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A New Class of Complex Water-soluble Polyelectrolytes

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The literature data on polyelectrolyte complexes (PEC), mainly non-stoichiometric PEC (N-PEC), are analysed. Interpolyelectrolyte reactions, leading to the formation of N-PEC as well as the methods of synthesis of these macromolecular compounds are examined. The structure of water-soluble N-PEC, which constitute a new class of complex water-soluble polymers, is discussed. A special section is devoted to the behaviour of N-PEC in aqueous salt media and to the description of the characteristics of the phase separation in such systems. The prospects for the development of the research into and the possible applications of this new class of polyelectrolytes are discussed.
The bibliography includes 64 references.

CONTENTS

I. Introduction 833
II. Interpolyelectrolyte reactions 834
III. Synthesis of water-soluble non-stoichiometric polyelectrolyte complexes 836
IV. Structure of water-soluble non-stoichiometric polyelectrolyte complexes 841
V. The influence of low-molecular-weight salts on the behaviour of polyelectrolyte complexes in aqueous solutions 848
VI. Prospects for the development of research into and the possible applications of the new class of polyelectrolytes 852

I INTRODUCTION

The increasing interest in the chemistry and physical chemistry of synthetic polyelectrolytes is due to the continuous expansion of their practical applications as highly effective flocculants, structure-forming agents and stabilisers for colloidal dispersions, ion-exchange materials, specific sorbents, biologically active compounds, etc. In addition, with their aid it is sometimes possible to simulate certain important features of the behaviour of biopolymers: enzymes and nucleic acids.

Polyelectrolytes belong to the class of reactive polymers. Among the reactions which they undergo, one of the most interesting is that between cationogenic and anionogenic macromolecules (polymeric acids, polymeric bases, and their salts) in aqueous solutions, leading to the formation of interpolymer salts or polyelectrolyte complexes (PEC), a term which is frequently applied to them. In a certain sense, this reaction has no analogies in the chemistry of low-molecular-weight substances, since the polymeric product (the PEC) is a compound whose stability is due mainly to entropy factors. Cationo- and aniono-genic macromolecules complement each other electrostatically. Therefore the interaction between them is fully analogous in the thermodynamic sense to the interaction between complementary biopolymers responsible for the self-assembly of the majority of biological structures.

As early as the 1930's, the attention of investigators was attracted to the fact that, when aqueous solutions of oppositely charged natural polyelectrolytes, characterised by a relatively low charge density on the macromolecules (for example, gelatines and gum arabic), are mixed, phase separation and the formation of living coacervates take place under certain conditions[1-4]. Subsequently the phase separation conditions were investigated[5-7]. On the other hand, the chemical and physicochemical aspects of the reactions between the macromolecules and particularly the structure of the PEC have not been investigated at the macromolecular level. The coacervates of natural polyelectrolytes still attract the attention of certain biochemists attempting to simulate the phenomena of prebiological evolution[8-10].

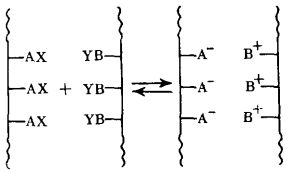
The next stage in the studies on the PEC refers to the 1960's [11-15] when strong polyelectrolytes with a high charge density on the chains became available as a consequence of advances in the synthesis of polymers. The interaction in solutions between electrostatically complementary polyelectrolytes, characterised by a high charge density, leads to the formation of PEC, which are usually precipitated from solution in the form of comparatively little solvated deposits. The ratio of the oppositely charged groups in these compounds is 1:1. Henceforth we shall refer to such PEC as stoichiometric (S-PEC). They are insoluble in any of the known solvents and are capable of limited swelling in water, resembling in some of their properties the well-known cross-linked hydrogels. The interest in the S-PEC is due mainly to the possibility of using them as membranes for the desalination of water[14-15], for haemodialysis[16-18], etc. A fairly large number of publications have been devoted to the formation reactions and properties of S-PEC (see, for example, Refs.19–27), a detailed description of which is outside the framework of our task.

The present review deals with a new field of research which has arisen as a result of the discovery of non-stoichiometric PEC (N-PEC). These interpolymer compounds are also the products of reactions between electrostatically complementary chains. However, in contrast to the S-PEC, when certain conditions are observed, they do not precipitate. Consequently they can be used like the usual soluble polyelectrolytes. At the same time, in contrast to the usual polyelectrolytes, the N-PEC also have a series of unique properties, which, as will be seen from the exposition below, make it possible to isolate them as a special class of water-soluble polymeric compounds.

However, before proceeding to the description of the N-PEC, it is necessary to consider certain general characteristics of interpolyelectrolyte reactions and their products.

II. INTERPOLYELECTROLYTE REACTIONS

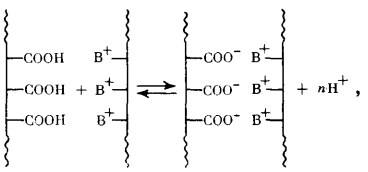
The reaction between polyelectrolytes can be represented schematically as follows:



(I)

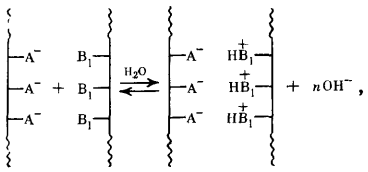
Here -AX- is a unit of a polymeric acid or its salt and -BY- is a unit of the polymeric base or its salt. As a result of the reaction between the units of the macromolecule, salt bonds are produced. The formation of each bond is accompanied by the liberation into the surrounding medium of a pair of low-molecular-weight ions.

Evidently equilibrium (I) can be displaced in one direction or another by altering the activity of the low-molecular-weight reaction product. Accordingly, one of the methods for the investigation of equilibrium (I) is based on the measurement of the activities of the low-molecular-weight ions in the system. This can be done particularly simply when the reaction is accompanied by the liberation of protons or hydroxide ions, which happens when one of the macromolecular reactants is a weak polymeric acid or a weak polymeric base, and the second is a polymeric cation or a polymeric anion respectively:



(Ia)

where B^+ is, for example, a charged amino-group and



(Ib)

where A^- is an anionic group in the unit of the polymer chain and B_1 is, for example, a primary, secondary, or tertiary amino-group. Reactions of types (Ia) and (Ib) can then be investigated by the potentiometric titration method[19-23].

The typical pH profiles of such reactions are illustrated in Fig. 1 The degree of conversion θ represents the fraction of the intermacromolecular salt bonds formed relative to their maximum possible number. An equilibrium value of θ corresponds to each pH. The value of θ can be readily calculated from potentiometric titration data. It is determined as the ratio of the concentrations of the salt bonds (c_s) and the initial concentration of the functional groups of any of the polyelectrolytes (c_0)† provided that the PEC species remain stoichiometric over the entire range of θ.

†Here and henceforth the concentration of the polyelectrolytes will be expressed in terms of the molar concentration of their units and will be designated as follows: basic mol litre^{-1}.

Since the formation of each intermacromolecular salt bond is accompanied by the liberation of a proton [reaction (Ia)] or a hydroxide ion [reaction (Ib)] into the surrounding medium, the following equation can be used to determine c_s and hence also θ:

$$c_c = \theta c_0 = q_{alk}/V + [H^+], \quad (1a)$$

where q_{alk} is the amount of the added titrant (alkali), $[H^+]$ the concentration of protons in solution, V the volume of the reaction mixture, and

$$c_c = \theta c_0 = q_{ac}/V + [OH^-], \quad (1b)$$

where q_{ac} is the amount of added titrant (acid) and $[OH^-]$ the concentration of hydroxide ions in solution. Reactions whose θ–pH profiles have a positive slope correspond to equilibrium (Ia) and those with a negative slope correspond to equilibrium (Ib).

Fig. 1 shows that the profiles of reactions (Ia) and (Ib) are very steep, which is usually characteristic of cooperative transformations. The transformation of a mixture of macromolecules which have not interacted ($\theta = 0$) into the product of the completed reaction ($\theta = 1$) takes place over a fairly narrow pH range. Correspondingly the pH range in which the PEC formed is stable proves to be fairly wide.

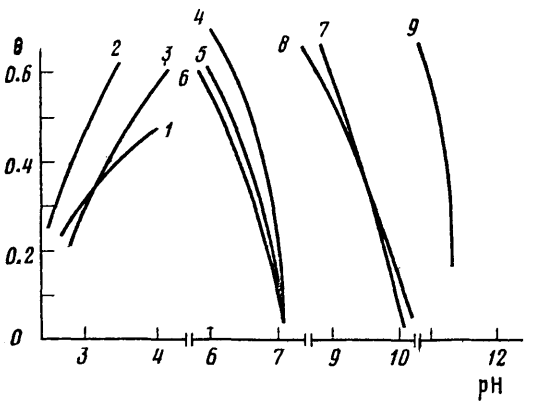
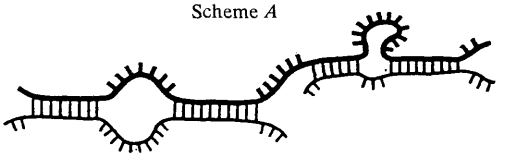


Figure 1. Dependence of the degree of conversion θ on the pH for reactions between polyelectrolytes: *1*) polyacrylic acid (PAA)–poly(dimethylaminoethyl methacrylate) hydrochloride (PDMAEMA.HCl); *2*) poly-L-glutamic acid–PDMAEMA.HCl; *3*) PAA–poly-L-lysine hydrobromide (PL.HBr); *4*) poly-4-vinylpyridine (PVP)–sodium polyphosphate (PP-Na); *5*) PVP–sodium polyethylenesulphonate; *6*) PVP–sodium polystyrenesulphonate; *7*) PDMAEMA–sodium polyacrylate (PA-Na); *8*) PDMAEMA–PP-Na; *9*) PL–PA-Na.[20]

The results of the study of the equilibria of the reactions involving the formation of PEC have led to the idea that the PEC are polymers with a ladder structure in which more or less long sequences of pairs of units, linked via salt bonds, alternate with loops consisting of sequences of disconnected units[22,26,27] (Scheme *A*). The fraction of units incorporated in the ladder sequences increases with θ. The average length of the ladder sequences also increases,

as shown by the results of the analysis of equilibria (Ia) and (Ib) in terms of model *A*:[27]

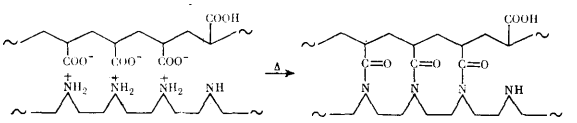
Scheme *A*



The study of the properties of S-PEC, which are products of completed reactions, indicates the presence in the latter of a considerable number of defects, which are represented in Scheme *A* by loops. Because of the presence of the defects, which contain disconnected hydrophilic units of the electrostatically complementary chains, the S-PEC swell appreciably in water. The hydrophobic ladder sections limit the capacity of the S-PEC for swelling in aqueous media. The non-polar interactions of these units with one another lead to the compaction of the PEC species in dilute aqueous solutions[28,29]. The electron micrograph in Fig.2 illustrates typical globular PEC particles formed as a result of the reaction between poly-L-lysine and polyacrylic acid (PAA) in a dilute aqueous solution. Structures of this type were first discovered in 1959.[30] The coiling of the S-PEC species into compact globules is possible by virtue of the marked bending of the two-stranded formations at the sites of the defects (loops).

The presence of defects in the products of the completed reactions can be due to different causes. One of these is the "freezing" of the random intermolecular contacts arising in the early stages of the rapid ionic reaction. After the deposition of the PEC, its subsequent rearrangement, tending to "heal" the defects, probably proceeds very slowly. Thus certain non-equilibrium states are fixed in the system. This is indicated by data obtained in studies[28,29] in which the relaxation of the PEC formed as a result of the neutralisation of strong polymeric acids by strong polymeric bases was observed. On the other hand, if the conditions for the occurrence of non-equilibrium structures are excluded, for example, by employing matrix polymer reactions for the preparation of the PEC, then the resulting PEC can prove to be highly ordered[31-33].

However, in the general case one has to bear in mind also another important factor determining the defectiveness of the PEC: the absence of a steric correspondence between the electrostatically complementary chains. The majority of the PEC described in the literature are products of the interaction of sterically irregular macromolecules. Such PEC are amorphous as regards X-ray diffraction and contain at least 20–30% of pairs of disconnected units, i.e. units incorporated in defects. This is demonstrated convincingly by the results of the study of ion-exchange equilibria with a series of different PEC.[34] Even in the product of the complete reaction between linear polyethyleneimine (PEI) and atactic PAA, whose chains are characterised by a fairly satisfactory steric correspondence, 20% of the units of each type are in the defects. The infrared spectra of the PEC dialysed against water indicate the presence of ~20% of protonated carboxy-groups[35]. On the other hand, the two-stranded ladder sections in such PEC have an extremely ordered structure. This is indicated by the fact that, in the products of the interaction of PAA and PEI in the vitreous state, the intermolecular salt bonds are quantitatively converted into covalent amide bonds at elevated temperatures[35-37]:



(II)

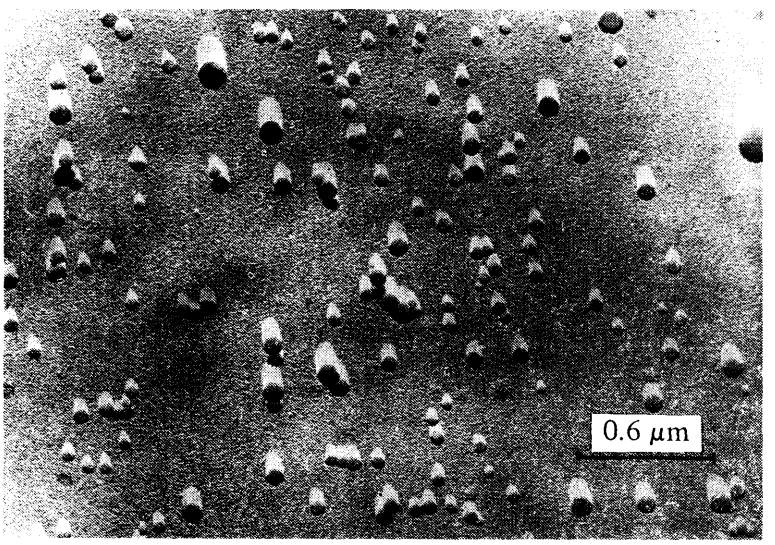
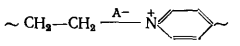


Figure 2. Photomicrograph of particles of the stoichiometric PEC formed as a result of the reaction between equivalent amounts of poly-L-lysine and polyacrylic acid at pH 4.2 and a concentration of polyelectrolytes of 10^{-5} basic M.[29]

The units located in the defects do not enter into this reaction.

The foregoing does not imply that the presence of a considerable number of defects is characteristic of all the PEC obtained by the direct mixing of solutions of electrostatically complementary polyelectrolytes. Crystalline PEC, i.e. low-defect PEC, obtained, for example, from ionene, which is a product of the 1,4-polymerisation of 4-vinylpyridine,

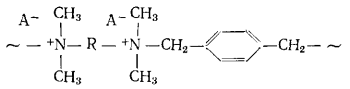


and isotactic PAA [38] and also from ionene and a polyphosphate (PP),[39] have been described in the literature. However, presumably the stereoregularity and the satisfactory steric correspondence of the initial components are essential conditions for the formation of highly-ordered crystalline PEC.

