented for the first time in (13). This paper provides the data on the solubility of the products of interpolymeric reaction in the system: poly-N,N-dimethylaminoethyl methacrylate hydrochloride (PDMAEMA·HCl)-sodium polyphosphate (NaPP) as a function of the degree of polymerization ($\bar{P}$) of the individual components. It follows from the data that soluble products are formed only if $\bar{P}_1/\bar{P}_2 \geqslant 1$. The subscript 1 corresponds to polyelectrolyte included in N-PEC in excess and this component will be listed first in the studied systems identification. Let us also note that the degree of conversion in reaction between polyelectrolytes(θ)is close to 1. It means that practically each unit of a polyelectrolyte, included in an N-PEC in deficient amount and referred to as the guest polyelectrolyte (GPE), forms a salt bond with a unit of a polyelectrolyte included in an N-PEC in excess and referred to as the host polyelectrolyte (HPE). Thus the degree of polymerization of the HPE ($\bar{P}_{HPE}$) must be higher than or equal to the degree of polymerization of the GPE ($\bar{P}_{GPE}$). In this paper the systems for which $\bar{P}_{HPE} \gg \bar{P}_{GPE}$ are considered.

However, the formulated condition $\bar{P}_1 \geqslant \bar{P}_2$ is not sufficient. It is also necessary for the solution in which the reaction between HPE and GPE is carried out to contain a certain amount of a low-molecular weight electro-lyte. This amount may vary over the range 0.002÷0.1mole/l (for example, NaCl) and depends on the chemical nature of the polyelectrolytes and their ratio. Generally speaking, the larger the excess of the HPE is, the smaller should be the concentration of the salt required for the formation of a water-soluble N-PEC (12).

For full solubility of the product of a completed interpolyelectrolyte reaction ($\theta \simeq 1$) between HPE and GPE, it is also necessary that their ratio in the system should not exceed a certain characteristic value. In the terms of the ratio between the number of GPE units to the number of HPE units φ =[GPE]/[HPE] is limited by a certain characteristic value, φ_c . If N-PEC components are taken in the ratio greater than φ_c , then a dissolved N-PEC of the characteristic composition φ_c and a corresponding amount of an undissolved S-PEC coexist in the reaction system. The value of φ_c for most of the systems investigated varies over the range of 0.5 to 0.2 and depends basically on the chemical nature of the polyelectrolytes constituting the N-PEC.

Even within the route indicated for N-PEC's preparation at least two different subroutes are possible. One of them consists of the addition of a solution of an HPE to a solution of a GPE, the other corresponds to the opposite sequence of mixing. In both cases the composition of intermediate products and the phase states of intermediate systems are quite different (16). However, the molecular characteristics of the resulting N-PEC are identical and, consequently, soluble N-PECs can be considered as equilibrium macromolecular compounds. This means, in particular, that the methods broadly used for the investigation of ordinary polymer solutions, particularly of polyelectrolyte solutions can be also used for N-PEC investigation.

Most detailed information on the structure of water-soluble N-PECs was obtained when their solutions were investigated by the light-scattering technique. Solutions containing a single macromolecular component – an N-PEC were studied. The condition $\bar{P}_{GPE}/\bar{P}_{HPE} < \varphi_c$ was maintained. The measurements, as a rule, were carried out in aqueous solutions of simple electrolytes at their concentrations not lower than 0.05M. N-PEC solutions of the different concentrations were dialyzed against the same salt solution. The plots of a double extrapolation had the form characteristic for the usual polymer solutions. Table 1 shows the results of an investigation of solutions of the N-PECs formed by PDMAEMA·HCl (HPE) and NaPP (GPE) (17). It is seen that when the N-PEC's composition changes over a quite broad range φ = 0.5 ÷ 0.067 their molecular weight only slightly changes and corresponds to the weight of the particles containing one HPE chain. The average number of GPE chains ($\bar{n}$) in each particle, calculated from the equation $\bar{n}_{GPE} = (\bar{P}_{HPE}/\bar{P}_{GPE})$ decreases from 10 to 1. Consequently a particle of N-PEC must be considered as a peculiar individual complex

Table 1
Effect of the composition of the nonstoichiometric PEC
PDMAEMA·HCl-PP on its molecular characteristics. $\bar{M}_w$ of
the PDMAEMA.HCl=$6.3\cdot10^5$; $\bar{M}_w$ of the NaPP=$1.7\cdot10^4$; pH=
4.0 in 0.1M NaCl at 20°

