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FORMATION OF POLYELECTROLYTE COMPLEXES AND THEIR STRUCTURES

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ABSTRACT

When a polycation and a polyanion are mixed together in an aqueous solution, a polyelectrolyte complex is formed. In general, an equimolar complex is formed by mixing oppositely charged strong polyelectrolytes. However, integral-type polycations provide nonstoichiometric complexes. In the case of the complexation of polycations with weak polyacids, the composition and the structure of the polyelectrolyte complexes obtained depend on the degree of neutralization of the polyacid, polymer structure, hydrophobicity, the concentration of the complex, pH, ionic strength, and so on. Complex formation proceeds cooperatively, and the stability constant increases with the degree of polymerization, i.e., the charge number on one chain. When a polyelectrolyte is added to the polymer complex, a cooperative interpolymer substitution occurs if the adding polymer can interact more strongly with the constituent of the complex. The process of polyelectrolyte complex leading to the supermolecular structure can be divided mainly into three classes: 1) primary complex formation, 2) formation process within intracomplexes, and 3) intercomplex aggregation.

INTRODUCTION

Biofunctions such as gene information, selective reactivity of enzymes, and antigen–antibody reactions are based principally on the complexation between biopolymers such as proteins, polysaccharides, and nucleic acids or complexation of

biopolymers with low-molecular-weight compounds. Since many secondary binding interaction forces (electrostatic, dipole, hydrogen-bonding, hydrophobic) govern the higher-ordered structure of proteins, it is difficult to understand the fundamental features of complexation in biological systems without basic knowledge about those interactions. Therefore, studies about the formation of interpolymer complexes of simple polymers and their structures are necessary [1]. Since synthetic polymers have simpler structures than biopolymers, the functional phenomena occurring in complicated reactions in living cells may be more easily understood. Therefore, suggestions about the design of functions on the polymer chains are given by the study of the mechanism of complexation between synthetic polymers.

This review summarizes the formation and structure of polyelectrolyte complexes. The cooperative phenomena of the complexation are mainly discussed.

CHARACTERISTICS OF POLYELECTROLYTE COMPLEXATION

Polyelectrolyte Complex between Strong Polyelectrolytes

There are two types of polycations. One is pendant-type polycations which have charges in the side groups and the other is integral-type polycations which have charges in the chain backbone. The characteristics of polyelectrolyte complexes between poly(sodium styrene sulfonate) (NaSS) and a series of integral-type polycations are described, and they are compared with pendant-type polycations [2]. Figure 1 shows the relationship between the yield of polyelectrolyte complexes and the mixing ratio of their components. By using a pendant-type polycation such as quarternarized poly(4-vinyl pyridine) [Fig. 1(a)], the yield of the complex reaches a maximum (about 100%) at a mixing ratio of 1, regardless of the mixing order. In other words, the complex can always be obtained as an equimolar complex. On the other hand, when NaSS is added to an integral type polycation (3X) [Fig. 1(b), open circles], the yield also reaches a maximum at a mixing ratio of 1. However, further addition of NaSS causes a linear decrease in the yield, followed by complete dissolution at $[\text{NaSS}]/[3\text{X}] = 3$. In a reverse order of the addition of 3X to NaSS [Fig. 1(b), filled circles], no precipitation of the complex was obtained at $[3\text{X}]/[\text{NaSS}]$ ratios less than $1/3$, and then the yield of the precipitation increases linearly until an equimolar mixture is reached.