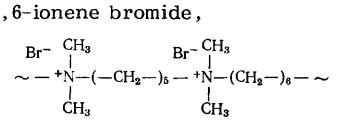
III. SYNTHESIS OF WATER-SOLUBLE NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

In contrast to the S-PEC, the history of the study of which covers a period of approximately 20 years as already mentioned, detailed and systematic studies of the N-PEC began less than 10 years ago. The publications by Tsuchida et al.[40] and Gulyaeva et al.[41] are some of the first in which N-PEC were described. The ability of the N-PEC to dissolve in aqueous media was noted as their main characteristic in the above publications.

Tsuchida et al.[40] were the first to describe in detail the procedures for the preparation of non-stoichiometric water-soluble PEC. They showed that N-PEC are formed as a result of the mixing of aqueous solutions of aromatic ionenes



and sodium polystyrenesulphonate (PSS-Na) taken in non-equivalent proportions. It was observed that the PEC dissolve only when PSS-Na is present in excess relative to ionene. The complete dissolution of the PEC is observed in the presence of a threefold excess of PSS-Na. When excess amounts of ionene are introduced into PSS-Na solutions, a soluble PEC is not formed. In the latter case, insoluble S-PEC is produced and excess ionene remains in solution. These observations led the authors[40] to the conclusion that polymers of the series of ionenes have a special ability to form soluble PEC, which in their view is associated with the localisation of the charged groups in the chain of the main valences of the macromolecules. The authors[40] were unable to obtain water-soluble PEC from PSS-Na and polybenzylvinyltrimethylammonium chloride, i.e. from polyelectrolytes in which the ionogenic groups are localised in the side-substituents. It was soon shown[41], in relation to the reaction between the sodium polyacrylate (PA-Na) and 5,6-ionene bromide,



that aliphatic ionenes are also capable of forming water-soluble N-PEC. The above facts are seemingly consistent with the hypothesis of the exceptional properties of ionenes which, if one follows the reasoning of Tsuchida et al.[40], are due to the steric "accessibility" of the positively charged quaternary nitrogen atoms.

However it was shown later[42–45] that water-soluble N-PEC can be obtained from oppositely charged polyelectrolytes of a wide variety of chemical structures when certain conditions are observed. The examples of the water-soluble N-PEC known at present are presented in Table 1. Evidently N-PEC can be formed by pairs of strong polyelectrolytes, pairs of weak polyelectrolytes, and by mixed pairs. It is also seen that N-PEC can be obtained by the reaction of two electrostatically complementary polyelectrolytes in each of which the charged compounds are localised in the side-substituents and not in the chain of the main valences of the macromolecule, for example, PA-Na–poly(dimethylaminoethyl methacrylate) hydrochloride (PDMAEMA.HCl) or PA-Na–poly-*N*-ethyl-4-vinylpyridinium bromide (PVP.C_2H_5Br). The polyelectrolyte incorporated in the N-PEC in excess can be both negatively and positively charged. It follows from Table 1 that the structural-chemical limitation introduced by Tsuchida[40] is erroneous. As will be shown later, the necessary and sufficient conditions for the formation of soluble N-PEC are not associated directly with the chemical structure of the units of the electrostatically complementary polyelectrolyte components.

Table 1. Non-stoichiometric polyelectrolyte complexes and methods for their preparation[41,42].

LPE	BPE	Examples	Methods of preparation
s. (–)	s. (+)	PP-ionenes	*a'*, *a''*
s. (–)	s. (+)	heparin-ionenes	*a'*, *a''*
s. (–)	s. (+)	PSSA-ionenes	*a'*, *a''*
s. (–)	s. (+)	PSSA-PVP.C_2H_5Br	*a'*, *a''*
s. (–)	w. (+)	PP-PDMAEMA	*a'*, *a''*
w. (–)	s. (+)	PAA-ionenes	*a'*, *a''*, *b'*
w. (–)	s. (+)	PAA-PVP.C_2H_5Br	*a'*, *a''*, *b'*
w. (–)	s. (+)	PMAA-ionenes	*a'*, *a''*, *b'*
w. (–)	s. (+)	PMAA-PVP.C_2H_5Br	*a'*, *a''*, *b'*
w. (–)	w. (+)	PAA-PDMAEMA	*a'*, *a''*, *b'*
w. (–)	w. (+)	PAA-PEI	*a'*, *a''*, *b'*
w. (–)	w. (+)	PMAA-PEI	*a'*, *a''*, *b'*
s. (+)	s. (–)	ionenes-PP	*a'*, *a''*
s. (+)	w. (–)	PVP.C_2H_5Br-PMAA	*a'*, *a''*
w. (+)	s. (–)	PDMAEMA-PP	*a'*, *a''*, *b''*
w. (+)	s. (–)	PDMAEMA-heparin	*a'*, *a''*, *b''*
w. (+)	s. (–)	PDMAEMA-lignosulphonate	*a'*, *a''*, *b''*
w. (+)	w. (–)	PDMAEMA-PAA	*a'*, *a''*, *b''*
w. (+)	w. (–)	PDMAEAA-PMAA	*a'*, *a''*, *b''*

Notation: LPE and BPE are the lyophilising and blocking polyelectrolytes; s.(–), s.(+), and w.(+) are respectively strong and weak polyelectrolytes charged negatively and positively; PMAA = polymethacrylic acid; the notation used for the other polyelectrolytes and for the methods of preparation of the PEC is described in the text.

The data permitting the formulation of one of the necessary conditions for the formation of water-soluble N-PEC were first obtained by Kasaikin et al.[43]. In the synthesis of N-PEC, non-equivalent amounts of the initial polyelectrolyte components are introduced into the reaction. We shall adopt the convention that the overall condition of the reaction system is henceforth characterised by the quantity Z, which represents the ratio of the concentration of the units of the component present in a deficient amount to the concentration of the units of the component present in excess. Kasaikin[43] presents data for the solubilities of

the products of the interpolymer reaction in the PDMAEMA.HCl–sodium polyphosphate (PP-Na) system# as a function of the degree of polymerisation of the initial components P.

It follows from these data that the soluble products are formed only for $\bar{P}_1/\bar{P}_2 \gtrsim 1$. In all cases the reaction conditions correspond to a virtually complete shift of equilibrium (Ib) to the right, i.e. the degree of conversion θ, calculated with respect to the component present in a deficient amount, is close to unity. Consequently the soluble product is an N-PEC with the composition Z. If $\bar{P}_1 < \bar{P}_2$, the reaction product precipitates; analysis of the compositions of the coexisting phases showed that the precipitate is an S-PEC which incorporates the entire deficient polyelectrolyte. Only the superstoichiometric amount of the polyelectrolyte component introduced in excess remains in solution.

A completely analogous situation is observed in the same system with the "reverse" ratio of the PDMAEMA.HCl and PP-Na concentrations with an excess of polyanions instead of polycations. In this system N-PEC is formed only for $\bar{P}_1 > \bar{P}_2$. However, this requirement implies that the polyanions introduced in excess must be longer than the polycations[43].

Turning again to the studies[40,41,44] in which the N-PEC were first described, one should note that the condition $\bar{P}_1 > \bar{P}_2$ was in fact observed, since the N-PEC were obtained when the high-molecular-weight polyanions predominated over the relatively low-molecular-weight polycations (ionenes).

Thus the necessary condition for the formation of the N-PEC, concerning the ratio of the degrees of polymerisation of the electrostatically complementary polyelectrolyte pairs, is $\bar{P}_1 \gtrsim \bar{P}_2$. To facilitate further exposition, we shall now introduce certain new definitions and characteristics. The relatively high-molecular-weight component present in the N-PEC in excess will be referred to as the lyophilising polyelectrolyte (LPE)§. The relatively low-molecular-weight component present in the N-PEC in a deficient amount will be called the blocking polyelectrolyte (BPE)¶.

Thus, by definition, the degree of polymerisation of the LPE ($\bar{P}_{LPE}$) is always greater than or equal to the degree of polymerisation of the BPE ($\bar{P}_{BPE}$). The composition of the N-PEC will be expressed in terms of the ratio of the number of units in the BPE to the number of units in the LPE incorporated in the N-PEC, designated by $\phi = [BPE]/.[LPE]$. Evidently ϕ can vary from 0 to 1. If the PEC is the product of a completed reaction, i.e. corresponds to $\theta \cong 1$ (such PEC will in fact be considered henceforth), the limiting value $\phi = 1$ corresponds to the transformation of the N-PEC into the S-PEC. Naturally $\phi = 0$ corresponds to a solution of the free LPE.

The condition $\bar{P}_1 \gtrsim \bar{P}_2$ formulated above is insufficient for the formation of N-PEC on direct mixing of salt-free dilute aqueous solutions of oppositely charged polyelectrolytes. It is also necessary that the solution in which the reaction is carried out contains a certain amount of a low-molecular-weight electrolyte. This amount may be comparatively small. The required concentration of the 1:1-valent electrolyte, for example NaCl, can vary in the range 0.002–0.12 M, depending on the chemical nature of the polyelectrolytes and their ratio in the system. Generally speaking, the greater the excess of the high-molecular-weight component, i.e. the lower the value of Z, the lower the concentration of the low-molecular-weight salt necessary for the formation of the water-soluble N-PEC (Fig.3).

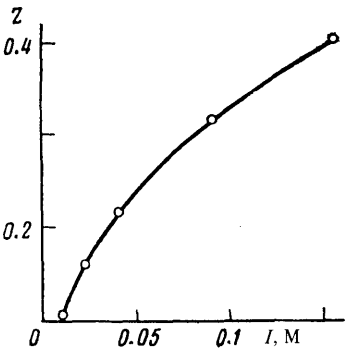


Figure 3. Dependence of the composition of a mixture of polyelectrolytes for which N-PEC dissolves in the sodium polymethacrylate (PMA-Na)–poly-*N*-ethyl-4-vinylpyridinium bromide (PVP.C_2H_5Br) system on the ionic strength of the solution I.[42]

For the complete dissolution of the product of the completed reaction between the BPE and the LPE, it is also necessary that their ratio in the system should not exceed a characteristic value: $Z \leqslant Z_{char}$. The characteristic composition of the N-PEC ($\phi_{char} = Z_{char}$) corresponds to this condition. If $Z > Z_{char}$, then the dissolved N-PEC with the characteristic composition ϕ_{char} and the corresponding amount of the insoluble S-PEC coexist in the reaction system. The value of ϕ_{char} for the majority of the systems studied varies in the range from 0.5 to 0.2 and depends mainly on the chemical nature of the polyelectrolytes constituting the PEC. It is still not altogether clear what determines the value of ϕ_{char}, but it presumably depends to a large extent on the steric correspondence of the units of the BPE and the LPE and also on the degree of hydration of the intermacromolecular salt linkages and the degree of binding of small counterions to the units of the LPE incorporated in excess in the PEC.

We shall now consider the specific procedures for the preparation of N-PEC. A general method for different pairs of polyelectrolytes whereby N-PEC can be synthesised consists in the direct mixing of solutions of fully ionised oppositely charged polyelectrolytes taken in appropriate proportions ($Z \leqslant Z_{char}$) and containing the necessary amounts of a low-molecular-weight salt (composition *a* in Table 1); such mixing can be achieved in two ways.

#Here and henceforth in the designation of the polyelectrolyte systems investigated we shall first indicate the component present in excess.

§In publications in English, for example in the book by Kabanov et al.[47], the term host-polyelectrolyte has also been adopted for LPE.

¶In the original publications[42,43,46,52,55] the BPE has also been called the reference polyelectrolyte and, in publications in English, the "guest-polyelectrolyte".[47]

Procedure *a'* consists in the gradual addition of a solution of the LPE to a solution of the BPE. The polyelectrolyte chosen as the LPE is then initially present in a deficient amount relative to the BPE. According to the above considerations, in this stage the N-PEC is not formed, since the reaction system is characterised by a ratio of the degrees of polymerisation of the reactants unfavourable for the formation of the N-PEC. Instead an insoluble S-PEC is formed and accumulated and the solution of the polyelectrolyte chosen as the BPE is in equilibrium with it. Fig.4*a* presents curves for the turbidimetric titration of a solution of 5,6-ionene bromide (BPE) with a solution of PP-Na (LPE) and for the titration of a solution of PP-Na (BPE) with a solution of PDMAEMA.HCl (LPE). The increase of turbidity with change in the composition of the mixture of polyelectrolytes is linear and corresponds to the accumulation of the insoluble S-PEC. The maximum turbidity corresponds to the equivalent proportions of the polyelectrolytes in the system ($Z = 1$). At the maximum both polyelectrolytes are quantitatively incorporated in the insoluble S-PEC. A further increase of the amount of the high-molecular-weight component chosen as the LPE is accompanied by a gradual, virtually linear decrease of turbidity.

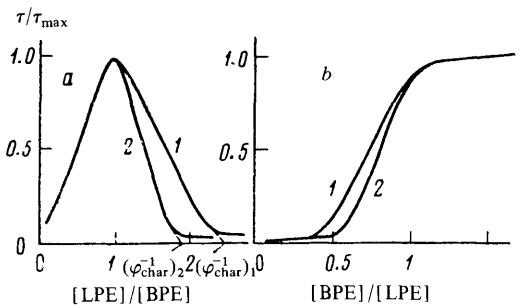


Figure 4. Turbidimetric titration curves: *a*) titration of an aqueous solution of 5,6-ionene bromide (BPE, $\bar{M}_w = 1.4 \times 10^4$) with a solution of PP-Na (LPE, $\bar{M}_w = 6.6 \times 10^4$) at pH 7.0 in 0.01 M NaBr (curve *1*) and of an aqueous solution of PP-Na (BPE, $\bar{M}_w = 1.7 \times 10^4$) with a solution of PDMAEMA.HCl (LPE, $\bar{M}_w = 6.3 \times 10^5$) at pH 4.5 in 0.1 M NaCl (curve *2*); *b*) ditto with the reverse order of mixing of the solutions; τ_{max}—maximum turbidity of the system[47].

Analysis of the composition of the coexisting phases shows that the concentrated phase contains the stoichiometric PEC. Its amount diminishes with increase of the excess of the LPE. The N-PEC accumulates in the dilute solution; its composition remains unaltered up to the complete dissolution of the precipitate and is specified by ϕ_{char}. The reciprocal ϕ^{-1}_{char} in Fig.4*a* corresponds to the intercept which the descending branch of the curve makes on the abscissa axis. Thus the procedure for the preparation of the N-PEC examined above virtually consists in the dissolution of the S-PEC under the influence of the excess of the LPE, i.e. in the transformation of the S-PEC into the N-PEC.

The second procedure (*a''*) leading to the preparation of the N-PEC consists in the addition of a solution of the BPE to that of the LPE. Fig.4*b* presents the corresponding turbidimetric titration curves for the same polyelectrolyte salt as in Fig.4*a*. Evidently the initial section of the curve corresponds to the homogeneous system. This is natural, since, in the given range of compositions of the polyelectrolyte mixtures, the condition $\bar{P}_1 > \bar{P}_2$, necessary for the formation of the soluble N-PEC, is satisfied; the LPE is present in excess at this stage. The system remains homogeneous over the entire range of compositions of the reaction mixture for $Z \leqslant Z_{char}$. Depending on the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$, the composition of the N-PEC can either vary within wide limits or can remain unaltered. The causes of this will be examined at the end of this Section.

