Kinetics and Mechanism of Interpolyelectrolyte Exchange and Addition Reactions

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ABSTRACT: Transfer of relatively short polycation chains (guest polyelectrolyte, GPE) from their polyelectrolyte complex (PEC) with a relatively long polyanion (host polyelectrolyte, HPE) to another polyanion of the same chemical structure and chain length but tagged with a fluorescent group has been investigated by the luminescence quenching technique. It has been shown that if only one polycation chain, on average, is transferred, the reaction follows irreversible second-order kinetics. The irreversibility of the reaction is due to additional selective nonelectrostatic interaction between the polycations and polyanion chains, carrying pyrenyl groups. The rate constant of the exchange reaction is independent of polyanion chain length and increases sharply with an increase of ionic strength of water–salt solution, a decrease of polycation chain length, and a decrease of the charge density. In accordance with the proposed mechanism, the rate-limiting step of the reaction is the transfer of a polycation chain from one polyanion to the other one in the united coil HPE–GPE–HPE*. The polyion addition reaction, i.e. the complexation between two oppositely charged polyanions, also has been studied by luminescence quenching and quasielastic light scattering techniques. The reaction can be considered as a multistage process, consisting first of the rapid coupling of the oppositely charged polyions with the formation of a nonequilibrium interpolyelectrolyte network followed by the slow relaxation process, leading finally to the formation of the individual PEC.

Introduction

The interpolyelectrolyte reactions represent a subject of increasing interest now. Basically, such reactions proceed in water–salt solutions with polyions of high charge density. The investigation of these reactions has a special interest first of all in obtaining different PEC, which have a wide range of practical applications as a new type of synthetic polymeric material in industry, agriculture, and medicine.[1-3] Meanwhile, the investigation of the exchange and substitution interpolyelectrolyte reactions[1,2] with the participation of water-soluble nonstoichiometric PEC (NPEC) may be important for modeling processes that take place in nature with the charged macromolecules and, especially, for understanding the action mechanism of biologically active substances containing linear synthetic polyions (artificial immunogenes, etc.).[4-6]

The first study of the kinetics of interpolyelectrolyte reactions was undertaken in ref 7. It was found that a low molecular weight electrolyte has a great influence on the rate of the exchange reactions. Lately, it has been shown[8] that, as a rule, the kinetics of such reactions have a complicated character and cannot be described in terms of formal kinetic schemes of the first- and second-order reactions. The same conclusion has been made by studying the reactions with polycomplexes stabilized by a cooperative system of hydrogen bonds.[9,10] The complicated empirical equations of the Kolraysh type or the sum of two exponentials[8,10] were used to describe the kinetics of intermacromolecular reactions. However, such an approach does not provide the possibility to better understand the mechanism of the reactions themselves, because these equations include empirical parameters having no direct physical sense.

The study of the kinetics and mechanism of the interpolyelectrolyte addition reaction is much less advanced at present. One can conclude[11] that such a reaction represents a quite complicated process and basically proceeds through the stage of macro-phase separation.

The investigation of kinetics of interpolyelectrolyte reactions was carried out on the qualitative level, mainly by evaluation of the total rate of the process.

In this work we have undertaken a systematic study of kinetic regularities of an interpolyelectrolyte exchange reaction. As a result we have found that such a reaction follows typical irreversible second-order kinetics. We have formulated the mechanism of the reaction on the basis of the analysis of the infuence of different parameters on the reaction rate constant. We will also discuss some results on the kinetics of the interpolyelectrolyte addition reaction, i.e. the reaction of direct NPEC formation and possible stages of such a reaction.

Experimental Section

Materials. The synthesis by radical polymerization and fractionation by dropwise precipitation of poly(methacrylic acid) (PMA) and poly(4-vinylpyridine) (PVP) samples were carried out according to the literature methods.[12,13] The samples of PMA* with the pyrenyl chromophoric groups were synthesized by interaction of pyrenyldiazomethane with poly(methacrylic acid) fractions, as is described in refs 14 and 15. PMA* fractions with weight average polymerization degrees DP_w = 4400, 980 (one pyrenyl group per 600 chain units, on the average), and 3900 (one pyrenyl group per 350 chain units) were used in our research. The contents of pyrenyl residues in PMA* chains have been evaluated by measuring UV spectra of PMA* water solutions at $\lambda = 342$ nm, assuming a characteristic molar absorption coefficient for pyrenyl groups equal to $\epsilon = 5 \times 10^4$ L mol^{-1} cm^{-1}. We also have used polycations with variable charge density, which are the products of PVP quaternization by ethyl bromide.[13] The degree of quaternization (β, %) (where β, % $= 100m/(m + n)$, m and n are the molar percent of 1-ethyl-4-vinylpyridinium chain units and 4-vinylpyridine chain units in PEVPB polycation, respectively) for such polycations (PEVPB) was measured by IR and UV spectroscopy.[15,16] PEVPB samples with β values of 60, 70, 84, 90 (DP_w = 200) and 95% (DP_w = 100, 200, 320, 600) were used in this study. Twice-distilled water was used in all experiments.