Composition of the N-PEC, φ	$\bar{M}_w$ of the N-PEC ($\cdot10^{-5}$)		Average number of macromolecules in a particle of the N-PEC, $\bar{n}$.		$(\overline{R_g^2})^{1/2}$, Å	$A_2\cdot10^4$
	Experimental value	Calculated value	HPE	GPE		
PDMAEMA·HCl						
(φ=0)	6.3	–	I	–	510	8.2
0.07	7.15	6.4	I	1.4	480	6.5
0.10	6.9	6.4	I	2.0	440	5.9
0.13	7.35	6.5	I	2.3	430	5.2
0.20	6.75	6.6	I	3.9	400	4.9
0.33	6.7	6.8	I	6.5	350	2.9
0.50	7.0	7.0	I	10	270	1.1

macromolecule which composition with respect to the polyelectrolyte
components can be easily varied, when their initial ratio is given.

It is seen from Table 1 and Fig.1 that the macromolecule average size
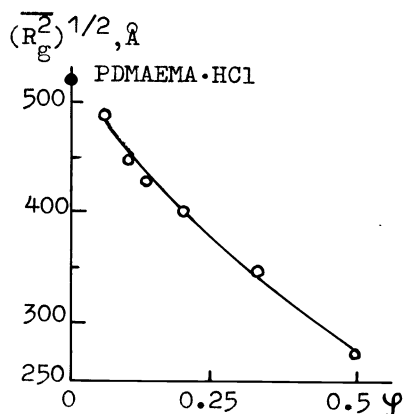

$(\overline{R_g^2})^{1/2}$, Å

PDMAEMA·HCl

Fig.1 Dependence of the value of $(\overline{R^2})^{1/2}$
of a particle of the N-PEC PDMAEMA·HCl-PP
on the composition of the N-PEC φ. $\bar{M}_w$
of PDMAEMA·HCl = $6.3\cdot10^5$; $\bar{M}_w$ of the NaPP=
$1.7\cdot10^4$, pH=4.0, in 0.1M NaCl at 20°.

increases monotonously with a decrease in the population of GPE chains in
the HPE chains approaching the average size of a coil of the free HPE. The
results of a measurement of mean-square radius of gyration $(\overline{R_g^2})^{1/2}$ are of
great importance for a basis of a general scheme of the structure of N-PEC
particles involving the existence of sufficiently extended double-strand
ladder sections. In fact, as seen from Table 1, the values of $(\overline{R_g^2})^{1/2}$
for N-PEC macromolecule with the composition φ = 0.067 and for a chain of
the free HPE differ very little, by ~5%. At the same time, in such N-PEC
particle every fifteenth unit of the HPE chain on average, participates in
formation of a salt bond with a unit of the GPE chain: for $\theta \simeq 1$, each
HPE chain, with a length of 3000units, is linked to the GPE chain 170
units in length. It is obvious, that when two chains are randomly
entangled with each other, a considerably larger decrease in $(\overline{R_g^2})^{1/2}$ should
be expected (16-19). Consequently, in water-soluble N-PEC the contour line
of a fragment of the HPE chain, occupied by a GPE chain, is close to the
contour length of the latter. However, it is not necessary to think that
double-strand ladder sections in N-PEC particles must necessarily have the
shape of extended rods. On the contrary, because of their increased
hydrophobicity, they must show a tendency to fold up at the sites of
intraladder loop-shaped defects, forming drop-shaped clusters. This
complex macromolecule is shown in Scheme A. This type of conformation
apparently corresponds to a minimum in free energy, or a maximum in
entropy, since a particle contains long continuous relatively flexible
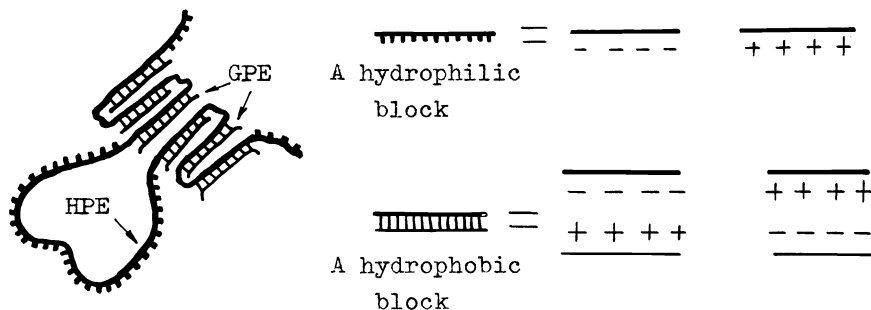
Scheme A

sections of the free HPE. Because of the reversibility of the intermole-
cular ionic reaction of the N-PEC formation, the system can find an optimum
set of conformations by a "trial and error" method.