A further alteration of the composition of the polyelectrolyte mixture is accompanied by the appearance and accumulation of a deposit of the S-PEC (up to $Z = 1$). In the range $Z_{char} < Z \leqslant 1$, the insoluble S-PEC coexists with the soluble N-PEC having the characteristic composition. Following the attainment of $Z = 1$, both polyelectrolytes are quantitatively incorporated in the particles of the insoluble S-PEC, after which further addition of the BPE no longer leads to such appreciable changes in the state of the system. The excess BPE simply accumulates in the solution. In this range of compositions the formation of the N-PEC is impossible, since we now have $\bar{P}_1 < \bar{P}_2$. In contrast to the previous method, this procedure presupposes the formation of the N-PEC in a homogeneous system and allows for the possibility of varying the composition of the N-PEC over a wide range.

The procedures described above consist in carrying out the reaction between wholly or almost wholly dissociated LPE and BPE taken in considerable proportions. The N-PEC are then formed immediately as products of the completed reactions ($\theta \cong 1$). However, other procedures are also possible whereby the N-PEC can be obtained from weak polyelectrolytes. They are based on the ability of pairs of polyelectrolytes, at least one of which is weak, to form the N-PEC for $\theta \ll 1$, i.e. under conditions where the interpolymer reaction is far from completion. Such N-PEC can be both soluble and insoluble in water. Insoluble S-PEC, formed in acid media by the reaction of PAA and polymethacrylic acid (PMAA) with various polymeric bases, have been described[24,44]. The virtually unionised units of the polymeric acid are incorporated in the N-PEC species in a 2–5-fold excess. It has been suggested that the solubility of these N-PEC is due to the compaction of their species. The compact conformations are stabilised by the hydrogen bonds formed by the excess carboxy groups. Non-polar interactions also play an important role in the stabilisation of these compounds.

Fig.5 presents curves for the potentiometric and turbidimetric titration of the PMAA–PVP.C_2H_5Br system with alkali (NaOH) for $Z = 0.2$. The degrees of neutralisation of the PMAA (α), calculated relative to the entire polymeric acid introduced into the reaction with the polycation, are plotted along the abscissa axis. The reaction product formed on mixing aqueous solutions of the polycation and free PMAA taken in a 5-fold excess was considered as the initial system. This reaction is accompanied by the liberation of protons into the solution [equilibrium (Ia)] and the formation of an insoluble N-PEC. Both polyelectrolytes are quantitatively incorporated in the species of the polymeric complex[45]. However, only ~25% of the units of the polycations functioning as the BPE form salt linkages with the macromolecules of the polymeric acid in the N-PEC formed. If alkali (for example, NaOH) is now added to the colloidal dispersion obtained, the reaction involving the formation of salt linkages between the BPE and the LPE is initially completed. The degree of ionisation of the PMAA then varies in the range between 0 and 0.2; at the same time there is a

slight increase of the pH to ~4, which is accompanied by an increase of the turbidity of the system. For $\alpha = 0.2$, an N-PEC in which virtually all the quaternary nitrogen atoms form salt linkages with an equivalent number of the charged carboxy-groups of the PMAA ($\theta \cong 1$) exists in the system.

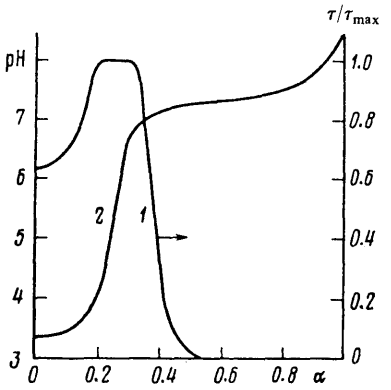


Figure 5. Curves for turbidimetric (curve *1*) and potentiometric (curve *2*) titration of an acid solution of a mixture of polymethacrylic acid (PMAA) (LPE, $\bar{M}_w = 2.6 \times 10^5$) and PVP.$C_2H_5Br$ (BPE, $\bar{M}_w = 2 \times 10^5$) having the composition $Z = 0.2$ with sodium hydroxide; [PVP.C_2H_5Br] $= 2 \times 10^{-3}$ basic M; α = degree of neutralisation[45].

However, such N-PEC is still insoluble in water, because the free PMAA units functioning as the LPE are not yet ionised and they do not therefore exhibit an adequate lyophilising capacity. The subsequent addition of alkali leads to the ionisation of the free carboxy-groups of the PMAA incorporated in excess in the N-PEC. After the attainment of $\alpha \cong 0.5$, the N-PEC dissolves. This follows from the form of the turbidimetric titration curve. On the other hand, the potentiometric titration curve exhibits a sharp rise, showing that the dissolution of the N-PEC is accompanied by a conformational transformation of its species: the compact conformations are converted into the uncoiled conformations characteristic of charged macromolecular chains. The degree of ionisation of the LPE necessary for the dissolution of the N-PEC is higher the smaller the excess of the LPE in the N-PEC species, i.e. the higher the value of ϕ. The dissolution of the N-PEC having the characteristic composition requires virtually complete charging of the units of the LPE chains. The method for the preparation of water-soluble N-PEC described above will henceforth be designated by *b'*.

An analogous procedure can be used also in cases where weak polymeric bases are used as the LPE. An example is provided by the PDMAEMA.HCl–PP-Na system[42]. When solutions of the polymeric components are mixed in an alkaline medium, where the amino-groups of the LPE are uncharged, the N-PEC formed initially is a product of the uncompleted reaction (but this time it is soluble). In the course of the subsequent titration of the reaction mixture with acid (HCl), the degree of completion of the interpolymer reaction θ increases to a value close to unity, but the excess free amino-groups of the LPE are still not protonated and the N-PEC formed in the intermediate titration range is precipitated. However, further addition of the acid leads to the charging of the free amino-groups of the LPE and to the formation of a soluble N-PEC. This method for the preparation of water-soluble N-PEC will be designated by *b''*.

Thus water-soluble N-PEC can be obtained in several ways. The possibility therefore arises of the solution of the fundamentally important problems of whether the water-soluble N-PEC are equilibrium compounds, i.e. whether their state depends on the way in which they have been obtained. In order to answer this question, it is necessary to compare the characteristics of the N-PEC formed by the same pair of polyelectrolytes having a fixed composition but prepared in different ways. Table 2 presents the weight-average molecular weights $\bar{M}_w$, the mean-square radii of inertia $(\bar{R}_g^2)^{1/2}$, the second virial coefficients of the solution A_2 obtained by the light scattering method, and the sedimentation coefficients S. It follows from Table 2 that the above characteristics of each of the N-PEC investigated are almost independent of the method of preparation. Consequently the soluble N-PEC must be regarded as equilibrium macromolecular compounds, which implies, in particular, that the methods widely used to investigate the usual polymer solutions, especially solutions of polyelectrolytes, can be employed for their investigation.

Table 2. Characteristics of the water-soluble non-stoichiometric PEC prepared by different methods[42].

PEC	Method	I, M	pH	$10^{-5}\bar{M}_w$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$	S
PA-Na-5,6-ionene	*a'*	0.025	7.2	3.80	300	0.18	—
ditto	*a''*	0.025	7.2	3.30	300	0.20	—
»	*b'*	0.025	7.2	3.30	260	0.17	—
PDMAEMA.HCl-PP	*a'*	0.100	4.0	7.70	390	2.9	5.8
ditto	*a''*	0.100	4.0	7.70	380	3.3	5.4
»	*b''*	0.100	4.0	7.20	370	2.8	5.5
PP-Na-5,6-ionene	*a'*	0.025	7.0	0.77	—	0.16	—
ditto	*a''*	0.025	7.0	0.77	—	0.15	—
PMA-Na-PVP.C_2H_5Br*	*a'*	0.125	7.5	12.50	420	1.1	—
ditto	*b'*	0.125	7.5	12.50	410	1.3	—
PDMAEMA.HCl-PAA	*a'*	0.100	4.5	5.60	435	8.6	3.2
ditto	*a''*	0.100	4.5	—	—	—	3.3
»	*b''*	0.100	4.5	—	—	—	3.2

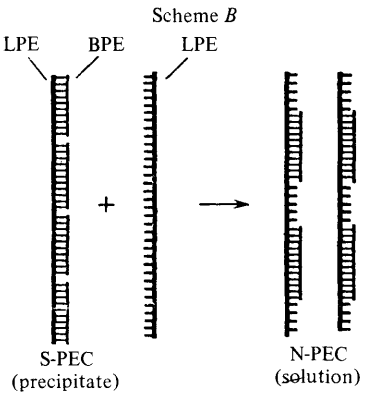
*$\phi = 0.25$; in the remaining cases $\phi = 0.33$.

Remarks: I = ionic strength of the solution; S = sedimentation coefficient (in Svedberg units) determined at a fixed concentration of the N-PEC (0.28 wt.%).

It was already noted above that in the reactions between polyelectrolytes, there is a possibility of the formation of both insoluble S-PEC and soluble N-PEC. Such situations are also observed when an insoluble S-PEC coexists with an N-PEC solution. It is significant that the characteristic composition of the N-PEC (ϕ_{char}) differs considerably from that of the stoichiometric polyelectrolyte. It has also been shown that, when an LPE is added to the S-PEC, the entire PEC gradually dissolves in the form of the N-PEC having

the characteristic composition[41]. In the case where $\bar{P}_{LPE} \gg \bar{P}_{BPE}$, this process can be represented by Scheme *B*.

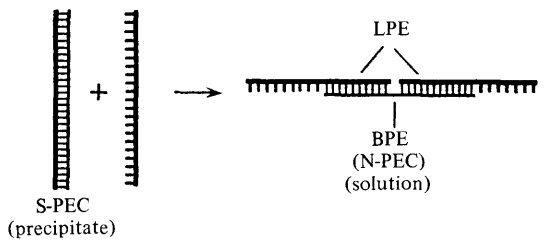
Scheme *B*



It must be supposed that the driving force of the spontaneous formation of the water-soluble N-PEC after the addition of the LPE is the increase of the entropy of the system by virtue of the additional increase of the number of species in solution compared with the number of the LPE molecules introduced. The number of intermolecular salt linkages then remains unaltered.

However, the increase in the number of species in solution is apparently not the only factor determing the conversion of the insoluble S-PEC into the soluble N-PEC. This transformation occurs also when the degrees of polymerisation of the polyelectrolyte components are similar ($\bar{P}_1 \cong \bar{P}_2$), although the number of N-PEC species formed in this situation cannot exceed the number of macromolecules of all of the components added in excess to the system containing the S-PEC. The formation of the water-soluble N-PEC for $\bar{P}_1 \cong \bar{P}_2$ can be represented by Scheme *C*.

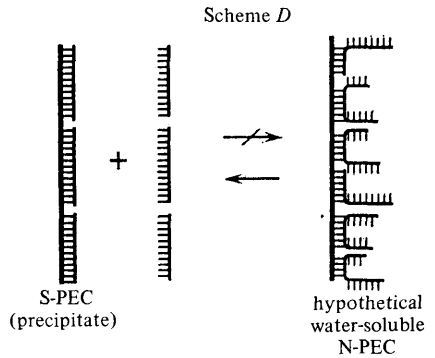
Scheme *C*



The number of interpolymer salt linkages remains unchanged after this transformation, as in the preceding case. However, reaction *C* can still be accompanied by an increase of the entropy of the system due to the transfer of the defects present both in the S-PEC and in the N-PEC from the precipitate to the solution. It was stated above that these defects, not illustrated in Schemes *B* and *C*, consist of loops made up of sequences of disconnected units of the electrostatically complementary chains (see Scheme *A*). The transfer of such loops from the concentrated to the dilute phase can be accompanied by an increase of the entropy of mixing of the system. The latter factor must naturally be taken into account also in considering processes described by Scheme (III). We may note that, for water-soluble N-PEC formed by chains with a similar degree of polymerisation, the concept of the LPE and BPE becomes degenerate. In this case the polyelectrolyte component present in excess actually plays the role of the LPE.

Finally, we shall consider the question why the water-soluble N-PEC are not formed when $\bar{P}_1 < \bar{P}_2$, i.e. why the excess of a polyelectrolyte having relatively short chains cannot lyophilise the oppositely charged long-chain polyelectrolyte. If one takes into account the fact that the PEC species acquires the ability to dissolve in the form of N-PEC only when its composition includes a considerable (at least two-fold) excess of LPE units, then the case under consideration may be reduced to Scheme *D*.

Scheme *D*



Evidently, the formation of the hypothetical N-PEC should result in a considerable decrease in the number of species in solution and the decrease should be greater the lower the degree of their polymerisation. When the total number of intermolecular salt contacts remains unchanged, this should be accompanied by a considerable decrease of the entropy of the system. Consequently process *D* can occur only from right to left, i.e. its occurrence from left to right is thermodynamically prohibited. An illustration of this situation is provided by the solubilities of the PEC and also the data in Fig.4*b*. It follows from Fig.4*b* that the introduction of an excess of the BPE into the reaction system relative to its content in the N-PEC for $\phi = \phi_{char}$ is accompanied by the formation of the S-PEC, which precipitates. After the attainment of the overall system composition $Z = 1$, a further addition of the BPE does not lead to any changes in the state of the insoluble S-PEC formed. The excess BPE simply accumulates in the solution over the precipitate.

Evidently the exact boundary between the polyelectrolyte pairs which are and are not capable of forming water-soluble N-PEC cannot be established exactly by an experimental procedure using only the average degrees of polymerisation of the electrostatically complementary polymeric components. This is due to the finite width of the molecular weight distribution of the fractions employed in the experiment. However, on the basis of the experimental data and their interpretation presented above, one can assume with an adequate degree of approximation that this boundary is in fact close to the ratio $P_1/P_2 = 1$. We may note that in all the examples considered the overall compositions Z were finite. One cannot rule out the possibility that, when a very large excess of even a relatively low-molecular-weight polyelectrolyte is used, it is possible to observe the spontaneous dispersion and peptisation of the PEC. However, the nature of such phenomena must be different and their consideration is outside the scope of our task.

In conclusion of this Section, we shall consider the question of the influence of the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$ on the characteristics of the compositions of the N-PEC formed. For this, it is sufficient to investigate two limiting cases: $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$ and $\bar{P}_{LPE}/\bar{P}_{BPE} \cong 1$.

We shall consider the system PDMAEMA.HCl (LPE)–PA-Na (BPE). In the first of the versions investigated $\bar{P}_{LPE} = 3200$ and $\bar{P}_{BPE} = 150$, i.e. $\bar{P}_{LPE}/\bar{P}_{BPE} = 21 \gg 1$. Fig.6*a* presents sedimentation diagrams for mixtures of the above polyelectrolytes in the composition range $0.13 < Z < 0.5$ and also for free LPE. Evidently the peaks on the sedimentation

diagrams are symmetrical and fairly narrow, which indicates the inhomogeneity of the species of the water-soluble N-PEC as regards composition. The sedimentation coefficient S of the N-PEC decreases appreciably with decrease of the relative content of the BPE in the polymeric complex, i.e. as ϕ diminishes. When ϕ becomes sufficiently small ($\phi < 0.1$), the sedimentation coefficients of the N-PEC and LPE hardly differ. Thus, in systems where $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$, the composition of the water-soluble N-PEC can be varied within fairly wide limits. The composition of the N-PEC then agrees with the overall composition of the mixture of polyelectrolytes, i.e. it can be readily specified in the experiments. The range of variation of the composition of the water-soluble N-PEC is determined by the inequality $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi < \phi_{char}$.