Sample Preparation. NPEC water-soluble complexes with the composition ϕ = [PEVPB]/[PMA] (where ϕ is the ratio of molar concentrations of corresponding polyelectrolyte chain units) were prepared by mixing water solutions of PEVPB, so-called guest polyelectrolyte (GPE), and PMA, host polyelectrolyte (HPE), at the proper concentration ratio with the subsequent addition of NaOH up to pH = 10 for dissolution of the initial product and giving finally NPEC (PMANa–PEVPB).[15,17]

The experiments on the interpolyelectrolyte exchange reaction were carried out by the fast ("dead" time 3 s) feeding of water–salt NPEC solution into water–salt PMA*Na solution so that in the reaction mixture [PMANa] = [PMA*Na] (the concentration of sodium poly(methacrylate) chain units in moles per liter). The reaction has been conducted with NPEC, having different ϕ values.

The addition reaction was carried out by fast mixing of 1.5 mL of aqueous PMA*Na solution, [PMA*Na] = 3.8×10^{-4} mol L^{-1}, with 0.02 mL of PEVPB solution so that the final composition of the mixture was about ϕ = 0.2. The homogenation time in this procedure was about 2–4 s.

In all experiments the solutions were constantly stirred.

Measurements. Fluorescence steady-state intensity measurements of the reaction mixtures (I) and free PMA*Na solutions (I_0) were carried out on a "JY-3CS" spectrofluorometer at room temperature.

Quasielastic light scattering experiments have been conducted by applying a laser goniometer "ALV-SP81" with the wavelength λ = 633 nm and a digital correlator "LFI-1096". Z-average diffusion coefficient D_f and the diameter of the effective hydrodynamic sphere $2R_0$ were calculated using the method of cumulants[18] and Stocks' approximation.

Results and Discussion

I. Interpolyelectrolyte Exchange Reaction. The ability of nonstoichiometric polyelectrolyte complexes to participate in interpolyelectrolyte reactions[7,19,20] is one of their most essential properties. These reactions proceed in water–salt solutions and represent the transfer of guest polyelectrolyte chains (GPE) from the NPEC particles to the host polyelectrolyte chains (HPE) fed into the solution. (Polyions present in NPEC in excess and in deficiency are called host and guest, respectively.)

We used the method of fluorescence quenching to study the interpolyelectrolyte exchange reaction between NPEC formed by HPE polyanion sodium poly(methacrylate) (PMANa) and GPE polycation poly(N-ethyl-4-vinylpyridium) bromide (PEVPB), with the free PMA*Na polyanion containing fluorescent pyrenyl groups:

$$\text{NPEC(PMANa–PEVPB)} + \text{PMA*Na} \rightarrow \text{NPEC*(PMA*Na–PEVPB)} + \text{PMANa} \quad (1)$$

The chain units of PEVPB are effective quenchers of pyrenyl group luminescence. Reaction 1 consists in the formation of NPEC* particles in which some part of luminescent groups are in contact with the chain units of PEVPB, i.e. quenchers of luminescence. The kinetics of this reaction can be followed by measuring the time decrease of luminescence intensity (I) of the reactive mixture.

We have recently found[21] that the presence in the PMA*Na chains of pyrenyl groups in the quantities indicated above is enough to achieve nearly complete selective interaction: all PMANa polyanions in the complex (reaction 1) are replaced by PMA*Na. It could be important for modeling molecular "recognition" in biopolymer sytems. This effect is due to the decrease of free energy resulting from charge-transfer complex formation between the pyrenyl chain unit (the donor) and the PEVPB pyridine ring (the acceptor) and the pyrenyl group plunging into the hydrophobic area, formed by hydrocarbon fragments of the coupled polyions. Thus, reaction 1 can be regarded as kinetically irreversible.