These data demonstrate that in the region of a $[3\text{X}]/[\text{NaSS}]$ ratio higher than unity, an equimolar water-insoluble polyelectrolyte complex is obtained, whereas in the presence of excess polyanions (NaSS) a water-soluble complex with the composition $[3\text{X}]/[\text{NaSS}] = 1/3$ should be formed. This implies that the effect of the position of the cationic site (pendant or integral type) on complex formation may be expressed by the complexation scheme shown in Fig. 2. Compared with the pendant-type polycation, cationic sites of the integral-type polycation are only slightly hindered. Thus, in the case of a pendant-type polycation, when an equimolar complex is once formed, excess NaSS cannot attack the cationic sites in the complex from the opposite direction, while in systems of integral-type polycations, excess NaSS can attack the cation sites of the equimolar complex from the other directions to form a soluble complex. In this system, Na^+ , counterions of NaSS, may weaken the electrostatic interaction between polyelectrolytes, leading to enhancement of the solubility of the complex.

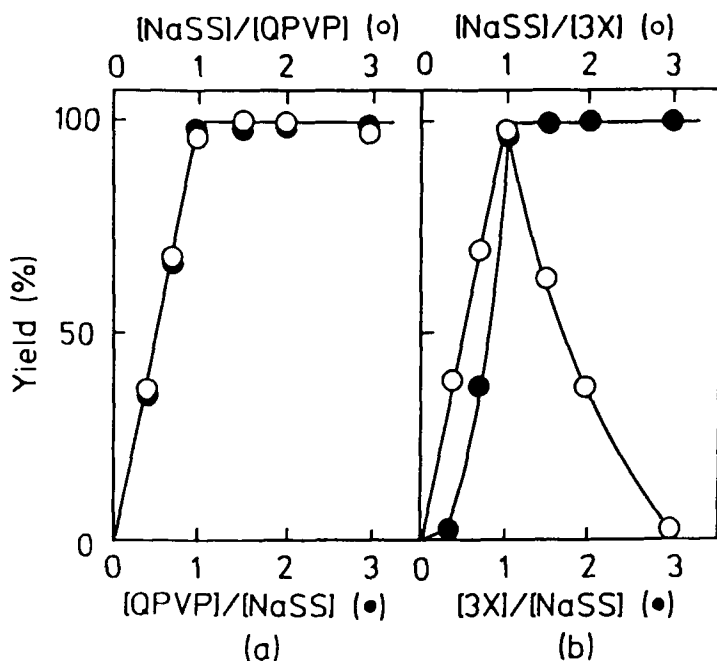
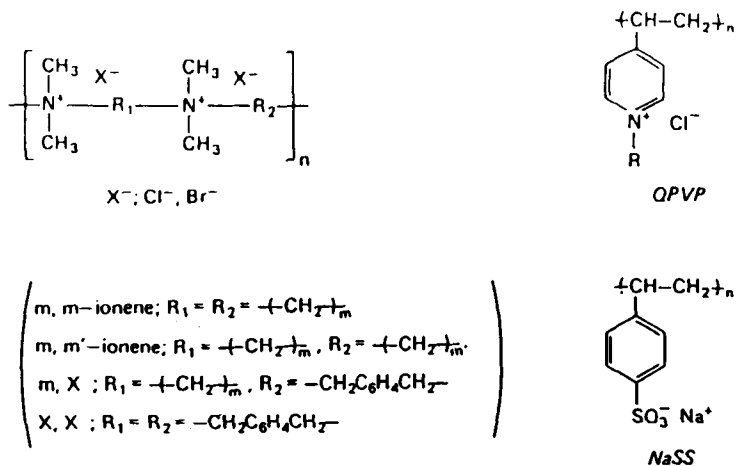
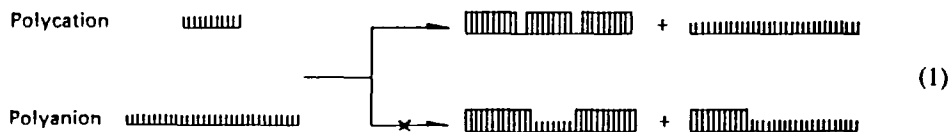


FIG. 1. Effect of the structure of polycations on the yield of polyelectrolyte complexes. (a) QPVP-NaSS system, (b) 3X-NaSS, (O) the NaSS solution was added to the polycation solution, (●) the polycation solution was added to the NaSS solution.