In the second version $\bar{P}_{LPE} = 3200$ and $\bar{P}_{BPE} = 3500$ in the same system, i.e. $\bar{P}_{LPE}/\bar{P}_{BPE} \approx 1$. Fig.6*b* presents the corresponding sedimentation diagrams. Evidently the water-soluble N-PEC with the compoistion $\phi = 0.5$, which is the characteristic composition, is sedimented as an individual compound. The sedimentation diagrams show only a single peak whose sedimentation coefficient is significantly higher than the sedimentation coefficients of each of the initial components. A further enrichment of the system in PDMAEMA.HCl (LPE) leads only to its accumulation in the solution in a free state. This is evident from the appearance of a second peak on the sedimentation diagram, which corresponds to free PDMAEMA.HCl. Some decrease of the sedimentation coefficients of the excess polyelectrolyte with increase of its concentration in solution as well as the decrease of the sedimentation coefficient of the N-PEC are due to the increase of the viscosity of the medium. The area of the slowly sedimenting PDMAEMA.HCl peak steadily increases with increased content of this component in the system, i.e. with decrease of Z. Thus, in systems made up of polyelectrolytes having similar degrees of polymerisation, there is a possibility of the formation of only the N-PEC having the characteristic compositions ϕ_{char}. Variation of the overall system composition Z leads in this case to the appearance and accumulation in solution of an excess of the LPE which coexists with the N-PEC having the characteristic composition.

The behaviour, described above, for mixtures of oppositely charged polyelectrolytes having different ratios of degrees of polymerisation, is characteristic of an extremely wide range of polyelectrolyte pairs[43]. Thus one may conclude that, when $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi_{char}$, the range of variation of the composition of the water-soluble N-PEC is determined by the inequality $\bar{P}_{BPE}/\bar{P}_{LPE} < \phi < \phi_{char}$. Evidently the composition of the species of the water-soluble N-PEC varies discretely with the overall mixture composition in the above range of ϕ by the amount $\bar{P}_{BPE}/\bar{P}_{LPE}$ or its multiple. On the other hand, if $1 \geq \bar{P}_{BPE}/\bar{P}_{LPE} > \phi_{char}$, then N-PEC with the characteristic composition only is always formed regardless of the overall mixture composition.

The above data on the methods of preparation of water-soluble N-PEC and the compositions of these macromolecular compounds are necessary for the correct choice of conditions in which their structures and properties can be usefully investigated.

IV. STRUCTURE OF WATER-SOLUBLE NON-STOICHIOMETRIC POLYELECTROLYTE COMPLEXES

In the first place we shall consider data obtained by light scattering[46,47]. We may note that solutions containing a single macromolecular component, namely N-PEC, have always been investigated. As stated above, in order to achieve this, the compositions of the corresponding polyelectrolyte mixture must satisfy the condition $\bar{P}_{BPE}/\bar{P}_{LPE} < Z < \phi_{char}$. The sedimentation diagrams for such mixtures are characterised by the presence of a single peak corresponding to the N-PEC. As a rule, light scattering measurements have been carried out in aqueous salt media (concentration of the low-molecular salt not less than 0.1 M) in order to suppress the polyelectrolyte effect. In order to be able to reduce the analysis of the experimental results to a canonical consideration of two-component polymer–solvent systems, in each series of experiments the activity of the low-molecular-weight salt in solutions of the N-PEC at different concentrations was kept constant. This was achieved by dialysing N-PEC in solution at different experimental concentrations against the same aqueous salt solution. The increment in the refractive index $(\partial n/\partial c)_I$ at an ionic strength I was measured making sure that the same requirements were satisfied[48].

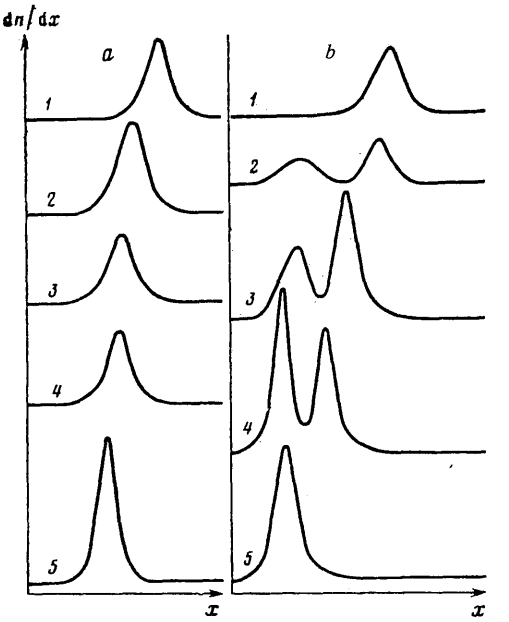


Figure 6. Sedimentation diagrams for mixtures of polyelectrolytes: *a*) PDMAEMA.HCl (LPE, $\bar{P} = 3.2 \times 10^3$) and PA-Na (BPE, $\bar{P} = 1.5 \times 10^2$) with different compositions Z [*1*) 0.5; *2*) 0.33; *3*) 0.2; *4*) 0.13; *5*) 0]; concentration of solutions 0.35 wt.%; time 100 min for a rate of rotation of rotor of 5600 min^{-1}; *b*) PDMAEMA.HCl (LPE, $\bar{P} = 3.2 \times 10^3$) and PA-Na (BPE, $P = 3.5 \times 10^3$) with different compositions Z [*1*) 0.4; *2*) 0.33; *3*) 0.2; *4*) 0.13; *5*) 0]; concentration of solutions 0.28 wt.%; time 70 min for a rate of spinning of 56000 min^{-1}. All the experiments were performed at pH 5.0 in 0.1 M NaCl at 20 °C.[43]

Fig.7 presents typical Zimm diagrams for N-PEC solutions obtained in the PDMAEMA.HCl–PP-Na systems for different ratios of the polyelectrolyte components. Evidently the double extrapolation plots do indeed have the form characteristic of normal polymer solutions. The relations between $(Kc/R_\theta)_\theta$ and c and between $(Kc/R_\theta)_c$ and $\sin^2(\theta/2)$ are

linear, which indicates the absence of polyelectrolyte swelling and dissociation of the N-PEC species into the initial components when the solutions are diluted.

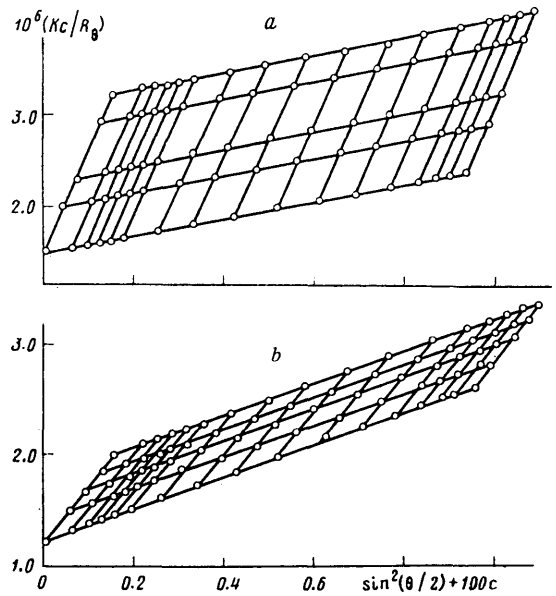


Figure 7. Zimm diagrams for solutions of the PDMAEMA.HCl ($\bar{M}_w = 6.3 \times 10^5$)–PP ($\bar{M}_w = 1.7 \times 10^4$) N-PEC at pH 4.0 in 0.1 M NaCl for different compositions ϕ: *a*) 0.13; *b*) 0.33.[46]

Table 3 presents the weight-average molecular weights $\bar{M}_w$ of a series of N-PEC having a fixed composition ϕ measured by the light scattering method. For comparison, the Table also includes the calculated molecular weights. In the calculation it was assumed that the N-PEC species have homogeneous compositions and that each contains only one LPE macromolecule and that the number of BPE macromolecules corresponds to the composition ϕ. Account was taken also of the fact that the formation of a single salt linkage between the LPE and BPE units is accompanied by the liberation of a pair of small ions present in solutions of the initial component as counterions. The degree of conversion θ relative to the BPE in the reaction involving the formation of the N-PEC was assumed to be unity. Next, assuming that the polyelectrolytes are monodisperse (relatively narrow LPE and BPE fractions were used by Kharenko et al.[46]) and that their true molecular weights are equal to the weight-average values listed in Table 3, we obtained the calculated M_{calc} from the formulae

$$M_{calc} = \bar{P}_{LPE}\bar{M}_{un}, \qquad (2)$$

where $\bar{M}_{un}$ is the average molecular weight of a unit of the N-PEC species, and

$$\bar{M}_{un} = \bar{M}_{(LPE)} + \varphi(M_{(BPE)} - M), \qquad (3)$$

where M is the molecular weight of the low-molecular-weight salt liberated on dissolution as a result of reaction (I). Table 3 shows that the measured values of $\bar{M}_w$ agree satisfactorily with those calculated by Eqns.(2) and (3), which convincingly demonstrate that the composition of each species of the N-PEC investigated does indeed incorporate in this instance a single LPE macromolecule and the corresponding number of BPE macromolecules ($\bar{n}_{BPE}$):

$$\bar{n}_{BPE} = \varphi(\bar{P}_{LPE}/\bar{P}_{BPE}). \qquad (4)$$

It will be shown below that the maintenance of specific conditions is necessary for the formation of such unassociated N-PEC. The results presented in Table 3 again confirm the conclusion that the N-PEC can be regarded as individual macromolecular compounds characterised by their specific molecular weights. It is seen from a comparison of the radii of inertia $(\bar{R}_g^2)^{1/2}$ for the N-PEC and the LPE that the dimensions of the N-PEC species are appreciably smaller than those of the charged chains of the corresponding LPE.

Table 3. Characteristics of the individual polyelectrolytes and the N-PEC formed from them and having the composition $\phi = 0.33$.[46]

(N-PEC)	$10^{-5}\bar{M}_w$ (LPE)	$10^{-5}\bar{M}_w$ (BPE)	pH	I, M	$10^{-5}\bar{M}_w$ N-PEC expt.	$10^{-5}\bar{M}_w$ N-PEC calc.	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 A_2$
PDMAEMA.HCl-PP	6.3	0.17	4.0	0.100	6.7	6.8	350 (520)	2.9 (8.2)
PDMAEMA.HCl-PAA	5.3	0.14	5.0	0.100	5.6	5.6	435 (485)	8.6 (9.4)
PP-Na-5,6-ionene	0.66	0.14	7.0	0.025	0.66	0.85	—	17 (143)

Remarks: The values in brackets refer to the LPE in the LPE–BPE systems.

It is also seen that the formation of the N-PEC is accompanied by a decrease of the second virial coefficient of the solution A_2. The causes of these changes will be examined below. Here we shall only note that the relative changes in the above parameters on formation of the N-PEC are not the same for different pairs of polyelectrolytes even if the polyelectrolyte complexes have the same composition expressed in terms of ϕ. It may be that this is associated with the characteristics of the structures of the initial polyelectrolyte, in particular, with the disposition of the ionogenic groups relative to the main chain and also with the ratio of the hydrophilic and hydrophobic groups in the units of the interacting polyelectrolyte components. The degree of the mutual steric correspondence of the polyions forming the N-PEC can apparently also play a definite role. These questions have not as yet been adequately investigated.

We shall now consider how the macromolecular parameters of the N-PEC in aqueous solution behave as a function of ϕ. Table 4 presents the results of a light-scattering study of N-PEC solutions obtained in the PDMAEMA.HCl—PP-Na system. Evidently, when the composition of the polyelectrolyte complexes ϕ is varied within a fairly wide range (from 0.5 to 0.067), their weight-average molecular weight hardly changes and is identical, within the limits of the error of the measurements, with the values calculated from Eqns.(2) and (3). Over the entire range of compositions, each PEC species contains a single LPE chain. The average number of BPE chains in each species, calculated from Eqn.(4), decreases from 10 to 1. Thus each N-PEC species, under conditions where it contains only one LPE chain, can be reasonably regarded as a kind of individual complex macromolecule whose composition with respect to the polyelectrolyte components can be readily varied within certain limits having specified their initial ratio Z. Clearly the constancy of the experimental molecular weights and the

slight variation of the calculated molecular weights, under the conditions of a 10-fold decrease of the population of the LPE chains by BPE chains is due to the compensation effect caused by the liberation of counterions into the solution as a result of the formation of the PEC.

Table 4. The influence of the composition of the N-PEC in the PDMAEMA.HCl ($\bar{M}_w = 6.3 \times 10^{-5}$)–PP-Na ($\bar{M}_w = 1.7 \times 10^{-4}$) system on its molecular characteristics (pH 4.0 in 0.1 M NaCl at 20 °C).[46]

φ	$\partial n/\partial c$, dl g^{-1}	$10^{-5}\,\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$(\overline{R_g^2})^{1/2}_z$, Å	$10^4 \cdot A_2$	S
		expt.	calc.				
0	0.161	6.3	—	—	510	8.2	2.5
0.07	0.158	7.15	6.4	1.4	480	6.5	2.7
0.10	0.158	6.9	6.4	2.0	440	5.9	2.8
0.13	0.158	7.35	6.5	2.3	430	5.2	—
0.20	0.158	6.75	6.6	3.9	400	4.9	3.7
0.33	0.154	6.7	6.8	6.5	350	2.9	6.0
0.50	0.156	7.0	7.0	10	270	1.1	5.9

Notation: $\bar{n}_{BPE}$ = average number of macromolecules in the N-PEC species ($\bar{n}_{LPE} = 1$); S = sedimentation coefficient (in Svedberg units) determined for [N-PEC] = [PDMAEMA.HCl] = 0.35 wt.%.

The mean square radius of inertia $(\overline{R_g^2})^{1/2}$ of the N-PEC is more sensitive to changes in composition than the molecular weight. In particular, $(\overline{R_g^2})^{1/2}$ of a complex macromolecule having the composition $\phi = 0.5$ is almost a factor of two smaller than the $(\overline{R_g^2})^{1/2}$ of the macromolecule of the free LPE (Table 4). The dependence of $(\overline{R_g^2})^{1/2}$ of the N-PEC macromolecules on ϕ, based on the data in Table 4, is illustrated in Fig.8*a*. Evidently their average size decreases monotonically with decrease of the population of the LPE chains by the BPE chains, approaching the average size of the statistical coil of the free LPE in the same solvent. The results on the measurement of the radius of inertia of the N-PEC macromolecule as a function of composition are important for the justification of the general scheme for the structure of the N-PEC species assuming the existence of sufficiently long two-stranded ladder sections. This scheme was assumed above *a priori* on the basis of indirect data concerning the structure of the S-PEC in the solid phase already mentioned. It can now be shown that the adopted fundamental motif of the ladder-like relative distribution of the chains constituting the PEC has in fact no alternative.

Indeed Table 4 shows that the values of $(\overline{R_g^2})^{1/2}$ for the N-PEC macromolecules with composition $\phi = 0.067$ and for the statistical coil of the free LPE differ by only 5–6%. At the same time, on average each 15th unit of the LPE chain of the N-PEC species having the composition $\phi = 0.067$ is involved in the formation of a salt linkage with a unit of the BPE chain: for $\theta \cong 1$, each LPE chain with a length equivalent to ~3000 units is linked to a BPE chain with a length equivalent to ~170 units. If it is assumed that the two chains are randomly intertwined, then, on passing from the free LPE to the N-PEC, one would have to expect a much greater relative decrease of the radius of inertia, which follows, for example, from calculations by the Monte Carlo method of the change in the average dimensions of a model chain on random formation of irreversible intramolecular cross-links[49]. In particular, it has been shown that, even for a Gaussian chain comprising 100 segments and existing under θ-conditions, the relative decrease of the radius of inertia accompanying the formation of on average five fixed cross-links should be ~35%. Naturally, in the case of the N-PEC one is dealing with the formation of reversible salt linkages within its species. However, if the statistical weight of the randomly formed cross-links in the N-PEC structure had been considerable, the experimentally observed relative change in the average dimensions of the macromolecular coil on passing from the free LPE to the N-PEC would have been significantly greater.