Typical kinetic curves of reaction 1 are shown in Figure 1 in the coordinates of relative fluorescent intensity (I/I_0) versus time. The values of I_0 and I conform to the solution of PMA*Na chains (I_0) and the reactive mixture (I). The I/I_0 relative fluorescence intensities in Figure 1, marked by the dotted lines, designate the equilibrium values in reaction 1. The equilibrium values of I_e/I_0 were measured in the independent experiments, and they correspond to the solutions, containing all three components of reaction 1 with the proper molar ratio of polyions and the same other conditions as in the reactive mixtures. The preparation of such a solution is identical to the procedure for obtaining water-soluble NPEC (Experimental Section). The decrease of I/I_0 of the reactive mixture takes place as a result of a successive increase of (PMA*Na–PEVPB) complex composition in the course of reaction 1. We have proved that the $I/I_0 = F(\phi)$ dependence has almost linear character for all experimental kinetic curves. Therefore one can pass from $[I/I_0, t]$ coordinates to $[q, t]$, where $q = (I_0 - I)/I_0 - I_e)$.

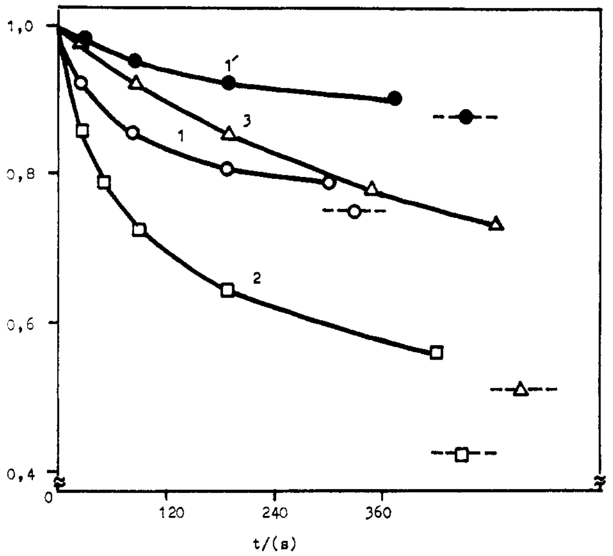

Figure 1. Kinetic curves of reaction 1 in the mixtures of PMA*Na and NPEC: DP$_w$(PMA*Na) = 3900 (1, 1', 2, 3); DP$_w$(PEVPB) = 320 (1, 1'), 100 (2), and 600 (3); [PMA*Na] = 1.28×10^{-4} (1, 1'), 3.2×10^{-5} (2), and 1.6×10^{-5} mol L^{-1} (3); [PEVPB] = 9.22×10^{-6} (1), 4.61×10^{-6} (1'), 8.19×10^{-6} (2), and 2.46×10^{-6} mol L^{-1} (3); [NaCl] = 0.07 (1, 1'), 0.04 (2), and 0.08 M (3).

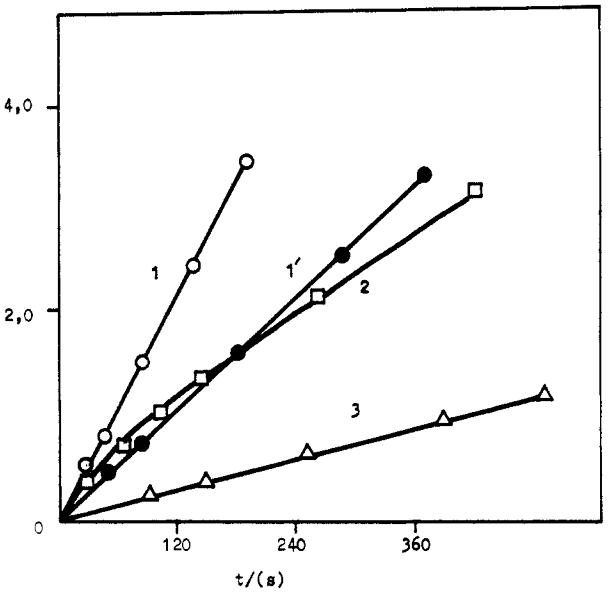

Figure 2. Dependence of $q/(1 - q)$ on the time of reaction 1 in the mixture of PMA*Na and NPEC.

The data on the kinetics of interpolyelectrolyte reaction 1 shown in Figure 2 are processed in accordance with the equation of the second-order irreversible reaction:

$$q/(1-q) = k_{\text{II}}at \qquad (2)$$

where q is the conversion degree, calculated from kinetic curves,[8] k_{II} is the rate constant of the bimolecular second-order reaction, a is the initial molar concentration of HPE* chains, and t is time.

The kinetic curves presented in Figure 2 have an important feature. While the transfer of several GPE chains takes place in reaction 1 (Figure 2, curve 2), the deviation from rectilinear dependence is observed in the coordinates of eq 2. However, in this case, when the exchange reaction is followed by the transfer of the only GPE chain, the kinetic curves straighten out in the coordinates of eq 2 and can be characterized by the only rate constant (k_{II}) (Figure 2, curves 1, 1′, 3).