Another interesting result obtained from these findings is that the yield is proportional to the added amount of each polymer component. Furthermore, even when the degrees of polymerization of the two polymer components differ, identical phenomena are observed. These results suggest an "all or none type" complex formation mechanism as shown in Eq. (1).



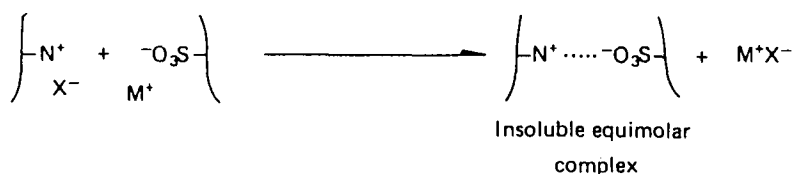
This implies that the reactivity of the polyanion chain partially covered with the polycation may be considered to be higher than that of the free chain, probably owing to the changes of conformation, dissociation, and microenvironment in the domain of the polymer chain. Therefore, there are only two species: one is completely neutralized polyelectrolyte complexes and the other is free polyelectrolytes in the solution.

Polyelectrolyte Complexes between Weak Polyacids and Polybases [3]

When a weak polyacid or a weak polybase is used as the polyelectrolyte component, the dissociation state of the weak polyelectrolyte directly affects the complexation ability and the composition of the complex obtained. The various compositions of polyelectrolyte complexes are formed in pairs of strong polybases and weak polyacids [the degree of neutralization (α) of the weak polyacids is zero] as listed in Table 1.

When α is zero, poly(carboxylic acid)s scarcely dissociate in solution. However, the addition of polycations can induce the dissociation of poly(carboxylic acid) up to about 20–25% (assuming that all dissociated ionic sites can react linearly with complementary active sites). The composition of PMAA–10,10-ionene of 9:1 and that of PAA–10,10-ionene of 1:1 may be explained from the fact that since 10,10-ionene forms a relatively rigid compact complex with PMAA due to its higher

(a) Pendant-type polycation/pendant-type polyanion



(b) Integral-type polycation/pendant-type polyanion

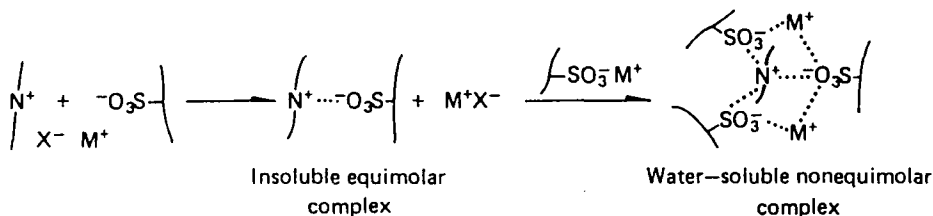


FIG. 2. Schematic representation of the effect of the position of cationic sites of polycations on the formation of polyelectrolyte complexes.

TABLE 1. Composition of the Complexes of Poly(Carboxylic Acid)s with Various Polycations^a

Poly(carboxylic acid)	Polycations	Composition ^b
PAA	QPVP	2:1
	PLL·HBr	2:1
	PDMAEMA·HCl	2:1
	5,6-Ionene	3:1
	2,5-Ionene	2:1
	10,10-Ionene	1:1
	2X	4:1
	3X	4:1
PMAA	PVBMA	2:1
	10,10-Ionene	9:1
	2X	5:1
	3X	5:1
PIA	2X	3:1
PGA	3X	6:1

^aThe degree of neutralization of poly(carboxylic acid)s is 0.

^bMolar ratio of repeating unit ([poly(carboxylic acid)]/[poly-cation]).

hydrophobicity than PAA, and the number of real active sites becomes very low. In other systems, in general, when the charge density of the polycation increases, the dissociation of poly(carboxylic acid) tends to be induced to form a complex with a composition close to unity.