Consequently, in the water-soluble N-PEC form the contour line of the fragment of the LPE chain is close to the contour line of the BPE chain interacting with it. In other

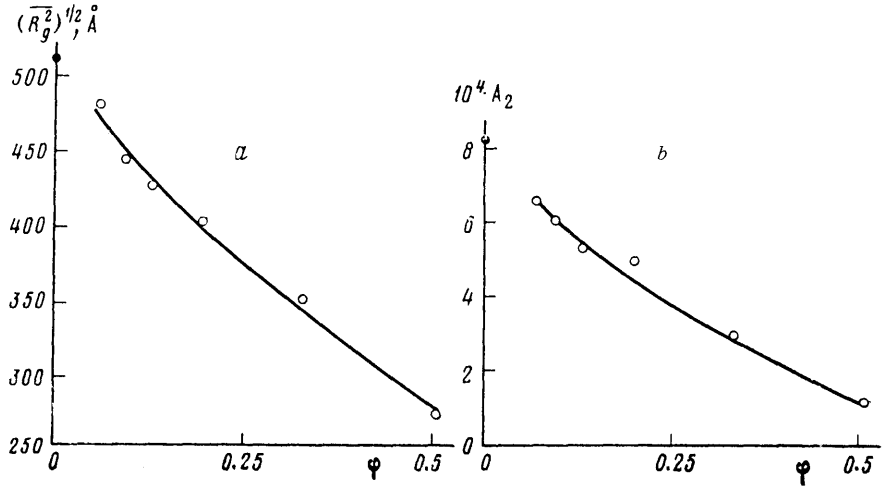
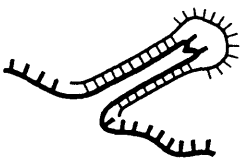


Figure 8. Dependence of the particle size $(\overline{R_g^2})^{1/2}$ (*a*) and of the second virial coefficient A_2 (*b*) for solutions of the PDMAEMA.HCl–PP N-PEC on the composition of the N-PEC (ϕ); for conditions, see caption to Fig.7.[46]

words, a structure in which both interacting chains are in the main distributed parallel to one another in all probability predominates in the N-PEC. At the same time, in the course of thermal movement, the BPE chains can in general migrate from one LPE section to another and different N-PEC macromolecules in solution can even exchange their constituent polyelectrolyte components†.

The two-stranded sections of the PEC species do not necessarily have the form of extended rods. On the other hand, by virtue of their increased hydrophobic properties, they should tend to fold at the sites of the "intraladder" loop-shaped defects already mentioned, forming drop-like clusters, as shown in Scheme *E*.

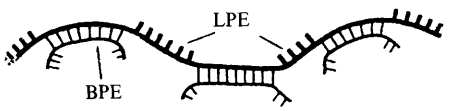
Scheme *E*



The conformation of the complex macromolecule of the water-soluble N-PEC illustrated in this Scheme appears probable also from general thermodynamic considerations. Conformations of this type for fixed values of ϕ and θ apparently correspond to the minimum free energy (maximum entropy), since they contain long sections of free LPE. By virtue of the reversibility of the formation reaction of the N-PEC, the system can "find" the optimum set of conformations by the method of "trial and error".

With increase of ϕ, i.e. with increase of the number of BPE chains incorporated in the N-PEC molecule, the number of two-stranded ladder sections in this molecule naturally also increases, as shown in Scheme *F*.

Scheme *F*

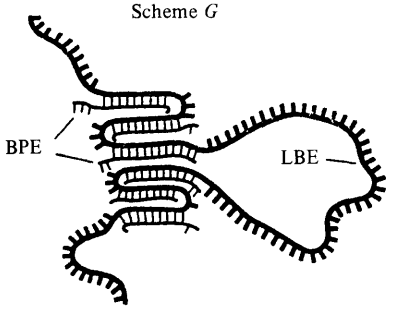


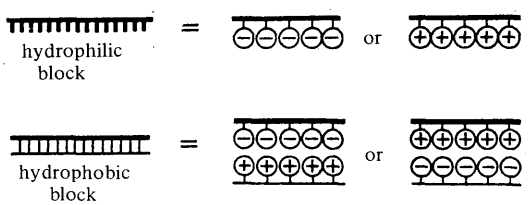
Each section of this kind constitutes a set of cooperatively interacting oppositely charged chain units. It exhibits an enhanced rigidity and relatively weak hydrophilic properties (i.e. relatively pronounced hydrophobic properties). This is why the N-PEC "overloaded" with the BPE for $\phi > \phi_{char}$ lose their solubility in water. The S-PEC are insoluble in water for the same reason. On the other hand, the BPE-free LPE sections in the N-PEC macromolecule are relatively flexible and hydrophilic. Consequently the N-PEC molecule can be regarded as a linear sequence of fairly long hydrophobic and hydrophilic blocks. In other words, the N-PEC constitutes a kind of block-copolymer. The hydrophilic blocks are carriers of properties typical for the usual linear polyelectrolytes. Water behaves as a good solvent in relation to one-stranded polyelectrolyte sequences and as a poor solvent in relation to two-stranded hydrophobic sequences. Consequently the hydrophobic blocks of the N-PEC macromolecules in an aqueous solution should collect together, i.e. should become segregated as a result of non-polar interactions.

†The question of the intramolecular and intermolecular dynamics of the PEC is of considerable interest and merits special study. Some primary information about this problem can be found in Kabanov's paper[21].

In fairly dilute solutions such segregation is intramolecular, which happens, in particular, in the systems presented in Table 4. The progressive decrease of the average dimensions, i.e. of the quantity $(\overline{R}_g^2)^{1/2}$, for complex N-PEC macromolecules as they become enriched in the BPE chains can serve as a quantitative measure of the intramolecular segregation. Scheme *G*, below, illustrates the intramolecular segregation of the hydrophobic blocks in water-soluble N-PEC,

Scheme *G*





A change in the composition of complex N-PEC macromolecules is also accompanied by a change in the thermodynamic characteristics of their solutions. It follows from Table 4 that the second virial coefficient of the solution A_2 increases with decrease of ϕ, i.e. with decrease of the fraction of LPE units incorporated in the hydrophobic blocks. With decrease of ϕ, the quantity A_2 tends to the value characteristic of the solution of the free LPE (Fig. 8*b*). The latter shows that the electrostatic repulsion between LPE units having like charges and forming one-stranded hydrophilic blocks makes the main contribution to the formation of the excluded volume in complex N-PEC macromolecules. According to the Donnan–Guggenheim theory[50], the contribution of the electrostatic repulsion of the polyion units to the overall second virial coefficient can be expressed as follows:

$$A_{2el} = 10^3 z^2/4M^2 I \ , \qquad (5)$$

where z is the effective charge of the polyion, M its molecular weight, and I the concentration of the low-molecular-weight (1:1) electrolyte. An important property of the parameter $A_{2,el}$ of an ordinary polyelectrolyte is its proportionality to the square of the degree of ionisation of the corresponding polyion. Evidently, for the N-PEC considered, this parameter can be varied within wide limits by altering the composition of the complex macromolecule ϕ. The effective charge on the N-PEC macromolecules in the pH range corresponding to the complete ionisation of the LPE units depends on the composition ϕ in the following manner:

$$z/M = \gamma(1-\varphi)/M_0 \ , \qquad (6)$$

where M_0 is the mass of the unit of the polyion and γ the degree of binding of the low-molecular-weight counterions. Thus the parameter $A_{2,el}$ should be proportional to the quantity $(1 - \phi)^2$ for a solution of N-PEC block macromolecules, in which the hydrophobic ladder blocks are combined into a system of compact intramolecular clusters and the

charged hydrophilic blocks are on the periphery of the species and are responsible for the solubility of the N-PEC. The dependence of A_2 on $(1 - \phi)^2$ is plotted in Fig.9 on the basis of the data in Table 4. It is evidently linear. The parameter A_2 tends to the value for the solution of the free LPE as ϕ diminishes. For $\phi \to \phi_{char} = 0.56$, the quantity A_2 tends to zero. The data presented convincingly confirm the applicability of Scheme *G* to the description of the behaviour of water-soluble N-PEC.

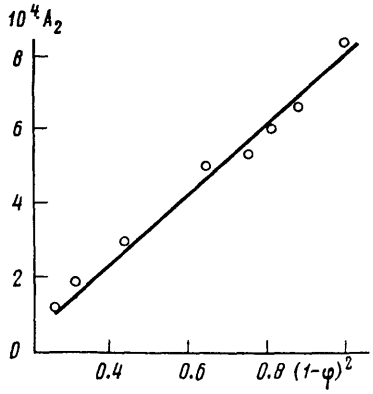


Figure 9. Dependence of the second virial coefficient A_2 for solutions of the PDMAEMA.HCl–PP N-PEC on $(1 - \phi)^2$; for conditions, see caption to Fig.7.[47]

Table 5. The influence of the composition of the PDMAEMA.HCl ($\bar{M}_w = 6.3 \times 10^5$)–PA-Na ($\bar{M}_w = 1.4 \times 10^4$) N-PEC on its molecular characteristics (pH 4.5 in 0.1 M NaCl at 20 °C).[46]

φ	$10^{-5}\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$	S
	expt.	calc.				
0	5.3	—	—	485	9.4	2.0
0.125	5.5	5.4	2.1	475	9.5	2.1
0.20	6.0	5.5	3.4	460	9.0	2.3
0.33	5.6	5.6	5.6	435	8.6	2.6
0.50	5.6	5.8	8.5	400	7.6	3.3

Notation: see Table 4.

The dependence of the sedimentation coefficient *S* on the composition of the N-PEC macromolecule for a fixed concentration of the solutions is also in good agreement with the ideas developed above (Table 4). The coefficient *S* steadily decreases with decrease of ϕ, approaching the value of *S* for the solution of free LPE. It is evident that, since the molecular weight of the N-PEC depends little on its composition ϕ, the main factor determining the behaviour of *S* is the average size of the sedimenting particles, which increases with decrease of ϕ as a consequence of the increased degree of swelling of the particles caused by the mutual electrostatic repulsion of the excess positively charged LPE units in the complex macromolecules.

Scheme *G*, describing the structure of the water-soluble N-PEC, is fairly general. It is apparently valid for a wide range of N-PEC with different chemical compositions, provided that they are products of completed interpolymer reactions, i.e. for $\theta \cong 1$. Tables 5 and 6 present the characteristics of two other varieties of the water-soluble N-PEC measured by the light-scattering and high-speed sedimentation methods. The dependences of $(\bar{R}_g^2)^{1/2}$, A_2, and *S* on ϕ obtained are also fully consistent with the ideas described above.

Table 6. The influence of the composition of water-soluble N-PEC formed from PP-Na ($\bar{M}_w = 6.6 \times 10^4$) and 5,6-ionene bromide ($M_w = 1.4 \times 10^4$) on their molecular characteristics (pH 7.0 in 0.025 M NaBr at 20 °C).[46]

φ	$10^{-4}\bar{M}_w$ (N-PEC)		$\bar{n}_{BPE}$	$10^3 \cdot A_2$	S
	expt.	calc.			
0	6.6	—	—	14.3	2.2
0.125	6.4	7.3	1.2	4.8	2.5
0.20	6.2	7.8	1.9	2.2	2.7
0.33	6.6	8.5	3.1	1.7	3.4

Notation; see Table 4.

The next important problem is that of the influence of the molecular weights of the LPE and the BPE on the macromolecular characteristics of the water-soluble N-PEC. Table 7 presents the values of $\bar{M}_w$, $(\bar{R}_g^2)^{1/2}$, and A_2 measured by the light-scattering method for the PDMAEMA.HCl–PP-Na N-PEC having the constant composition $\phi = 0.33$. The condition $\bar{P}_{LPE}/\bar{P}_{BPE} \gg 1$ holds for the entire series of systems. The systems differ from one another only by the molecular weights of the initial polyelectrolyte components. Table 7 shows that, when the ratio $\bar{P}_{LPE}/\bar{P}_{BPE}$ is varied within wide limits (from 5 to 20) by varying the values of both $\bar{P}_{LPE}$ and $\bar{P}_{BPE}$, only one LPE macromolecule is incorporated in the N-PEC species. In other words, in this case too the N-PEC species can be regarded as individual complex macromolecules in the dilute solution at fixed concentrations of the components and ionic strengths over the entire experimental range of molecular weights.

Table 7. The influence of the molecular weights of the LPE and the BPE on the molecular characteristics of the PDMAEMA.HCl–PP-Na N-PEC ($\phi = 0.33$; pH 4.0 in 0.1 M NaCl at 20 °C).[46]

$10^{-5}\bar{M}_w$ (PDMAEMA.HCl)	$10^{-4}\bar{M}_w$ (PP-Na)	$\bar{P}_1/\bar{P}_2$	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$	$(\bar{R}_g^2)^{1/2}$, Å	$10^4 \cdot A_2$
1.64	1.7	5.1	1.9	1.7	—	2.9
6.3	1.7	19.5	6.7	6.4	350	2.9
6.3	5.7	5.8	7.3	1.9	380	2.7
6.3	6.6	5.0	7.2	1.5	370	2.8

Notation: $\bar{n}$ is the average number of macromolecules in the N-PEC species; the values for PP are indicated, those for PDMAEMA.HCl being unity.

It is significant that the average dimensions of the N-PEC macromolecules and the second virial coefficients of their solutions with the specified values of $\bar{P}_{LPE}$ and ϕ are almost independent of $\bar{P}_{BPE}$. This agrees with ideas concerning

the structure of the complex macromolecules summarised in Scheme *G*. The segregation of the hydrophobic block in these macromolecules is again intramolecular. However, in other cases the change in the hydrophilic–hydrophobic balance in the N-PEC macromolecules with increase of ϕ and hence of the number of hydrophobic blocks can naturally lead also to their intermolecular segregation, i.e. to the formation of N-PEC species containing more than one LPE chain. Such species must be regarded as associated and consisting of individual N-PEC macromolecules.

At the beginning of this Section (Table 4) it was shown, in particular, that solutions of the N-PEC obtained from PDMAEMA.HCl and PP-Na with the composition $\phi \leqslant 0.5$ contain individual complex PEC macromolecules under the chosen conditions. However, when a comparatively small additional amount of the BPE, which is insufficient to cause phase separation in the system, is added to such a solution, the situation changes sharply. This is expressed primarily by a change in the Zimm diagram which assumes a form characteristic of solutions containing associated macromolecules (Fig.10). The double extrapolation plot shows that such associated species are entirely stable on dilution. The N-PEC species with the composition $\phi = 0.56$ has $\bar{M}_w = 2.8 \times 10^6$ according to light scattering data, which exceeds by a factor of four the $\bar{M}_w$ for the individual complex macromolecule with the composition $\phi = 0.5$. Consequently each such N-PEC species actually consists on average of four N-PEC macromolecules with the same composition ϕ.