Rate constants k_{II} were calculated from the obtained kinetic curves of reaction 1, in the variant of one-chain transfer. The range of k_{II} variation under the corresponding change of the experimental conditions (GPE polymerization degree and its charge density, low molecular weight electrolyte concentration) was $10^4 < k_{\text{II}} < 10^7$.

If one assumes that interpolyelectrolyte reaction 1 is limited by translational diffusion of NPEC and HPE coils, then k_{II} should be determined by the frequency of collisions of polymeric coils, in other words the constant rate of the reaction which is controlled by the translational diffusion of the coils (k_{diff}), can be evaluated by the well-known ratio

$$k_{\text{diff}} = 4\pi N_A D_\epsilon R_\epsilon \qquad (3)$$

where N_A is Avogadro's number, D_ϵ is the total diffusion coefficient of the polymeric coils, and R_ϵ is the total radius of equivalent spheres of the components. Accepting D_ϵ and R_ϵ as being equal to 10^{-7} cm^2/s and 100 Å, respectively, and with the data obtained by Mandel[22] for the diluted water–salt solutions of sodium poly(styrenesulfonate), one can get $K_{\text{diff}} \sim 10^9$ M^{-1} s^{-1}.

Thus, the calculated diffusion rate constant appears to be at least 2 orders of magnitude higher than k_{II}. Therefore, the translational diffusion of polymeric reagents does not represent the limiting stage of reaction 1. The data on k_{II} independence from HPE* (HPE) molecular weight agreed with this conclusion. The reaction 1 kinetic curves were obtained for NPEC particles containing GPE of similar chain length DP$_w$ = 100 and HPE with the polymerization degrees DP$_w$ = 4400 and 980. It turned out that under the conditions of one-chain transfer, the reaction kinetic curves coincided completely, despite their 4.5-fold difference in HPE molecular weight (Figure 3).

Rate constant k_{II} grows strongly with the increase of low molecular weight electrolyte concentration in reaction 1 (Table I). One has to stress that NPECs themselves do not dissociate to the components in the interval of ionic strength variation, indicated in Table I.

As the dissociation degree on polymeric components of the studied NPEC is nearly equal to zero, one should suppose that the mutual penetration of NPEC and HPE* coils is the necessary condition of reaction 1. In such a case, the transfer of GPE from HPE into HPE* in the united NPEC–HPE* coil should be the limiting stage of reaction 1. This also can be proven by a strong k_{II} dependence on the GPE degree of polymerization: k_{II} decreases with the increase of GPE DP$_w$ value (Table II). There is a sharp increase of k_{II} with the increase of salt concentration (Table I) or the decrease of GPE charge density, % β (Table III).

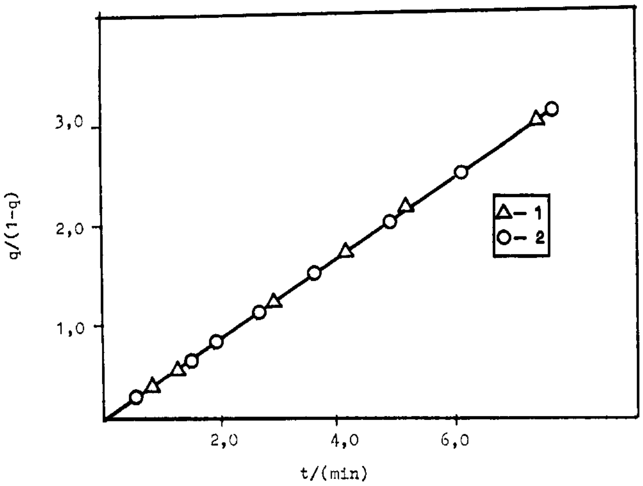

Figure 3. Dependence of $q/(1-q)$ on the time of reaction 1 in the mixture of PMA*Na and NPEC: DP$_w$(PMA*Na) = 4400 (1) and 1000 (2); DP$_w$(PEVPB) = 100 (1, 2); [PMA*Na] = 1.44 × 10^{-4} (1) and 3.2 × 10^{-5} mol L^{-1} (2); [PEVPB] = 3.27 × 10^{-6} (1) and 3.2 × 10^{-6} mol L^{-1} (2); [NaCl] = 0.04 M.