Double-strand sections represent a set of cooperatively interacting
oppositely charged units. It shows an increased rigidity and a relatively
high hydrophobicity. Precisely for this reason, N-PECs overloaded with GPE
(when $\varphi > \varphi_c$), lose their solubility in water. For the same reason, S-PEC are
also insoluble in water. The sections of HPE, free of GPE, on the contrary,
are relatively flexible and hydrophilic. Consequently, an N-PEC macro-
molecule may be considered as a peculiar block-copolymer. Water behaves as
a good solvent with respect to single-strand polyelectrolyte sequences and
as a poor solvent for hydrophobic double-strand sequences. It means that
hydrophobic blocks of N-PEC in an aqueous solution must segregate due to
nonpolar interaction. In dilute solutions such segregation, as is shown in
Scheme A and is seen from Table 1, is intramolecular in nature. Its
quantitative measure is a progressive decrease in the average size of N-PEC
complex macromolecules with an increase in GPE population, as is shown in
Fig.1 and Table 1.

Hydrophilic blocks, apparently, are responsible for the properties typical
for usual polyelectrolytes. It follows from the character of a change in
the thermodynamic characteristics of N-PEC solutions with a change in the
composition of complex macromolecules. From Table 1 it follows that the
second virial coefficient, A_2, increases with decreasing φ , i.e., with a
decreasing fraction of HPE units included in hydrophobic blocks and tends
toward a value characteristic for a solution of the free HPE. This is
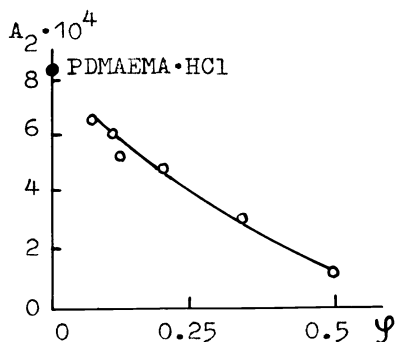shown in Fig.2. The said above means that the main contribution to an

Fig.2. Dependence of the second virial
coefficient A_2 of solutions of the N-PEC
PDMAEMA·HCl-PP on the composition of the
N-PEC, φ _. $\overline{M}_w$ of the PDMAEMA·HCl=
$6.3·10^5$; $\overline{M}_w$ of the NaPP=$1.7·10^4$, pH=4.0
in 0.1M NaCl at 20°.

excluded volume of N-PEC, being the products of completed reactions, is
made by electrostatic repulsion of similarly charged HPE units forming
single-strand hydrophilic blocks. This contribution is expressed as (20):

$$A_{2el} = 10^3 x^2 / 4M^2 I \qquad (1)$$

where x is the effective charge of polyion, M is its molecular weight,
I is the concentration of a low-molecular (1:1) electrolyte. It is
important that A_{2el} for an ordinary polyelectrolyte is proportional to
the square of the degree of ionization of macromolecules. It is obvious,
that for the N-PEC under consideration the value of this parameter can be
varied in a wide range by changing the composition of the complex

macromolecules $\mathcal{Y}$. The effective charge of N-PEC macromolecules in a pH range corresponding to complete ionization of the HPE units depends on the composition in the following manner:

$$z/M = \mathcal{Y}(1-\mathcal{Y})/M_o \qquad (2)$$

where M_o is the weight of the polyion unit, $\mathcal{Y}$ is the degree of bonding of low-molecular counterions. Thus, for a solution of block N-PEC macromolecules in which the hydrophobic ladder blocks are joined into a system of compact intramolecular clusters and the hydrophilic charged blocks are located at the periphery of the particle and are responsible for the solubility of the N-PEC, the parameter A_{2ef} must be proportional to the value of $(1-\mathcal{Y})^2$. This dependence is shown in FiG.3. It is seen that this relationship is indeed linear.
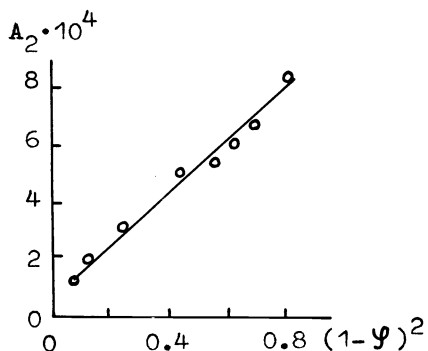

Fig.3. Dependence of the second virial coefficient A_2 of solutions of the N-PEC PDMAEMA·HCl-PP on the square of their charge $(1-\mathcal{Y})^2$. $\overline{M}_w$ of the PDMAEMA·HCl= $6.3\cdot10^5$; $\overline{M}_w$ of the NaPP=$1.7\cdot10^4$, pH=4.0 in 0.1M NaCl at 20°.