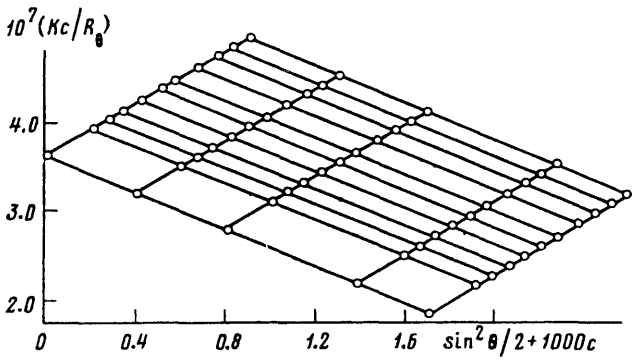
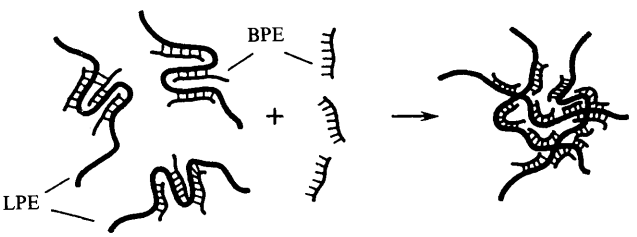


Figure 10. Zimm diagram for a solution of the PDMAEMA.HCl–PP N-PEC having the composition $\phi = 0.56$ at pH 4.0 in 0.01 M NaCl at 20 °C; for the values of $\bar{M}_w$, see Fig.7.[52]

The association phenomena can be represented by Scheme *H*.

Scheme *H*



The formation of the associated species is accompanied by a sharp decrease of the second virial coefficient A_2 and its becoming negative ($A_2 = -4.5 \times 10^{-5}$). The species comprising associated N-PEC macromolecules with $\phi = 0.56$ is extremely compact and its average size $[(\bar{R}_g^2)^{1/2} = 270$ Å] is virtually identical with the average size of the N-PEC macromolecule of similar composition ($\phi = 0.5$). The behaviour described is characteristic of soluble N-PEC, which do not exhibit a great tendency towards association and give rise to associated species only in the vicinity of characteristic compositions defining their solubility limit. The association phenomena in solutions of such N-PEC resemble the pre-critical phenomena in solutions of ordinary high-molecular-weight compounds, which occur within narrow ranges of conditions near the phase separation points[51].

However, there exists an extensive group of soluble N-PEC which tend to form associated species over an extremely wide range of compositions[52]. In particular, such N-PEC include polyelectrolyte complexes formed by PA-Na and ionenes, for example, by PA-Na and 5,6-ionene bromide. Table 8 presents the characteristics of these N-PEC with the constant composition $\phi = 0.33$, which are formed by PA-Na fractions of different molecular weights. Knowing the molecular weights of the initial polyelectrolyte components and the N-PEC species, the average number of the LPE and BPE chains incorporated in the N-PEC species can be calculated with the aid of the procedures described above. Table 8 shows that, regardless of the molecular weight of the LPE, which was varied by more than an order of magnitude, the N-PEC associated species, formed under the experimental conditions, each incorporate three PA-Na macromolecules. The number of 5,6-ionene macromolecules per associated species corresponds to the composition $\phi = 0.33$ and increases in proportion to the molecular weight of the LPE. The second virial coefficient of the solution then remains virtually constant, while the size of the N-PEC species increases with increase of their mass. This shows that the structure of the species of the polyelectrolyte complex does not undergo qualitative changes with increased length of the LPE chains. Thus each N-PEC species in the systems described can be formally regarded as an associated species formed by three individual complex N-PEC macromolecules. The structure of such an associated species is represented on the right-hand side of Scheme *H*.

Table 8. The influence of the molecular weight of PA-Na (LPE) on the molecular characteristics of the PA-Na–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC ($\phi = 0.33$; pH 7.2 in 0.025 M NaBr at 20 °C; $n_{LPE} = 3$ [52]).

$10^{-4}\,\bar{M}_w$ (PA-Na)	$10^{-4}\,\bar{M}_w$ (N-PEC)	$\bar{n}$BPE	$(\bar{R}_g^2)^{1/2}$, Å	$10^3 \cdot A_2$
1.4	5.0	2.2	—	2.0
7.5	28	11.3	290	1.8
12	38	18.1	300	1.9
18	69	27.2	400	1.9
41	150	61.7	750	1.9

The phenomena involving the association of complex macromolecules in N-PEC solutions are analogous to the micelle-formation processes in solutions of the usual block-copolymers in selective solvents. The degree of association of the N-PEC for the specified composition ϕ is little sensitive to changes in the molecular weight of the LPE. It is determined primarily by the ratio of the numbers of the LPE units incorporated in the hydrophilic and hydrophobic blocks, i.e. by the composition of the N-PEC. It is known

that the degree of association of the macromolecules of the usual block-copolymer in solutions also depends little on their molecular weights. It is largely determined by the ratio of the lyophobic and lyophilic blocks[53]. The change in the composition of the N-PEC is accompanied in exactly the same manner by a change in the degree of association of their species. This follows from Table 9. It is seen that an increase in the relative content of the LPE units in the N-PEC species, i.e. a decrease of ϕ, leads to a gradual decomposition of the associated species into the individual complex macromolecules.

Table 9. The influence of the composition of the N-PEC on its molecular characteristics[52].

φ	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$LPE	$\bar{n}$BPE	$10^8 \cdot A^2$
PA-Na ($\bar{M}_w = 1.2 \times 10^5$)–5,6-ionene bromide ($\bar{M}_w = 1.4 \times 10^4$), pH 7.2 in 0.025 M NaBr at 20 °C				
0.07	1.8	1	1.4	11.8
0.10	1.8	1	1.8	10.3
0.13	1.8	1	2.4	7.4
0.20	2.6	2	7.3	3.8
0.33	3.8	3	18.1	1.9
PA-Na ($\bar{M}_w = 2.0 \times 10^5$)–PDMAEMA.HCl ($\bar{M}_w = 7.7 \times 10^4$), pH 8.2 in 0.03 M NaCl at 20 °C				
0.2	2.9	1	1	4.1
0.33	4.8	2	3.4	1.8

The N-PEC formed by high-molecular-weight sodium polymethacrylate (LPE) and PVP-C_2H_5Br (BPE) also exhibit a high tendency towards association[52]; the characteristics of their behaviour are analogous to those considered above.

As shown above, the processes involving the formation and decomposition of the N-PEC associated species can be controlled by altering the composition of the N-PEC. The degree of ionisation of the LPE units incorporated in one-stranded hydrophilic blocks exerts a significant influence on these processes. If the LPE is a weak polyelectrolyte, a decrease in the degree of ionisation is accompanied by a decrease in its lyophilising capacity and leads to a progressive association of the N-PEC macromolecules up to their precipitation from the solution. This is why the N-PEC in which a polycarboxylic acid plays the role of the LPE and which have nearly the characteristic composition are soluble only in alkaline media at pH > 7. Correspondingly the N-PEC incorporating weak polymeric bases as the LPE acquire a capacity for dissolution only in acid media at pH < 7. The degree of association depends also on the degree of binding of the counterions to the free sections of the LPE. Table 10 presents the characteristics, in the presence of 0.025 M NaCl and KCl, of the N-PEC formed from PA-Na and 5,6-ionene bromide ($\phi = 0.33$). Evidently the replacement of the Na^+ counterions by the K^+ counterions, which are less strongly bound to the carboxylate groups of the LPE, entails the decomposition of the N-PEC associated species.

The capacity for association is also determined by the chemical structure of the LPE and BPE constituting the N-PEC. This question has been hardly discussed in the literature partly owing to the insufficiency of rigorous experimental data. Nevertheless, the pairs of polyelectrolytes forming the N-PEC can apparently be divided into two large groups. The subdivision can be based on a comparison of the distances between the neighbouring ionogenic groups in the LPE and BPE chains.

The first group includes pairs for which the neighbouring ionogenic groups in the LPE are separated by larger distances than in the BPE, for example, PDMAEMA.HCl–PA-Na and PDMAEMA.HCl–PP-Na. The amino-groups in PDMAEMA.HCl are far from the main chain and hence from one another. In the PA and PP chains the negatively charged units are closer to one another. Presumably in the corresponding PEC the BPE chain "spreads" over the LPE chains, occupying the section of the latter containing a relatively smaller number of units than in the BPE. Some of the BPE units are then not included in the system of intermolecular salt linkages, i.e. they are, as it were, overlooked. The effective fraction of the units incorporated in the hydrophilic blocks can then prove to be greater than the values calculated on the basis of stoichiometry. In fact, in the case under consideration the hydrophobic blocks should include a smaller number of the LPE units than the BPE units. The reduced tendency of the complex macromolecules towards association for compositions differing from the characteristic compositions ($\phi < \phi_{char}$) may be a consequence of this. Another consequence is the relatively high values of ϕ_{char}, for example, for the N-PEC formed from PDMAEMA.HCl and PA-Na ($\phi_{char} > 0.5$, Table 5).

Table 10. The influence of the nature of the LPE counterion on the molecular characteristics of the PA-Na ($\bar{M}_w = 1.2 \times 10^5$)–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC ($\phi = 0.33$; pH 8.0; salt concentration 0.025 M; 20 °C).[52]

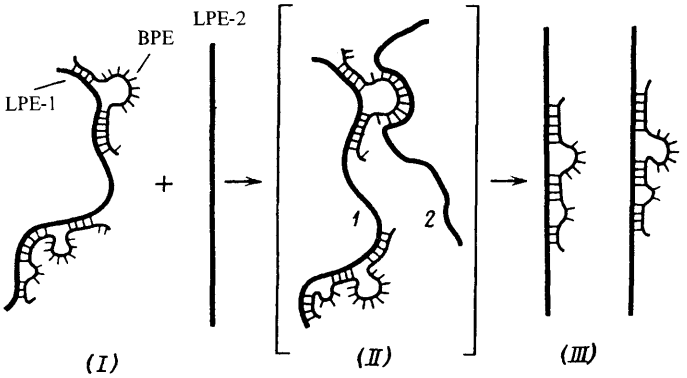
Salt	$10^{-5}\bar{M}_w$ (N-PEC)	$\bar{n}$LPE	$\bar{n}$BPE
NaCl	4.00	3	18.2
KCl	2.25	2	12.1

The second group of the N-PEC includes those for which the opposite condition holds, i.e. the distances between the neighbouring ionogenic groups in the LPE are smaller than in the BPE. Evidently such systems include particularly those which are symmetrical in relation to the systems examined above in which the LPE and BPE have changed places. Table 9 shows that the corresponding N-PEC have smaller values of ϕ_{char}. Presumably the number of units in the LPE section occupied by the BPE chain is greater than $\bar{P}_{BPE}$. The effective fraction of the LPE units incorporated in the hydrophilic blocks then falls, which actually implies a decreased lyophilising capacity of the LPE. A typical example of such a system is the PA-Na–5,6-ionene N-PEC examined in detail previously. The distance between the neighbouring quaternary nitrogen atoms in the BPE chain is much greater than the distance between the neighbouring COO^- groups in the LPE. Accordingly, the complex macromolecules formed by the above pair exhibit an enhanced tendency towards association.

In concluding this Section, we shall consider in broad outline the mechanism of the decomposition of the N-PEC associated species induced by a change in their composition. If the free LPE is added to solutions of the associated N-PEC, a gradual decomposition of the associated species is observed. For a certain ratio of the LPE and the BPE characteristic of each pair of the initial polyelectrolytes, the associated species decompose to the individual N-PEC complex macromolecules. This is illustrated by the data in Table 9.

The decomposition of the N-PEC associated species is accompanied by a redistribution of the BPE chains among a large number of the LPE chains. This leads ultimately to the formation of individual N-PEC species containing one LPE chain. However, their composition is significantly different from that of the initial associated species. The process described naturally presupposes the transfer of the BPE chains from one set of LPE chains to another. It is of interest that such transfer takes place in solutions from which free BPE macromolecules are absent. This is indicated by both light-scattering data and high-speed sedimentation data. Consequently the transfer of BPE takes place via the formation of intermediate macromolecular compounds, which then decompose to form the final products. The transfer can be represented by Scheme *I*.[21]

Scheme *I*



The intermediate polyelectrolyte complex (II) is formed via the addition of units of the free chain 2 to the section of the BPE chain incorporated in a defect of the N-PEC. The compound formed is unstable, since it possesses an increased electrostatic free energy. It therefore decomposes into two new N-PEC species having a different composition. This mechanism of the exchange of the BPE chains by the N-PEC species containing them is apparently fairly general for a wide variety of processes occurring with participation of polyelectrolyte complexes[54].

We emphasise yet again that the soluble N-PEC are macromolecular compounds formed as a result of reversible interpolymer reactions. This is why the reversible nature of the interaction of the macromolecules forming the N-PEC species presupposes the possibility of the interchange of the hydrophilic and hydrophobic blocks within such species and also between different species.

V. THE INFLUENCE OF LOW-MOLECULAR-WEIGHT SALTS ON THE BEHAVIOUR OF POLYELECTROLYTE COMPLEXES IN AQUEOUS SOLUTIONS

Certain properties of aqueous N-PEC solutions were briefly considered in the preceding two sections, mainly in connection with the factors altering the lyophilising capacity of the LPE. In particular, it was found that a decrease in the effective charge on the hydrophobic N-PEC blocks, which can be achieved by altering the pH of the solution or the nature of the LPE counterions, is accompanied by a change in the degree of association of the N-PEC species and ultimately by the loss of the solubility of the N-PEC. Situations were described where the precipitation of the PEC is not accompanied by a change in its composition.

However, the behaviour of the N-PEC in aqueous solutions of low-molecular-weight salts is of greatest interest. In the investigations summarised above mainly uni-univalent electrolytes—alkali metal halides and quaternary ammonium salts—were used[55]. Fig.11 presents as an example the curve for the turbidimetric titration of a solution of the PMA-Na–PVP.C_2H_5Br N-PEC having $\phi = 0.33$ with an NaBr solution. It is possible to distinguish three ranges of variation of the ionic strength of the solution to which regions I, II, and III in Fig.11 correspond.

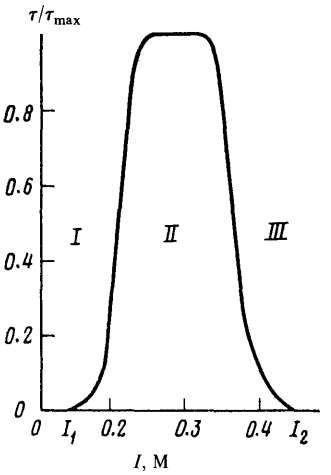


Figure 11. Curves for the turbidimetric titration of a solution of the PMA-Na ($\bar{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\bar{M}_w = 6 \times 10^4$) N-PEC having the composition $\phi = 0.33$ with NaBr solution; at pH 7.5 and 20 °C.[55]

In region I an increase in the salt concentration in solution is not accompanied by a change in the phase state of the system—the latter remains homogeneous. After the attainment of a certain ionic strength I_1, the system begins to turn turbid and a further increase of the ionic strength is accompanied by a progressive increase of turbidity. In region II the system is of the heterophase type. A fairly broad range of variation of the salt concentration corresponds to this region. The right-hand boundary of region II is characterised by a decrease of turbidity. Finally, at an ionic strength of the solution $I = I_2$, the system again becomes homogeneous. Region III corresponds to ionic strengths $I > I_2$; here the system remains homogeneous.