Figure 3(a) shows the potentiometric titration curves of PMAA in the absence and the presence of polycations 2X and XX in comparison with their low molecular weight analogs 2B and BT. Figure 3(b) shows the ratios of the proton concentration in the absence and the presence of polycations. In the presence of polycations, the pH of the PMAA aqueous solution is remarkably lowered. This phenomenon is caused by the release of protons accompanied by the formation of the polyelectrolyte complexes. On the other hand, in the presence of low molecular weight analogs, the pH changes only slightly, meaning that a stable complex is not formed in these systems. These results support the belief that the chain length of the polymer component is one of the most important factors for the control of complexation.

As shown in Fig. 3(b), only in the PMAA system is a large peak observed at a degree of neutralization of 0.1. It is known that the dissociation of PMAA is greatly depressed in the low pH region by its comparatively rigid conformation. Thus, a large peak at $\alpha = 0.1$ means that polycations can effectively eliminate the inter-chain hydrophobic interaction of PMAA, resulting in facile dissociation of PMAA. In this region, XX is more effective than 2X. However, in the region of higher degrees of neutralization, 2X forms complexes more readily than XX because of the higher charge density of 2X. Tsuchida et al. found that the strength of hydrophobicity of integral-type polycations increases in the order 10,10 > 8,8 > 6,6 = XX = 6X > 2X > 4,4-ionenes [2].

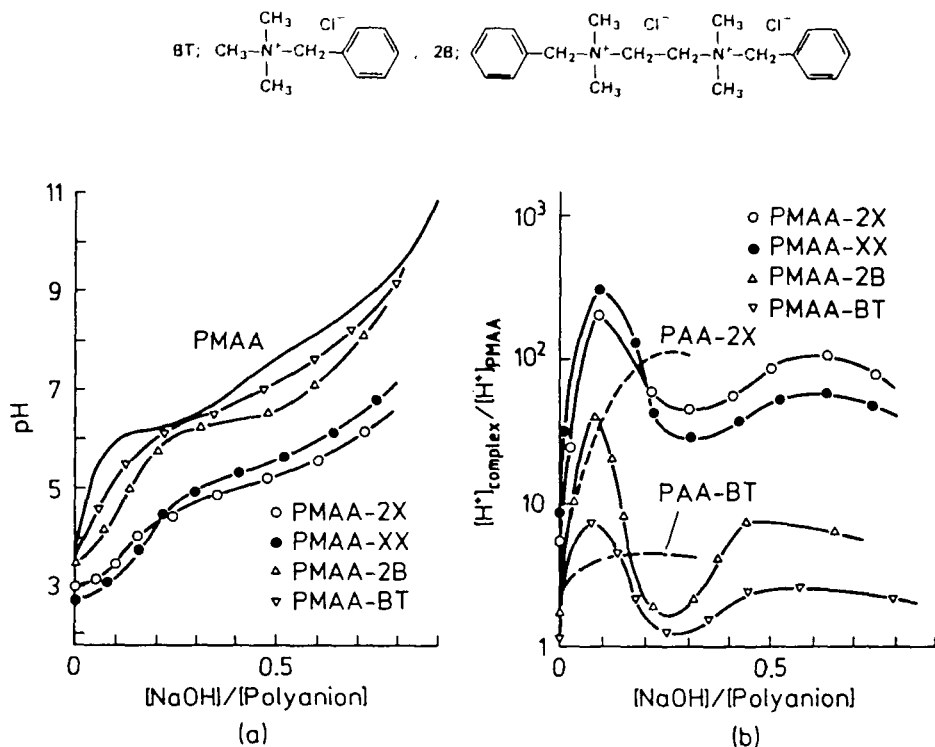


FIG. 3. Acceleration of dissociation of poly(carboxylic acid) at complexation. (a) Potentiometric titration, (b) amount of released protons.