If HPE is a weak polyelectrolyte, an N-PEC particle charge at fixed composition can be changed by a change in the degree of ionization of HPE units included in single-strand blocks. A decrease in the degree of ionization of the HPE is accompanied by a decrease in its lyophilizing capacity and results in progressive agglomeration of N-PEC particles going as far as their separation from the solution (15). It is precisely for this reason that N-PEC in which the role of the HPE is played by a polycarboxylic acid are soluble only in alkaline media at pH above 7 when they are close to their characteristic compositions. Correspondingly N-PEC containing weak polymeric bases as HPE, acquire the ability to dissolve only in acidic media at a pH< 7.

Proceeding from the data presented above it is possible to conclude that addition of simple salts to N-PEC solutions must be accompanied by a typical for ordinary polyelectrolytes decrease in the size of the polyion due to a screening of the electrostatic repulsion between HPE units contained in single-strand blocks. These effects actually exist. However, in addition there are some other effects much more pronounced and characteristic only of this class of macromolecular polyelectrolyte compounds. As it will be shown below, this unique properties are due to the reverisible character of an interaction between HPE and GPE units. We shall consider them, particularly, taking as an example the N-PEC formed by sodium salt of polyacrylic acid (Na PA) and linear polyethyleneimine (PEI). The turbidimetric titration curve of an aqueous solution of this N-PEC with a composition $\mathcal{Y}$= 0.5 with NaCl solution is represented in Fig.4.

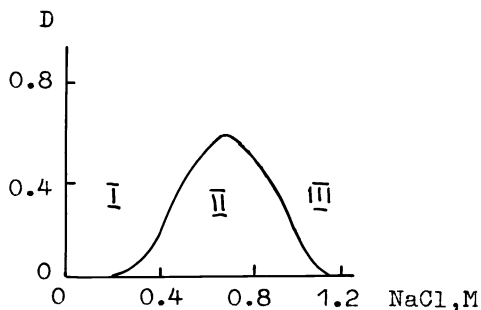Fig.4. Curve of the turbidimetric titration of a solution of the N-PEC NaPA ($\overline{M}_w=3\cdot10^5$)-PEI($\overline{M}_w=1.6\cdot10^4$) with the composition $\mathcal{Y}$ =0.5 with NaCl solution, [N-PEC]= $2\cdot10^{-3}$ mole/l, pH=7.0, at 20°C.

One can distinguish three regions of the change in ionic strength of the solution to which there correspond three regions on the diagram designated by the numbers I, II, and III.

In region I, an increase in the salt concentration is not accompanied by a change in the phase state of the system, which remains homogeneous. When a certain value of the ionic strength I_1 is reached the system becomes turbid and in region II it is heterogeneous. At an ionic strength I_2 the system again becomes homogeneous and remains homogeneous in region III. It should be noted that these transitions take place in dilute solutions of N-PEC with the concentration of $10^{-2} \div 10^{-3}$ mole/l. Such behavior, generally speaking, is not characteristic of solutions of ordinary linear polyelectrolytes, but it is characteristic for all N-PEC investigated (21,22).

Let us consider in succession the behavior of the N-PEC in the regions I, II and III. Fig.5 shows the dependence of the sedimentation coefficient
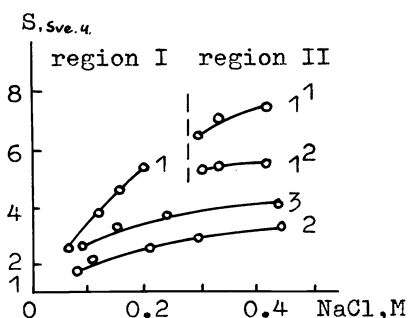

Fig.5. Dependence of the sedimentation coefficients of the N-PEC NaPA-PEI with the composition $\varphi = 0.5$ (curves 1, 1^1 and 1^2); of NaPA (curve 2) and of the N-PEC* NaPA-PEI with the composition $\varphi = 0.5$ (curve 3) on the concentration of NaCl in the solution. Curves 1,2,3 correspond to the homogeneous systems, 1^1 and 1^2 to the heterogeneous system [N-PEC*] = [NaPA] = 0.5mole/l, pH=7.0. The rotational speed of the rotor is 56100rpm, at20°.