The behaviour described is characteristic of all the N-PEC investigated at the present time. It can be illustrated in relation to examples of associated N-PEC, in particular PA-Na–5,6-ionene and PA-Na–PDMAEMA as well as non-associated N-PEC such as PDMAEMA.HCl–PP and PDMAEMA.HCl-PAA. However, one should note that the positions of the boundaries between regions I, II, and III, i.e. the values of I_1 and I_2, depend markedly on the nature of the polyelectrolytes forming the N-PEC and also on the nature of the low-molecular-weight salts inducing the transformations considered.

We shall follow in succession the changes in the state of the PEC in the above three regions corresponding to the variation of the ionic strength of the solution. For this purpose, we shall return to the PMA-Na–PVP.C_2H_5Br system. Fig.12

presents the results of the study by the light-scattering method of the corresponding aqueous salt solutions in region I (cf.Fig.11). It is seen that an increase in the ionic strength of the solution (an increase of the NaBr concentration) is not accompanied by a change in the molecular weights of the N-PEC associated species (curve *1*). In the range of ionic strengths indicated each associated species retains the composition $\phi = 0.33$ and each contains on average three LPE (PMA-Na) chains. The sedimentation diagrams for the solutions contain a single peak (see Fig.16 below). Thus, for $I < I_1$, the N-PEC investigated behaves like an individual macromolecular compound. On the other hand, an increase in the ionic strength of the solution in region I leads to a considerable decrease in $(\overline{R}_g^2)^{1/2}$, i.e. to a decreased average particle size (curve *2*). The second virial coefficient then also decreases and, as the boundary between regions I and II, i.e. the point $I = I_1$, is approached, it tends to zero, which indicates an impairment of the thermodynamic properties of the solvent.

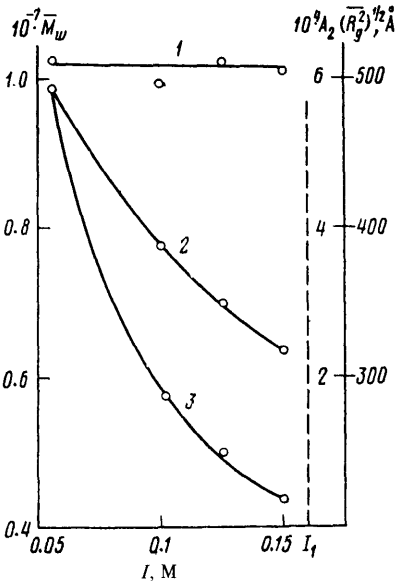


Figure 12. Molecular characteristics of the PMA-Na–PVP.C_2H_5Br N-PEC having the composition $\phi = 0.33$ as a function of the NaBr concentration in solution: *1*) $\overline{M}_w$ (N-PEC); *2*) $(\overline{R}_g^2)^{1/2}$; *3*) A_2; for conditions, see caption to Fig.11.[55].

Solutions of the unassociated N-PEC, an example of which may be provided by the PDMAEMA.HCl–PAA and PDMAEMA.HCl–PP systems, also behave analogously in region I. Such behaviour is typical for solutions of the usual flexible-chain polyelectrolytes. It is a consequence of the shielding of sections of the macromolecule by the counterions and of the decrease of the electrostatic repulsion between the LPE units with like charges incorporated in one-stranded hydrophilic blocks. The dependence of the second virial coefficients A_2 of solutions of different N-PEC on the reciprocal of the ionic strength is linear (Fig.13), which is also typical for the usual linear polyelectrolytes [see Eqn.(5)]. Thus the behaviour of the N-PEC in aqueous solutions containing comparatively low concentrations of low-molecular-weight salts is determined mainly by the properties of the charged one-stranded LPE blocks.

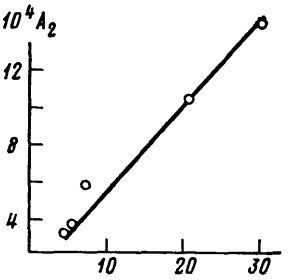


Figure 13. Dependence of the second virial coefficient A_2 for the PDMAEMA.HCl ($\overline{M}_w = 6.3 \times 10^5$)–PP ($\overline{M}_w = 1.7 \times 10^4$) N-PEC solution having the composition $\phi = 0.33$ on the reciprocal of the ionic strength of the solution $1/I$ (NaCl, pH 4.0 at 20 °C).[47]

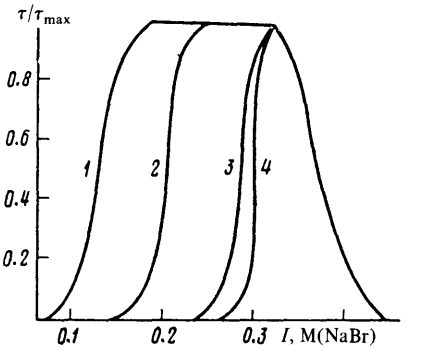


Figure 14. Curves for the turbidimetric titration of solutions of the PMA-Na ($\overline{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\overline{M}_w = 6 \times 10^4$) N-PEC having different compositions ϕ [*1*) 0.4; *2*) 0.33; *3*) 0.25; *4*) 0.2] with an NaBr solution at pH 7.5 and 20 °C.[55]

The position of the boundary between regions I and II, i.e. the value of I_1, depends greatly on the composition ϕ of the N-PEC. This is shown in Fig.14 in relation to the PMA-Na–PVP.C_2H_5Br N-PEC. Evidently, with increase of the BPE content in the polyelectrolyte complex species. i.e. with decrease of the fraction of the free LPE units, the boundary between regions I and II shifts towards lower ionic strengths of the solutions. This is also true of the PDMAEMA.HCl–PP and PA-Na–5,6-ionene systems. However, for fairly low values of ϕ, the majority of the N-PEC investigated remain soluble over the entire range of ionic strengths (for $\phi < 0.15$). This result is natural, since a decrease of ϕ implies an increase of the relative content of the hydrophilic blocks made up of ionised LPE units. The ionic strength I_1 also depends on the chemical nature of the low-molecular-weight salt, more precisely on the nature of the LPE counterions.

Fig. 15 presents curves for the turbidimetric titration of the PA-Na–5,6-ionene N-PEC having a fixed composition by various salts. In the series of selected counterions, the ionic strength I_1 varies as follows: $Li^+ < Na^+ < K^+ < TMA^+$ (TMA^+ is the tetramethylammonium ion), i.e. increases with decrease in the constant for the binding of the counterions to the polymeric carboxylic acids[56]. At the same time, I_1 is independent of the nature of the low-molecular-weight LPE ion, whose charge has the same sign as that of the ionised LPE units. Evidently curves *2'*, *2''*, and *2'''*, which refer to cases where an increase of the ionic strength is attained by the addition of the corresponding sodium fluoride, chloride, and bromide, coincide. All the facts presented show that in region I the behaviour of the N-PEC is indeed mainly determined by the properties of the free LPE units. The position of the boundary between regions I and II depends strongly, other conditions being equal, on the chemical nature of the LPE and BPE constituting the complex[5]. However, the available experimental data are as yet insufficient to trace any consistent relations.

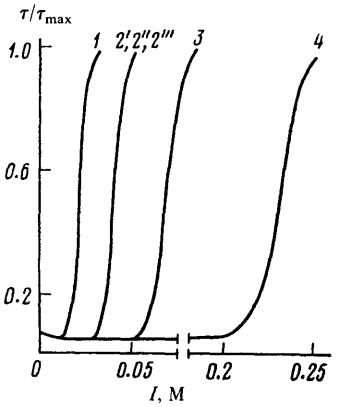


Figure 15. Curve for the turbidimetric titration of solutions of the PA-Na ($\bar{M}_w = 1.8 \times 10^5$)–5,6-ionene ($\bar{M}_w = 1.4 \times 10^4$) N-PEC having the composition $\phi = 0.33$ with solutions of LiCl (curve *1*), NaX [X: *2'*) F^-; *2''*) Cl^-; *2'''*) Br^-], KCl (curve *3*), and $(CH_3)_4NCl$ (curve *4*). Concentration of the N-PEC solution 0.01 wt.% at pH 8.5 and 20 °C.[55]

In region II ($I_1 < I < I_2$) the systems investigated are of the heterophase type for not unduly low values of ϕ. The soluble N-PEC must therefore be synthesised at ionic strengths of the solutions, not exceeding I_1. The behaviour of the PEC in region II differs significantly from the behaviour of the usual individual polyelectrolytes in aqueous salt media, for example, on salting-out. This is manifested primarily by a sharp difference between the compositions of the polymeric products in the coexisting phases. Table 11 presents the results of the analysis of the compositions of the dilute phase for the PDMAEMA.HCl–PP-Na system and the calculated compositions of the concentrated phase, i.e. the precipitate. It is found that, regardless of the composition of the initial system *Z*, for $\bar{P}_{LPE} \gg \bar{P}_{BPE}$, the S-PEC deposit coexists with a solution of complex macromolecules having the composition $\phi = 0.12–0.14$ (Table 11). For this composition, the N-PEC remains soluble over the entire range of ionic strengths. In the case where $\bar{P}_{LPE} \cong \bar{P}_{BPE}$ the S-PEC deposit coexists with a solution of free LPE (Table 11). Accordingly, the position of the turbidimetric titration curves for solutions of the N-PEC formed by electrostatically complementary polyelectrolytes with similar degrees of polymerisation is independent of the composition *Z* of the initial system.

Table 11. The composition of the phases coexisting in region II for the PDMAEMA.HCl ($\bar{P}_1 = 3200$)–PP-Na system at pH 4.0 at 20 °C.[55]

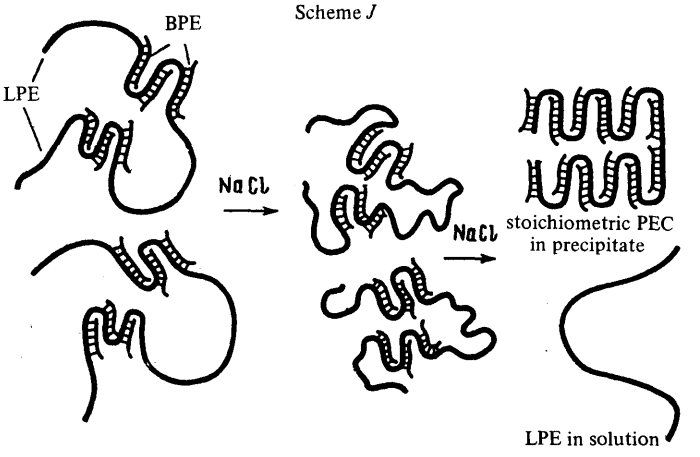
Z	$10^3 \cdot c_1$	$10^3 \cdot c_1'$	$10^3 \cdot c_2'$	ϕ
		$\bar{P}_2 = 170$; 0.57 M NaCl		
0.17	15.0	11.0	1.5	0.14
0.20	17.5	14.2	1.7	0.12
0.22	20.0	17.1	2.2	0.13
0.25	22.5	20.1	2.5	0.12
0.29	25.0	22.8	2.9	0.13
0.33	30.0	28.5	3.8	0.13
		$\bar{P}_2 = 3000$; 0.85 M NaCl		
0.2	10	4.8	traces	*
0.25	15	9.8	»	*
0.33	20	15	»	*
0.5	25	20	»	*

Notation: c_1 and c_1' are the PDMAEMA.HCl concentrations in the initial mixture and in the supernatant and c_2 and c_2' are the respective concentrations of PP-Na (in basic M) ($c_2 = 5.0 \times 10^{-3}$ basic M); ϕ is the composition of the PEC in solution; in the precipitate $\phi = 1$.

*Free PDMAEMA.HCl.

Thus, on passing from region I to region II, a distinct disproportionation phenomenon is observed, i.e. an inhomogeneous distribution of the BPE chains between the LPE chains. Disproportionation phenomena in interpolymer reactions are known[57]. In the cases considered here the disproportionation is due to the insolubility of the S-PEC. The transition from the uniform to the non-uniform population of the LPE chains by the BPE chains can be represented by Scheme *J*.

Scheme *J*



Evidently the entropy of the two-phase system where S-PEC is present in the concentrated phase (i.e. in the deposit), while in the dilute phase (i.e. in the solution) the N-PEC is depleted in the BPE or simply the free LPE is present, is

higher than the entropy of the system containing the N-PEC precipitate. For a constant total number of interpolymer salt linkages, a minimum in the free energy of the system should correspond to the first state.

The mechanism of the rearrangement of the N-PEC in aqueous salt media in region II is still not entirely clear. Presumably there are at least two pathways leading to disproportionation. One of these presupposes the preliminary salting-out of the N-PEC and its subsequent rearrangement in the concentrated phase with formation of the S-PEC and the liberation of the excess LPE into the solution. Another possible pathway consists in the formation of the S-PEC still in the solution as a result of the chemical reaction involving the transfer of BPE chains from one set of N-PEC species to another with subsequent precipitation of the S-PEC. In the case of associated N-PEC, the latter process can occur within the limits of each individual initial species. None of the postulated pathways excludes the other when applied to the given system—they can occur simultaneously. However, it must be emphasised that the characteristics of the behaviour of the N-PEC in region II are determined by the occurrence of two coupled processes: the physical process of phase separation and the chemical reaction involving the rearrangement of the PEC species.

The state of the species of the polyelectrolyte complex in region II varies with the ionic strength. An increase in the salt concentration is accompanied by the rupture of some of the interchain salt linkages as a consequence of ion exchange, i.e. as a consequence of the replacement of the "LPE unit–BPE unit" bond by two "chain unit–counterion" bonds[34]. For us, it is important that in region II the extent of the ion exchange is not sufficient for the dissociation of the PEC species into individual polyelectrolyte components. This is indicated particularly by the presence of the S-PEC deposit in the system.

Finally we shall consider the transition from the heterogeneous region II to the homogeneous region III. We may note in the first place that the position of the boundary between these regions, i.e. the value of I_2, depends little on the composition Z of the mixture of polyelectrolytes, in contrast to I_1 (Fig.14). The latter can be understood by taking into account the fact that, on passing from region II to region III and further, an increase in the ionic strength entails a far-reaching decomposition of the PEC. In fact I_2 is determined by the initial conditions for the separation of the polyelectrolyte components in the S-PEC, whose composition is naturally constant and independent of the initial ratio of the BPE and the LPE. In region III the fraction of the units θ linked by salt bonds greatly diminishes. There is a corresponding increase of the fraction of disconnected units. For the critical value of θ characteristic of each pair of polyelectrolytes, a sufficient number of hydrophilic sequences, i.e. loops incorporating disconnected units (see Scheme *A*), have accumulated in the S-PEC species. The precipitate then dissolves. The dissolution does not necessarily imply a complete separation of the electrostatically complementary chains in space. They can still be retained near one another by a relatively small number of salt linkages. However, with increase in the ionic strength in region III this number continuously falls. Finally, after the attainment of a sufficiently high concentration of low-molecular-weight salt, the polyelectrolyte complex dissociates completely into the individual polyelectrolyte components.