The degree of induction of the dissociation of PMAA in the presence of various polycations is estimated from its apparent dissociation constant ($\text{p}K_a$) as calculated from the potentiometric titration results (shown in Fig. 3) by using the Henderson-Hasselbach equation as listed in Table 2 [4]. In the presence of polycations, $\text{p}K_a$ and n' (one of the interaction parameters relative to adjacent ionic sites) decrease, and this shows the higher influence on $\text{p}K_a$ in comparison with the corresponding monomers.

Polyelectrolyte Complex with Polycation and Polyacid with Different Degree of Neutralization [5]

When a weak polyacid and/or a weak polybase are used as polyelectrolyte components, the dissociation state of the weak polyelectrolyte directly effects the complexation ability and the composition of the complex obtained. Figure 4(a) summarizes the relationship between the composition of a polyelectrolyte complex ($[\text{cation}]/[\text{carboxylic acid}]$) and the degree of neutralization (α) of poly(carboxylic acid). On the assumption that polyelectrolyte complexes are formed upon complete neutralization, their composition r is denoted by the following equations:

TABLE 2. Dissociation Constants (pK_a) of PMAA and Its Complexes^a

Sample	pK_a	n'
PMAA	7.3	2.3
PMAA-BT	6.3	2.2
PMAA-2B	6.4	2.2
PMAA-2X	4.3	1.4
PMAA-3X	5.5	—
PMAA-XX	4.8	—
PMAA-PEO ($\overline{M}_w = 1,300$)	7.5	—
PMAA-PEO ($\overline{M}_w = 25,000$)	7.9	—
MAA ^b	3.5	1.0

^aHenderson-Hasselbach equation: $pH = pK_a - n' \log [(1 - \alpha)/\alpha]$.

^bMethacrylic acid monomer.

$$[PC] = [PA]\alpha' \tag{2}$$

$$r = [PC]/[PA] = \alpha' \tag{3}$$

where [PC] and [PA] are the molar concentrations of the polycation and the polyanion [in this system poly(carboxylic acid)], respectively, and α' is the degree of dissociation of PA in the presence of PC (calculated from pK_a in Table 2), provided that the degree of dissociation of PC is unity. The value of r ([cation]/[carboxylic acid]) is 1/5 at $\alpha = 0$, and the ratio approaches unity with α . Finally, it becomes unity at $\alpha = 1$. The complex having a [cation]/[carboxylic acid] ratio of 1/5 is

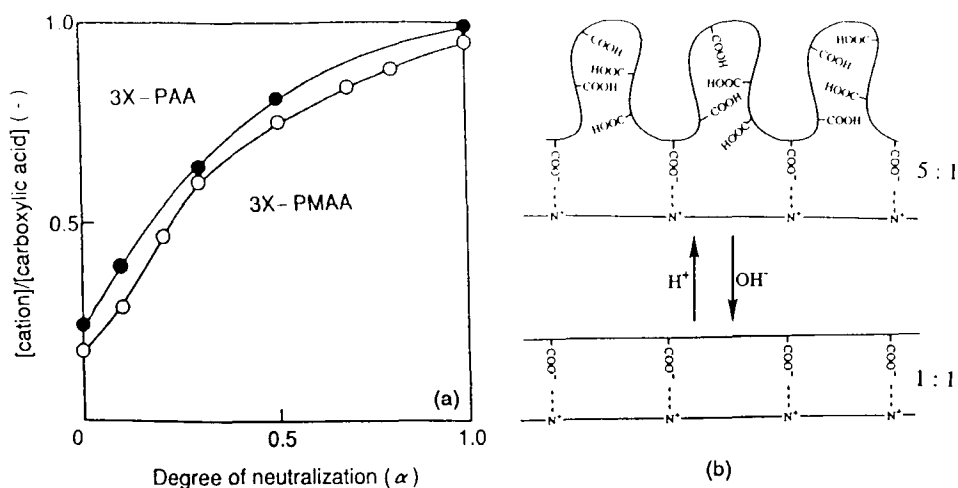


FIG. 4. (a) Relationship between the composition of polyelectrolyte complex and the degree of neutralization. (b) Structural change of polyelectrolyte complex.

considered to have a loop structure, as shown in Fig. 4(b). It converts to the ladder structure as neutralization proceeds. In the case of PAA, the experimental values of r are in good agreements with the theoretical values, as shown in Fig. 4(a).