(S) of N-PEC NaPA-PEI with the composition $\varphi = 0.5$. It is seen that in region I addition of NaCl results in a strong increase in compactness of the N-PEC particles. It follows from a strong increase in S when the salt concentration is increased from 0.05 to 0.3M, curve 1 in Fig.5. The increase in S , is precisely due to a change in conformation of the N-PEC particles, since their molecular weight measured by the light scattering technique remains unchanged over the indicated range of a change in the NaCl concentration ($\overline{M}_w = 2.7 \cdot 10^5$), and that corresponds to an N-PEC particle containing one HPE chain. The change in conformations of the N-PEC particles is directly shown by the results of light scattering measurements of $(\overline{R_g^2})^{1/2}$ for the N-PEC with the composition $\varphi = 0.25$. A considerable decrease in $(\overline{R_g^2})^{1/2}$ from 700Å to 270Å is observed when NaCl concentration is increased from 0.05M to 0.2M. It is of interest that the considerable decrease in the N-PEC particle size cannot be explained only by the screening of electrostatic repulsion between the ionized COO^--groups of the HPE, because S increase in the free HPE is much smaller, see curve 2 in Fig.5. Curve 3 in Fig.5 shows a change in the sedimentation coefficient for an N-PEC* with the same composition as the N-PEC normal, but specially modified by inter-HPE-GPE chemical cross-linking. It is seen that no considerable increase in N-PEC* compactness is observed if the salt is added. The behavior of the N-PEC* solution is quite close to that of the free HPE solution. A considerable difference between the N-PEC and N-PEC* is that between the HPE and GPE chains of the latter, in addition to the salt bonds, a certain number of covalent amide bonds does exist. They play a role of permanently fixed cross-links. The route of introduction of these covalent cross-links is described in (22,23). The cross-links restrict redistribution of the reversibly dissociating salt bonds and consequently the possibility of the GPE-HPE fragments rearrangement within an N-PEC particle. In the case of the normal N-PEC such restrictions do not exist. In both cases addition of the salt results in dissociation of a certain fraction of interchain salt bonds, the greater the higher the added salt concentration is (24). However, the consequences of this dissociation are different for the N-PEC and N-PEC*. It follows from the experimental results that the electrolyte addition is followed by a much greater increase in compactness of the N-PEC particles in comparison with that of N-PEC*. The increase in compactness is accompanied by a considerable decrease in the second virial coefficient of the solution, i.e. by a decrease in a thermodynamic affinity of the N-PEC to the solvent (16). The driving force of a compactization at the unchanged composition of N-PEC particles "damaged" with the salt, is apparently, due to an increase in the internal combinatorial entropy, because of the realization of b -type structures containing loop-shaped defects shown in

Scheme B. The defects of this type are in general typical for polycomplexes

$$\ominus = {+}COO^- \qquad \equiv = {+}COO^{-+}NH_2$$
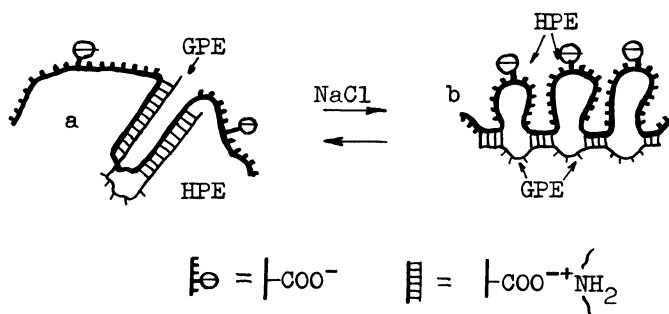
Scheme B

(19). The loops are asymmetric and include HPE units in a considerable excess; they are formed as a result of "shrinking" of long sections of an HPE chain along relatively short GPE chains. The greatest number of ways by which the sequences of intermolecular salt bonds (short double-strand blocks) can be distributed in an N-PEC particle, i.e. the highest combinatorial entropy, corresponds to the $\mathit{6}$-structure. A decrease in the size of N-PEC particles is due to a considerable contribution of these structures, which naturally cannot exist in the case of the N-PEC*.