Fig.16 presents the sedimentation diagrams for the PMA-Na–PVP.C_2H_5Br N-PEC with the composition $\phi = 0.14$ in aqueous salt media. The polyelectrolyte complex having this composition is soluble over the entire range of experimental ionic strengths, i.e. the system is homogeneous at all the ionic strengths investigated. The characteristics of the behaviour of the N-PEC in the vicinity of the boundary between regions II and III and in region III are therefore particularly clearly manifested in relation to this system. Evidently, in the homogeneous system up to the ionic strength $I = 0.4$ M, the N-PEC species sediment with a single peak, i.e. they retain their individuality (curves *1* and *2*). However, on further increase in the concentration of the low-molecular-weight salt, the N-PEC dissociates into the free LPE and BPE. This is indicated by the appearance of two peaks on the sedimentation diagram (Fig.16, curve *3*), corresponding to the individual initial polyelectrolyte components#. It follows from the data presented that the disproportionation phenomenon is not observed in the homogeneous system, i.e. that the disproportionation is indeed closely related to the phase separation occurring on transition from region I to region II. Hence it also follows that, after the attainment of I_2 (Fig.14), the S-PEC still does not decompose fully into the individual components and dissolves actually in the form of the products of the incomplete interpolymer reaction. The complete dissociation of the polyelectrolyte complex into the LPE and the BPE occurs only in region III at high ionic strengths corresponding precisely to the appearance of two peaks on the sedimentation diagram for the solution.

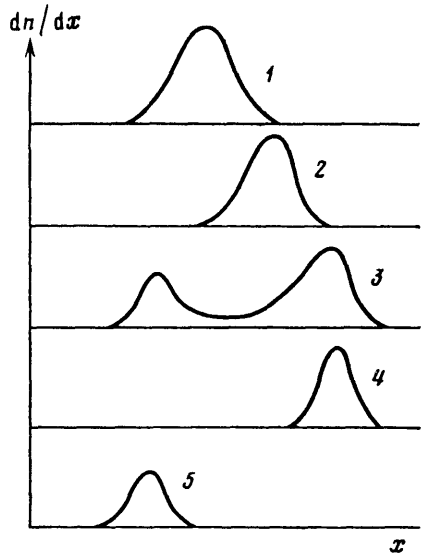


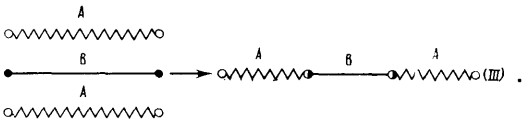
Figure 16. Sedimentation diagram for solutions of PMA-Na ($\bar{M}_w = 2.6 \times 10^5$)–PVP.$C_2H_5Br$ ($\bar{M}_w = 6 \times 10^4$) mixtures having the composition $Z = 0.14$ at different ionic strengths I(NaBr) [*1*) 0.2; *2*) 0.35; *3*) 0.48], PMA-Na (curve *4*), and PVP.C_2H_5Br (curve *5*). Concentration of solutions 0.3 wt.% at pH 7.5 and 20 °C. Time 60 min for a rate of spinning of 56000 min^{-1}.[55]

#In the experimental range of ionic strengths the individual polymeric components of the PMA-Na–PVP.C_2H_5Br system are not salted out, as happens, for example, in the sodium polystyrenesulphonate–polybenzylvinyltrimethylammonium chloride system[14].

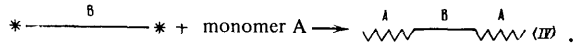
The other pairs of the electrostatically complementary polyelectrolytes taken in non-stoichiometric proportions and capable of forming the N-PEC (i.e. for $P_1 \gg P_2$) also behave analogously in aqueous salt media. This behaviour is caused by the thermodynamic reversibility of the interpolymer PEC formation reaction.

VI. PROSPECTS FOR THE DEVELOPMENT OF RESEARCH INTO AND THE POSSIBLE APPLICATIONS OF THE NEW CLASS OF POLYELECTROLYTES

The experimental data and considerations described in the review make it possible to regard the water-soluble N-PEC as an unusual variety of block-copolymers. Its unusual nature is manifested in the very synthesis of the N-PEC. In the classical chemistry of polymers one of two approaches is used for the synthesis of block-copolymers. According to the first of these, one synthesises initially the individual blocks A and B with the reactive groups at the ends, which are then linked to one another by a covalent bond as shown in the following scheme:



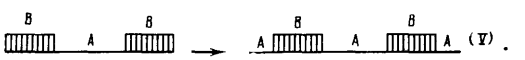
The second approach consists of the preliminary synthesis of blocks of, for example, type B whose terminal groups are capable of inducing the polymerisation of the corresponding monomer and the growth of blocks of type A:



In contrast to this, a fundamentally different approach is used in the synthesis of N-PEC, consisting in the lateral pairing of chemically complementary chains of different lengths.

The N-PEC is formed as a result of a very rapid ion-exchange reaction on simple mixing of aqueous solutions of the initial polyelectrolyte components. The process terminates almost instantaneously even at very high dilutions. The synthesis of the N-PEC can be achieved without any experimental tricks in the same working system where it is intended to function subsequently. The unusual nature and simplicity of the synthesis of hydrophilic-hydrophobic block macromolecules naturally lead to their new practical applications.

This is not all. In the block-copolymer synthesised by the usual method, the sequence of the alternation of the blocks and their lengths, i.e. the primary structure of the block macromolecules, are specified at the synthesis stage. Subsequently the structure can no longer be altered without the rupture of covalent chemical bonds. The macromolecules of the usual block-copolymer therefore attain thermodynamically optimum states in their interaction with one another and with the surrounding medium only by a change in their conformations, i.e. in their secondary structure. The situation is different in the case of the block N-PEC. By virtue of the reversibility of the reactions between the LPE and the BPE, the BPE chains can migrate along the LPE chains and can even move from one chain to another. Such migration actually implies an alteration of the relative lengths and number of hydrophilic and hydrophobic blocks in the complex macromolecule, for example, in accordance with the scheme



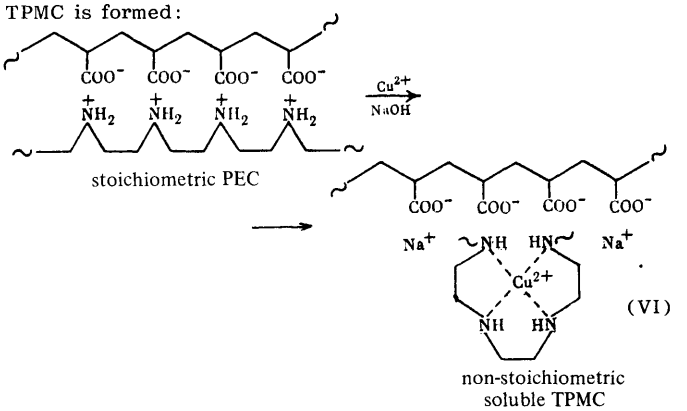
Consequently the complex block macromolecules of the N-PEC can "seek" thermodynamically optimum versions of the interaction with the surrounding medium not only by changing their secondary structure but also their primary structure. The unique ability of the N-PEC, which follows from this, which is to change as a function of the conditions its hydrophilic-hydrophobic balance and to become adjusted to the hydrophilic-hydrophobic balance of the surrounding species and surfaces, should also have important practical consequences, for example, in the solution of problems of flocculation or the stabilisation of colloidal systems.

The study of the structure and properties of N-PEC is extremely useful for the development of ideas concerning the behaviour of linear polyelectrolytes in classical highly disperse colloidal systems.

Non-stoichiometric polyelectrolyte complexes are of considerable interest also as the simplest model of polyelectrolyte complexes of biological origin, such as nucleoprotein, glycoprotein, etc. complexes. It has also been shown[47,58,59] that synthetic linear polyelectrolytes are capable of forming water-soluble complexes with oppositely charged proteins (albumin, globulins, etc.). Such complexes are characterised by a definite composition and molecular weight and are in many respects similar to the water-soluble N-PEC described above. They are of independent interest as fundamentally new biologically active macromolecular compounds, for example artificial antigens[60].

One rational explanation of the high physiological activity manifested by synthetic polyelectrolytes is based on the idea of their ability to interact cooperatively with oppositely charged biopolymers (nucleic acids, proteins, heparin, etc.) and also with cell membranes. Clearly, the polyelectrolyte complexes formed under these conditions can be both stoichiometric and non-stoichiometric.

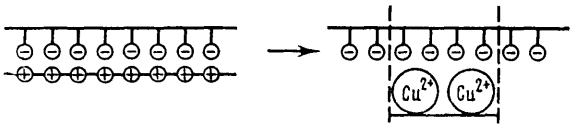
The reversible interpolymer reaction leading to the formation of an N-PEC can find applications in the creation of most varied functional macromolecular systems. In particular, we shall consider an example in which the ability of the PEC to bind strongly transition metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, etc. is used. The ternary polymer–metal complexes (TPMC) thus formed can be both stoichiometric and water-soluble and non-stoichiometric and can be interconverted. The TPMC of linear polyethyleneimine (PEI), PA-Na, and Cu^{2+} has been studied in greatest detail[61–63]. If an aqueous solution of a bivalent salt is added to the insoluble PAA–PEI S-PEC with $\theta \cong 1$, the deposit of the polyelectrolyte complex is coloured an intense blue. For the ratio $[Cu^{2+}]:[\text{polyelectrolyte unit}] \cong 1:5$, a water-soluble TPMC is formed:



Each Cu^{2+} ion in the TPMC is then bound by coordinate bonds to four non-protonated amino-groups belonging to four neighbouring PEI units. The TPMC can therefore be characterised as a polyelectrolyte complex formed by the negatively

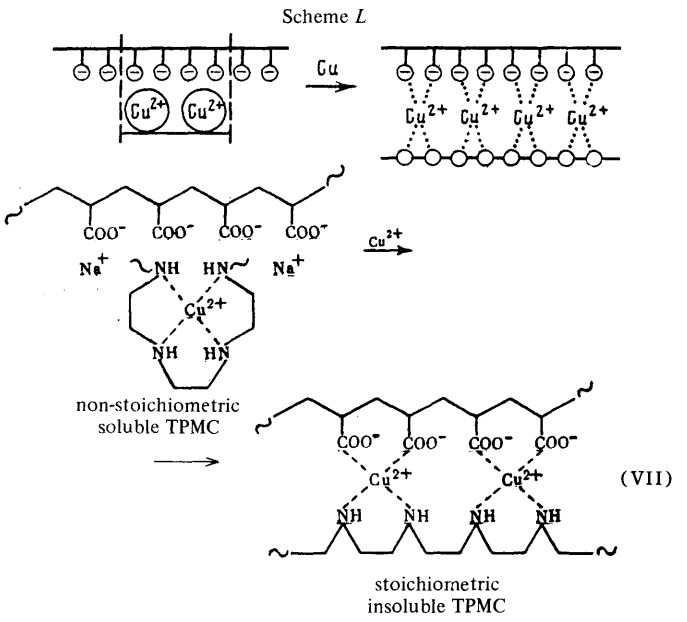
charged PA-Na chain and the positively charged chain of the copper complex of PEI. In the initial binary S-PEC there is one PEI unit per PAA unit. In contrast to this, in the TPMC for each two PAA units there are four PEI units, constituting the coordination sphere of the bivalent ion Cu^{2+}. Thus, on formation of the TPMC, the effective length of each PEI chain decreases. The PEI chains, as it were, "shrink" relative to the PA-Na chains. One-stranded sequences of the negatively charged PA-Na units are then liberated, as shown in Scheme *K*.

Scheme *K*



As a result, the TPMC acquires the block structure characteristic of the N-PEC and dissolves. However, if the addition of the copper salt to a solution of this TPMC is continued, then, for the ratio $[Cu^{2+}]/[\text{polyelectrolyte unit}] = 0.5$, phase separation occurs again. It is due to a rearrangement of the coordination sphere of the Cu^{2+} ion; in the presence of an excess of Cu^{2+}, only two PEI units remain in the TPMC molecule and two additional PAA units are incorporated. As a result, the TPMC acquires the continuous two-stranded structure characteristic of the S-PEC.[62] This is illustrated by reaction (VII) and Scheme *L*.

Scheme *L*



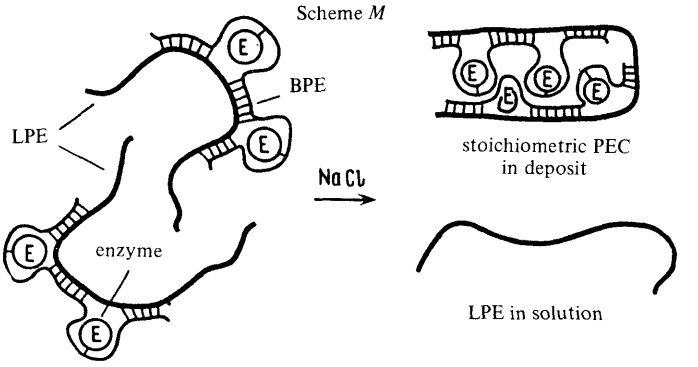
(VII)

The transformations of the TPMC as the concentration of transition metal ions in the surrounding solution is varied, described above, can be used, for example, for the creation of chemomechanical machines. The study of the above phenomena is of undoubted interest also for the creation of effective complex-forming ion-exchangers based on polyelectrolyte complexes.

Another example of functional macromolecular systems based on the N-PEC can be provided by the N-PEC–enzymes conjugated systems. The properties of penicillin amidase (*E*) from *E.coli*, incorporated in particles of the PMA-Na–$PVP.C_2H_5Br$ N-PEC, have been described[64]. The enzyme molecules were initially linked covalently to the BPE chains ($PVP.C_2H_5Br$) and then, using the procedures described above, the N-PEC was obtained ($\phi = 0.33$). The inclusion of the enzymes in the N-PEC species having an excess negative charge was accompanied by a considerable shift and distortion of the pH optimum in the enzyme activity induced by the Donnan exclusion effect. The activity of the enzyme hardly altered under these conditions. An important property of this three-component system is its ability to pass reversibly from the soluble to the insoluble state as the ionic strength of the solution is varied. The precipitation curve for the enzyme-containing PEC is very similar to the precipitation curve for the PMA-Na–$PVP.C_2H_5$ binary N-PEC having the same composition and presented in Fig.15.

The complete transition to the insoluble state takes place over a narrow range of salt concentrations (*I*), amounting to 0.01 M. The process is illustrated schematically in Scheme *M*.

Scheme *M*



The enzymes linked to the S-PEC formed are entrained together in the precipitate. It is remarkable that the formation of the deposit is accompanied by a virtually complete cessation of the enzymatic reaction. Since the phase separation process is reversible, it can be frequently repeated without loss of enzyme activity. Hence arises the possibility of creating self-regulating enzyme systems. If, for example, the enzymatic process involving the cleavage of the substrate leads to the formation of charged products, the ionic strength of the solution increases in the course of the reaction. After the attainment of an ionic strength I^* linked directly to the degree of conversion of the corresponding substrate, the N-PEC containing the enzyme is converted into the insoluble S-PEC. The enzymatic reaction should then stop independently. This has been demonstrated in relation to the hydrolysis of the sodium salt of benzylpenicillin by enzyme-containing N-PEC. The hydrolysis results in the formation of the sodium salt of 6-aminopenicillanic acid and the sodium salt of phenylacetic acid, which ultimately "stop" the reaction. By varying the initial ionic strength of the solution and (or) the composition of the N-PEC, it is possible to force the enzymatic reaction to stop automatically at any specified degree of conversion of the substrate.

* * *

The example presented naturally by no means exhaust all the theoretical and practical prospects for the employment of the N-PEC as a new class of water-soluble ionogenic macromolecular compounds. The very fact that the examples described refer to such varied and sometimes remote fields demonstrates convincingly the usefulness of further studies and research. Only the first steps have so far been taken in this direction.

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