Table I
Dependence of the Reaction 1 Rate Constant k_{II} on Salt Concentration [NaCl] in the Mixtures of PMA*Na and NPEC ([PMA*Na] = 3.2 × 10^{-5} mol L^{-1}, [PEVPB] = 4.9 × 10^{-6} mol L^{-1})

[NaCl], M	0.06	0.07	0.08	0.09
$10^{-5}k_{11}$, M^{-1} s^{-1}	1.3	2.7	5.2	9.0

Table II
Dependence of the Reaction 1 Rate Constant k_{II} on DP$_w$(PEVPB) in the Mixtures of PMA*Na and NPEC ([PMA*Na] = 1.28 × 10^{-4} mol L^{-1}; [PEVPB] = 2.89 × 10^{-6} (1), 5.76 × 10^{-6} (2), 9.22 × 10^{-6} (3), and 1.56 × 10^{-5} mol L^{-1} (4); DP$_w$(PMA*Na) = 4400; [NaCl] = 0.07 M)

NN	1	2	3	4
DP$_w$(PEVPB)	100	200	320	600
$10^{-5}k_{11}$, M^{-1} s^{-1}	23.0	11.0	5.7	1.8

Table III
Dependence of the Reaction 1 Rate Constant k_{II} on Percent β in the Mixtures of PMA*Na and NPEC ([PMA*Na] = 6.4 × 10^{-5} mol L^{-1}, [PEVPB] = 3.28 × 10^{-6} mol L^{-1}, [NaCl] = 0.035 M; DP$_w$(PMA*Na) = 3900, DP$_w$(PEVPB) = 200)

β, %	60	70	84	90
$10^{-6}k_{11}$, M^{-1} s^{-1}	11.5	0.8	0.2	0.05

Mutual penetration of NPEC and HPE* coils in the diluted solution leads, in this variant, to the increase of free energy. Otherwise, one has to expect the aggregation of polymeric coils in the system, which actually does not proceed (measurements were carried out by the quasielastic light scattering technique). The united HPE–GPE–HPE* coil appears as the result of fluctuations with the lifetime, much less than the half-conversion time in reaction 1.

The reaction 1 mechanism can be presented in the following way. First, the translational diffusion makes NPEC and HPE* coils approach each other and mutual penetration of NPEC and HPE* proceeds with the formation of the united coil which has all three polyion components. Then, as a result of conformational transformations, which are followed by redistribution of salt bonds between polyions during the lifetime of the united coil, the polycation transfer from one polyanion to the other one may occur. As follows from Tables I and III the possibility of such a transfer increases sharply with the increase of the solution ionic strength and decrease of polycation charge density. One can attribute it mainly to a decrease of cooperativity of electrostatic binding between guest and host polyelectrolytes and therefore to an increase of their segmental flexibility in the united coil. It follows from the comparison of k_{diff} and k_{II} values that there is one such transfer, or one effective collision, per 10^2–10^5 collisions of HPE* and NPEC coils.

The rate constant k_{II} in case of one-chain transfer can be interpreted in terms of the theory of absolute reaction rates, assuming the effective collision of NPEC and HPE* coils to be the "elementary" act of reaction 1. The transitional state in this reaction and overcoming of the free-energy barrier is achieved via segmental diffusion of components in the united coil.

We have studied the influence of temperature on k_{II}. It follows from the experimental data, that in the 13–42 °C interval, k_{II} is independent of temperature. This permits us to conclude that the activation enthalpy in reaction 1 is close to zero and the basic contribution into the activation free energy ΔG^* when the transitional state is formed is made by the change of the entropy.

In the variant of multichain transfer, the kinetics of reaction 1, naturally, do not follow a simple kinetic scheme of the second-order reaction (see Figure 2, curve 2). The probability of GPE to HPE* transfer decreases as the HPE* chains are being filled with GPE chains and the brutto process can no longer be characterized only by the kinetic constant k_{II}. A corresponding set of kinetic constants is necessary for its description.

II. Interpolyelectrolyte Addition Reaction. We have studied the kinetics of the addition reaction between poly(methacrylate) anions and poly(*N*-ethyl-4-vinylpyridinium) cations in the diluted aqueous solutions by the fluorescence quenching technique. The addition reaction of the oppositely charged polyions can be presented by the following scheme:

$$\text{PMA*Na} + \text{PEVPB} \rightarrow \text{NPEC(PMA*Na–PEVPB)} \quad (4)$$

The conversion degree, q, in this reaction is determined as a part of the ultimate number of salt bonds between polyions PMA*Na and PEVPB under the formation of a NPEC water-soluble complex. We have managed to carry out this reaction without macro-phase separation in the system by mixing quite diluted polyelectrolyte solutions with a concentration about 10^{-4} mol L^{-1} chain units. The addition of the chain fragment of PMA*Na containing the luminescent pyrenyl groups with PEVPB chains, the pyridinium units of which are the quenchers of luminescence, is followed by a decrease of the solution luminescence intensity (I). The ratio of chain units in the reaction mixture has been given as [PEVPB]/[PMA*Na] = 0.2. The experiments were carried out at pH = 10, i.e. under conditions when both polyelectrolytes were completely ionized. It has been shown before that the soluble NPEC with the composition ϕ = [PEVPB]/[PMA*Na] = 0.2[17] is formed in the system after the reaction is completed. The kinetics data on exchange reaction 1 between NPEC with $\phi = 0.2$ and PMA*Na chains also will be given here for comparison with the kinetics of addition reaction 4.

Dependencies of the relative luminescence intensity I/I_0 on time (I_0 is the luminescence intensity of the PMA*Na initial solution) are presented in Figure 4. Curves 1 and 2 correspond to addition reaction 4 which proceeds in the salt-free medium and in 0.03 M NaCl solution, respectively. One can see that in both cases there is a discontinuity on the curves; this corresponds to the fast process which does not exceed in time the process of mixing of polyelectrolyte solutions. The discontinuity value, i.e. the conversion degree at the initial stage of reaction 4 in the salt-free solution, is much less than that in 0.03 M NaCl solution. The threshold I/I_0 values, which correspond to the ultimately possible q values in reaction 4 under the above mentioned conditions are marked in Figure 4 by horizontal dotted lines 1′ and 2′. These values are determined via measurement of I/I_0 of NPEC solutions with the composition $\phi = 0.2$, prepared in the salt-free aqueous solution and 0.03 M NaCl solution, respectively, according to the methods described in refs 7 and 20. From the comparison of curves 1 and 2 (Figure 4) it can also be seen that the conversion degree in reaction 4 for the salt-free solution being achieved during the mixing of polyelectrolyte solutions undergoes no significant changes, at least during 10 min. On the contrary, in 0.03 M NaCl solution, the increase of the conversion degree continues after the initial discontinuity. The I/I_0 value here approaches the yield point, marked by dotted line 2, which is reached in several hours. The kinetics of the slow stage of reaction 4 in 0.03 M NaCl solution (curve 2) correlates rather well with the kinetics of exchange reaction 1, proceeding under the same conditions (curve 4) between NPEC of $\phi = 0.2$ composition and PMA*Na. It follows from the same Figure 4 that there is no slow stage of addition reaction 4 (curve 1) in the salt-free media if exchange reaction 1 does not proceed (curve 3). That is why it is natural to connect the slow part of curve 2 with the redistribution of PEVPB chains between PEC particles randomly formed during the first (fast) stage and the final formation of equilibrium NPEC particles which have a composition, ϕ, which is predetermined by the concentration ratio of the components in the reaction mixture.

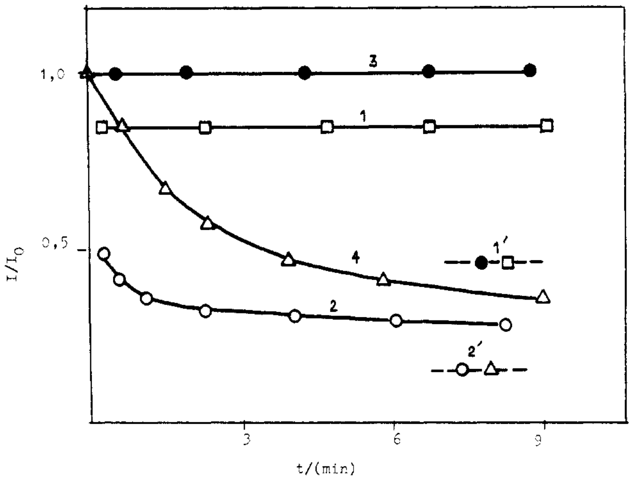

Figure 4. Kinetic curves of reactions 1 and 4 in the mixtures: (1, 2) PMA*Na and PEVPB; (3, 4) PMA*Na and NPEC; [PMA*Na] = 3.8×10^{-4} mol L^{-1}; [PEVPB] = 7.6×10^{-5} mol L^{-1}, [NaCl] = 0 (1, 1′, 3) and 0.03 M (2′, 2, 4). (1′ and 2′) the values of I/I_0 in reactions 1 and 4 for t.