The fate of the N-PEC* particles is quite different if the salt is added. With the increasing salt concentration, progressive dissociation of inter-HPE-GPE salt bonds takes place, but due to the existence of intracomplex covalent cross-links, the GPE chains remain immobilized, this eliminates the compactization phenomena. The conformations of N-PEC* particles gradually transform as it is shown in Scheme C, i.e. they change only within the α-structure shown in Scheme B to the left.

$$\blacksquare = {+}\overset{O}{\overset{\|}{C}}{-}N$$
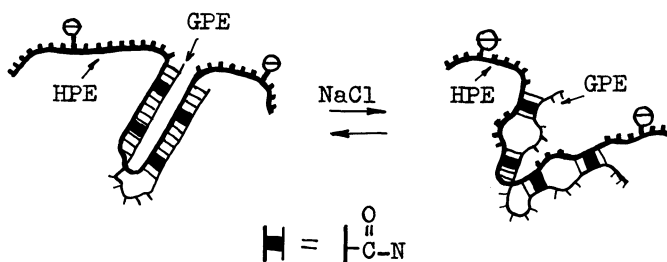
Scheme C

In region II at rather high salt concentrations $(\mathit{I} > 0.3M)$ a phase separation is observed. An analysis of the composition of the coexisting phases shows that the S-PEC is present in the precipitate while the N-PEC is present in the dilute phase, considerably depleted in PEI (GPE). Thus, in the system under consideration a physical process of phase separation and a chemical ionic reaction of redistribution of the salt bonds resulting in N-PEC particles disproportionation are carried out simultaneously and result in appearance in the coexisting phases of the two different N-PEC with quite different compositions. If to compare the behavior of an N-PEC and that of an N-PEC* one can see that these two processes are actually conjugated. In contrast to the N-PEC, if low-molecular salts are added to the N-PEC* solutions no phase separation is observed up to the salt concentration sufficient for the complete dissociation of the intermacromolecular salt bonds ($\mathit{I} \cong 2M$) (22). Hence it follows that prohibition of transfer of GPE chains from some N-PEC particles to others excludes the phase separation. Consequently the reason for phase separation in a mixture N-PEC-water-salt is disproportionation of the N-PEC particles taking place in the solution because of the action of the low-molecular electrolyte.

Thus, the understanding of the features of the phase separation in N-PEC solutions is directly related to investigation of further transformations of compacted N-PEC particles when a salt concentration is increased. These transformations can be followed in region II by following the properties of a polycomplex in dilute phase being in contact with the S-PEC

precipitate. As an example Fig.6 shows a sedimentogram of the supernatant
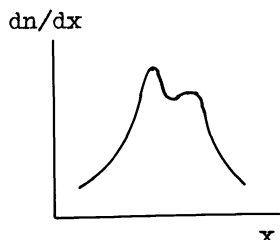liquid formed after the phase separation in the N-PEC solution (φ =0.5)

dn/dx

Fig.6. Sedimentogram of an aqueous salt
solution of the N-PEC NaPA-PEI with the
composition φ =0.5, the concentration
of NaCl is 0.35 M and of the N-PEC is
0.05mole/l, pH=7.0, at 20°. The
rotational speed of the rotor is
561000rpm.

x

caused by addition of NaCl (0.45M). It is seen that the dilute phase
contains two types of polymer particles: N-PEC[1] and N-PEC[2]. In Fig.5 in the
right hand top corner the dependences of the sedimentation coefficient on
NaCl concentration are given for the both types of particles formed in
region II. The S -values of these particles as it follows from curves 1[1]
and 1[2] differ by more than 2 Svedberg units and considerably exceed the
S -value of the free HPE (curve 2). The character of distribution of
GPE(PEI) among the particles of the rapidly sedimenting N-PEC[1] and the
slowly sedimenting N-PEC[2] was concluded from comparison of the sedimentation
data obtained by using refractometric detection technique, and the data of
the scanning sedimentation, the former are shown in Fig.6. In the latter
case the absorbance of the solution at 265nm was measured. The absorption
in this region is caused by benzamide groups present in PEI used in the
amount of 2% (25).

From these data it follows that the two types of particles found in the
dilute phase correspond to polycomplexes with considerably different
compositions. The composition of N-PEC[1] is close to stoichiometric one.
N-PEC[2] is considerably depleted in PEI, in comparison with the original
N-PEC. Thus disproportionation of the N-PEC into two polycomplexes N-PEC[1]
and N-PEC[2] with quite different relative contents of GPE particles
preceeds the phase separation. The disproportionation phenomena are found
in aqueous salt solutions of N-PEC with different original compositions.
The salt concentration required to reach phase separation is the higher
the smaller φ is.

In contrast to this in aqueous-salt solutions of N-PEC* only one polymer
component is found. The corresponding single peak in the sedimentograms
is observed over the whole range of NaCl concentration up to 1.5M.

The experimental results presented above can be summarized in the following
manner. If low-molecular weight salts, which are competitors in the
reaction between polyelectrolytes are added to aqueous solutions of N-PEC,
dissociation of intermolecular salt bonds takes place. This is accompanied
by corresponding rearrangement of HPE and GPE segments and appearance
of compact conformations of N-PEC particles, shown in Scheme B, b -structure.
An increase in compactness of N-PEC, apparently, must be accompanied by a
decrease in entropy of mixing in the polymer-solvent system. However, this
decrease is compensated by an increase in the internal combinatorial
entropy of the N-PEC due to realization of conformations and structures
containing increasing number of loop-shaped defects. At last when the
fraction of interchain salt bonds becomes sufficiently small, an increase
in the combinatorial entropy already cannot compensate a decrease in the
entropy of mixing of compact particles with the solvent. Under these
conditions in region II, interchange by GPE short chains between different
N-PEC particles takes place, which is forbidden for cross-linked particles
of N-PEC*. As a result of this interchange some particles of N-PEC are
depleted in GPE and become considerably more extended. A considerable
contribution made by these particles to the increase in entropy of
mixing compensates the loss in the entropy of mixing caused by the
appearance of very compact N-PEC[1] particles with the composition close to
the stoichiometric one. Apparently, these N-PEC[1] particles then form S-PEC
precipitating in aqueous salt solutions. Thus, the phase separation,
observed in aqueous salt solutions of N-PEC, is a consequence of dispropor-
tionation of N-PEC particles taking place in homogeneous solutions.

It should be noted that disproportionation phenomena are broadly
encountered in the reactions between chemically complementary macromolecules
for example, in interaction of linear polyelectrolytes with globular

proteins (16), of polyelectrolytes with polysilicic acid sols (26), of polyethylene glycol with polymethacrylic acid in aqueous solutions (5,27). The disproportionation of N-PEC in aqueous salt solutions described in this paper is the first observed example of disproportionation in the reactions between two linear flexible polyelectrolytes.

In connection with the disproportionation phenomena observed in N-PEC solutions, an investigation of the kinetics and the mechanism of GPE chains transfer from some N-PEC particles to others is of obvious interest. The study of this kind are of independent importance for the development of theoretical concepts concerning the dynamics of cooperative reactions between chemically complementary macromolecules. One of the peculiar properties of polymer-polymer complexes closely related to the phenomena considered above, is their ability to enter the reactions of macromolecular substitution and exchange in solutions (2,19,28-31). This is also characteristic for complexes formed by linear polyions and globular proteins (32-34). The first quantitative investigation of the kinetics of intermolecular exchange was carried out in (35) with the systems PAA-poly-N-vinylpyrrolidone and polymethacrylic acid - polyethylenoxide (PEO). These pairs form the complexes in which the complementary macromolecular partners are linked with cooperative hydrogen bonds. The interpolymer reaction was followed by a change in depolarization of luminescence in solutions of the polymers containing the polyacids labeled with anthryl labels. Recently the results of (35) have been confirmed for PAA-PEO system (36). As far as we know any data related to the kinetics of interpolyelectrolyte reactions are not available in the literature.

Naturally, most accessible for kinetic study are macromolecular reactions not accompanied by phase separation, i.e. the reactions in homogeneous systems. Recently found macromolecular exchange with participation of water-soluble N-PEC is one of such reactions (19,31). It can be represented by Scheme D. This reaction consists of transfer of relatively short GPE

Scheme D

The intermediate ternary polycomplex

chains from the original N-PEC particles to the free HPE chains. As a result an N-PEC with the composition equal to the composition of the reaction mixture is formed. It is important that when the reaction completes, no free GPE and HPE chains are found in the reaction systems. In this connection a mechanism for such reactions was supposed assuming the formation of ternary intermediate shown in Scheme D.

In this paper we consider the results of the kinetic study of the exchange reactions (Scheme D) between N-PEC with different composition φ , formed by sodium polymethacrylate (NaPMA) HPE and poly-N-ethyl-4-vinylpyridinium bromide (PVP). The kinetics was followed by measurements of luminescence quenching. Anthryl groups were used as luminescent label. These groups were introduced in HPE (NaPMA) chains: one label per 480 units of the polymer (NaPMA*) on average. The PVP units played a role of luminescence quenchers (37).

We have found that addition of simple salts to the solution of the reaction mixtures results in an enormous acceleration of the reaction shown in Scheme D. In a salt-free system this reaction was not observed

at all. These facts are explained in terms of formation of intermediate
product, shown in Scheme D. Apparently, it is necessary to have a
sufficient number of separated units, included in the loops present in the
original N-PEC particles to form a ternary intermediate N-PEC and then a
new N-PEC product with a changed composition. It seems that the reaction
under consideration cannot proceed if an average size of a loop partici-
pating in "nucleation" is smaller than a certain critical value. It is
clear that a successive addition of NaCl to N-PEC solutions is accompanied
by an increase in a number and a size of loops due to the competition
between small ions and charged polyion units in salt bonds formation
reaction.