However, the behavior of the system cannot be always explained within the framework of this scheme. The kinetic curves of addition reaction 4 (curve 1) and of exchange reaction 1 (curve 2) at the intermediate value of [NaCl] = 0.01 M are shown in Figure 5. One can see that under these conditions there is actually no exchange of PEVPB chains between the NPEC particles (curve 2). However, during the same time interval, the conversion degree in the addition reaction reaches substantial values, and not only at the initial discontinuity interval but also at the slow stage (curve 1). Thus, in the last case the increase of conversion degree, i.e. of the number of salt bonds between PMA*Na and PEVPB, during the slow stage takes place mainly due to the conformational rearrangements inside the primary nonequilibrium PEC particles formed during the fast initial stage.

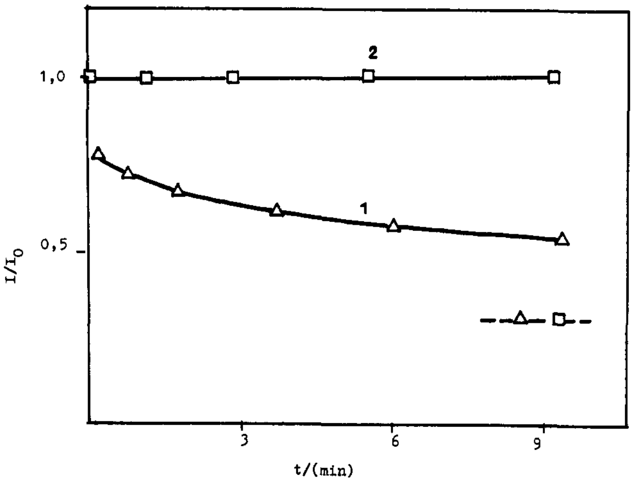

Figure 5. Kinetic curves of reactions 1 and 4 in the mixtures: (1) PMA*Na and PEVP; (2) PMA*Na and NPEC; [NaCl] = 0.01 M; other conditions are the same, see Figure 1.

We have failed to investigate the kinetics of the fast reaction 4 stage by the stopped flow method using the spectrofluorometer "Union Giken" (Japan). This stage is over in less than 5 ms (the "dead" time of the equipment); i.e. the low limit of the corresponding rate constant for a bimolecular reaction is on the order of magnitude 10 L $M^{-1} s^{-1}$. The rate constant of the diffusion collisions, k_{diff}, of macromolecular coils in the diluted solution which can be evaluated by formula 3 and the same approximations for D_Σ and R_Σ is of the same order of magnitude.

Making this comparison, it is possible to conclude that the rate of the fast stage of addition reaction 4 resulting in formation of the primary PEC particles, is probably determined by the diffusion rate of the oppositely charged coils toward each other. Nonequilibrium PEC aggregates can be formed during this stage. Their equilibration requires some rearrangement of interpolyion electrostatic bonds via an intraspecies exchange reaction. However, as it was shown before, the exchange rate strongly depends on ionic strength and is practically zero at zero concentration of a low molecular weight salt. The nonideal regime of mixing of polyelectrolyte solution is obviously conducive to formation of such aggregates including the considerable number of electrostatically complementary chains.

We have discovered such aggregates experimentally while studing the corresponding reaction mixtures by means of quasielastic light scattering technique.

Particles with $D_f = 3.3 \times 10^{-8}$ cm^2 s^{-1} and $2R_\theta = 1300$ Å are detected in the reaction system in 10 s (dead time) after the standard procedure of mixing of polyelectrolyte solutions. These parameters remain almost unchanged during the time when a considerable change in the reaction 4 conversion degree is observed (the flat part of curve 1, Figure 4). This means that the slow stage of reaction 4 does really proceed inside the primarily associated PEC particles. As the equilibrium state is approached, the total intensity of light scattering decreases. Then, 15 h after the beginning of the reaction, it reaches a value too small to measure precisely the size of the PEC particles in the experiment. The intensity of light scattering by specially prepared NPEC solutions with the composition $\phi = 0.2$ and the same concentration as in the reaction mixtures turns out to be too small as well. These facts reveal the rearrangements and disaggregation of the primary associated particles. However such rearrangements one can observe when rather high (more than 70–80%) conversion degrees are achieved in reaction 4.

The picture described above is in accordance with the results obtained while the influence of the reagents mixing technique on the reaction kinetics was studied. Kinetic curve 1, which is presented in Figure 6, corresponds to the formation of NPEC with the composition $\phi = 0.33$ in 0.01 M NaCl solution. The above described method of reagents mixing is used here, i.e. the fast feeding of a small solution volume of one of the polyions (PMA*Na in this case) into the cell with the relatively diluted solution of the other one (PEVPB). Fast and slow parts are well determined on this curve. The kinetic curve undergoes significant changes under the mixing of almost equal volumes of diluted PMA*Na and PEVPB (curve 2) solutions: a much higher degree of conversion is achieved during the formation of primary PEC particles at the fast stage. The slow stage is still present here, but it covers a much smaller interval of the conversion degree.

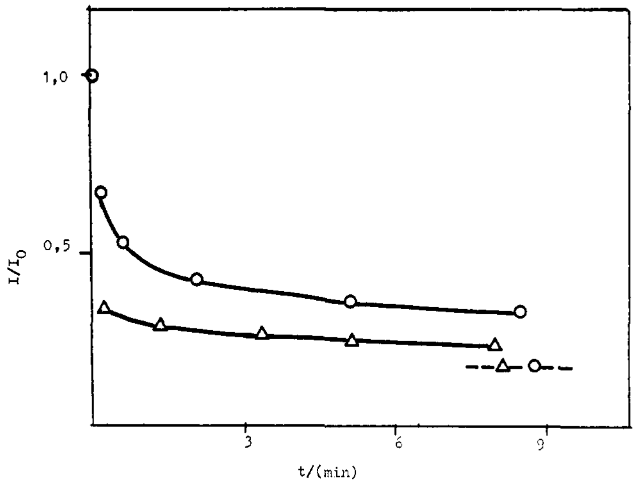

Figure 6. Kinetic curves of reaction 4 in the mixtures: (1) PMA*Na (0.02 mL) and PEVPB (2.0 mL); (2) PMA*Na (1.5 mL) and PEVP (1.0 mL). [PMA*Na] = 3.8×10^{-4} (mol L^{-1}); [PEVPB] = 1.25×10^{-4} (mol L^{-1}). [NaCl] = 0.01 M.

Concluding Remarks

One can point out that interpolyelectrolyte exchange and addition reactions are similar to each other. First, they both proceed with the same set of polyions, and then, the slow stage of the addition reaction may be considered as a special kind of exchange reaction, which is accompanied by the transfer of a GPE chain from one HPE chain to the other one. Meanwhile one must stress the substantial differences and some specific features of reactions. As a result of the exchange reaction proceeding, the total number of interpolymeric salt bonds in the system remains unchangeable, while the addition reaction leads to the formation of NPEC, i.e. interchain salt bonds appear as the result of this reaction. It can be seen that such differences cause the difference in driving forces of these reactions. In the case of the addition reaction, the driving force is connected to a great extent with the increase of the system entropy due to an increase of the fraction of noncondensed low molecular weight counterions and the final formation of equilibrium NPEC. In the case of the exchange reaction, the driving force of the reaction is due to a decrease of free energy in the reaction as a result of redistribution of interpolymeric salt bonds between NPEC and free HPE* chains. The distinction mentioned above causes (in turn) the peculiar feature of the kinetics and proceeding regularities of addition and exchange reactions. The kinetics of interpolyelectrolyte exchange reaction can be described in terms of an irreversible second-order reaction and characterized by only one rate constant. The transfer of a GPE chain from HPE to HPE*, i.e. the elementary act of this reaction, takes place in the united

HPE*–NPEC coil, the lifetime of which is much less than the half-conversion time in the exchange reaction itself.

As regards the interpolyelectrolyte addition reaction, the kinetics of such a reaction have a sophisticated character and cannot be described in terms of formal kinetic schemes of the first- and second-order reactions. One can consider the slow stage of this reaction as a peculiar relaxation process which is accompanied by the increase of the conversion degree within the initial associated complex particles, having appeared at the first, fast stage of the reaction. It is essential to point out that the lifetime of such associated complex particles is comparable with the half-conversion time in this reaction itself, and self-disaggregation of the associated particles takes place only with the completion of the addition reaction.

The generally accepted terminology for interpolyelectrolyte reactions,[1-3,23] which has been used here for definition of the exchange reaction, has a dubious sense in our variant. The exchange reaction, in our case, proceeds as an irreversible one and from this point of view cannot be called an exchange one. However, from the terminological point of view, this reaction proceeds with the chemically identical HPE chains, the only difference consists in the presence of a small amount, less than 1 molar %, of pyrenyl chromophoric groups in HPE* coils, which basically predetermined the irreversible character of such a reaction. The differences here deal mainly with terminology of interpolyelectrolyte reactions. We believe that the mechanism of the exchange reaction is more general and may be applied to reversible as well as irreversible interpolyelectrolyte exchange reactions.

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Registry No. NaCl, 7647-14-5; PMANa/PEVPB complex, 86073-99-6.