Fig.7 represents the kinetic curves corresponding to the reaction between
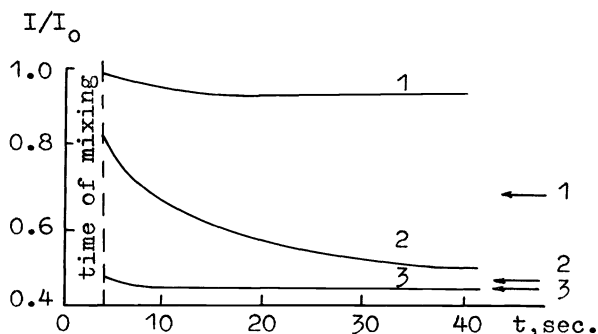the N-PEC (NaPMA-PVP) with the composition $\mathcal{Y}$ =0.33 and NaPMA* in solutions

Fig.7. Time dependence of the
relative intensity of
luminescence, for an exchange
reaction between the N-PEC
NaPMA ($\overline{M}_w$=2.7·10^5)-PVP($\overline{M}_w$=6·10^4)
with the composition $\mathcal{Y}$ =0.33 and
the labeled NaPMA* ($\overline{M}_w$=2.7·10^5)
at 20°. The NaCl concentration
in the solution: 1 - 0.036 M,
2 - 0.07 M,3 - 0.1 M.[N-PEC]=
[NaPMA*] = 0.004mole/l. Arrows
show the value ofI/I_oat the NaCl
concentrations indicated,
corresponding to the products
of the completed reaction.

with different NaCl content. The salt-less solutions of polymeric reagents
with equal concentrations, of the labeled and the unlabeled HPE were
prepared. Then the calculated amounts of 2M NaCl solution were rapidly
(less than for 1sec) injected into reaction vessel by the diluter. The
intensity of luminescence at λ =420nm was followed continuously by
spectrafluorimeter. The arrows show the values of the relative intensity
of luminescence, I /I_o , at chosen NaCl concentrations, corresponding to
the product of the completed reaction, i.e. to the N-PEC with the
composition $\mathcal{Y}$ =0.165. It is seen that the simple electrolyte quite strongly
influences the rate of macromolecular exchange with the participation of
cooperative polyelectrolyte complexes. As it was already mentioned above
in the absence of the salt the reaction practically does not proceed.
However, in 0.1M NaCl solutions only some seconds are enough for the
reaction to reach an equilibrium. The effect we found can be important
for understanding the mechanism of interpolymer reactions involving those
between biologically significant polyelectrolytes.

                    *   *

                              *

The experimental data and the considerations presented above permit to
consider water-soluble N-PEC as a distinctive variety of block copolymers
belonging to the class of polyelectrolytes. This peculiarity already
shows up during the synthesis of the N-PEC, in which a fundamentally new
approach is used, consisting of the lateral pairing of chemically
complementary chains of different length.

In addition, in contrast to block copolymers synthesized by the usual
methods, as a result of the reversibility of the reactions between HPE
and GPE, the GPE chains can migrate along the HPE chains and can even
move from one chain to another. A migration of this type actually means
a change in the relative length and number of hydrophilic and hydrophobic
blocks in the complex macromolecule. Consequently, complex block macro-
molecules of N-PEC can "seek" thermodynamically optimal variations of an
interaction with the surrounding medium by changing not only their
secondary, but also their primary structure. The unique possibility for
N-PEC to change their hydrophilic-hydrophobic balance in accordance with
conditions, which arise from this, and to adjust themselves to the
hydrophilic-hydrophobic balance surrounding their particles and surfaces,
must also have important practical consequences, for example, for the
solution of problems related to the flocculation or stabilization of
colloidal systems. N-PEC are also of considerable interest as the simplest
models of polycomplexes of biological origin.

The formation of N-PEC takes place as a result of a very rapid ion-exchange reaction by the simple mixing of aqueous solutions of the starting polyelectrolyte components. The process is completed practically instantaneously, even at very high dilutions. The synthesis of N-PEC may be carried out without any experimental devices, in the same working system in which its later operation is assumed. The originality and simplicity of the synthesis of block diphilic polyelectrolytes naturally will open up new areas for their practical application.

The rate of interchange reactions of N-PEC is dramatically controlled by simple electrolytes. The kinetics and mechanism of such reactions undoubtedly form a new facinating area for research.

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