Phase Diagrams of Polyelectrolyte Complexes

Figure 5 shows the phase diagrams of the complex of PMAA with 2X [6]. The complex is formed in dilute solution but it is not formed in a concentrated solution at low pH because of the suppression of the dissociation of PMAA. At concentrations around 10^{-2} mol/L in repeating units, the complex is obtained as a curdy precipitate at $\alpha = 0$, whereas it separates as a complex coacervate at $\alpha = 1$. The effects of ionic strength in a wide pH range on complexation is shown in Fig. 5(c). A boundary line between complex coacervates and precipitates is drawn at about pH 6. At higher pH, the composition of the complex is unity. When the ionic strength is increased to more than 0.7, the complex coacervates are dissociated into the individual polyelectrolyte components because of the shielding effect of microsalts. In contrast to this phenomenon, the precipitate is not dissociated.

Figure 6 shows the schematic diagrams of such phase changes of the polyelectrolyte complexes composed of a weak polyacid and a strong polybase [1]. PMAA cannot dissociate at extremely low pH and very high concentration (I). Under these conditions, the complex is not formed because the amount of dissociated carboxylate anions is insufficient for the generation of a stable complex. On increasing pH or upon dilution (II), PMAA can form a stable complex with a polycation because the amount of carboxylate anionic sites exceeds a certain critical value. At this stage

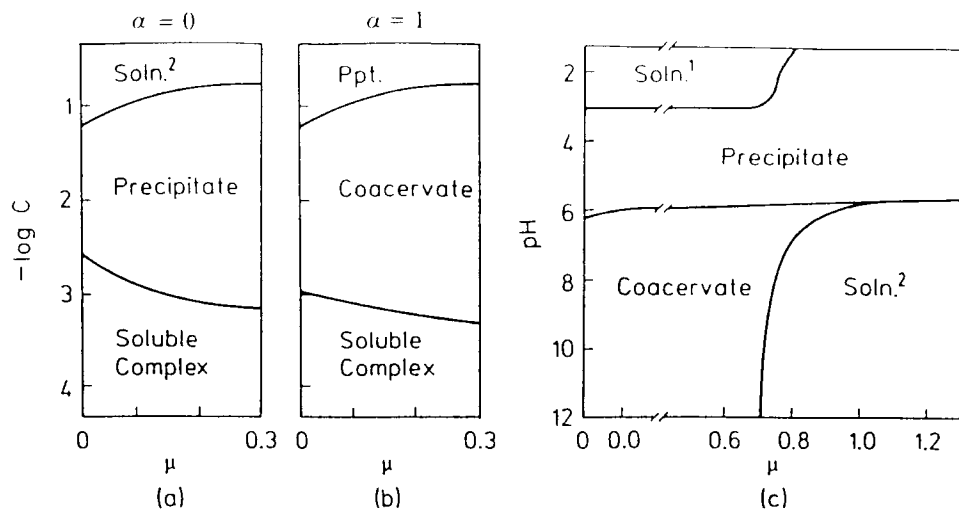


FIG. 5. Phase diagrams of PMAA-2X complex. (a) and (b): Ionic strength (μ) as a function of the concentration of the complex at the degree of neutralization of PMAA (α) = 0 and (α) = 1, respectively. (c): Dependence of pH on μ at 25°C. Concentration of the complex is 5×10^{-3} (mol/L). Soln.¹ = complex is formed (soluble under this condition), Soln.² = complex is not formed.

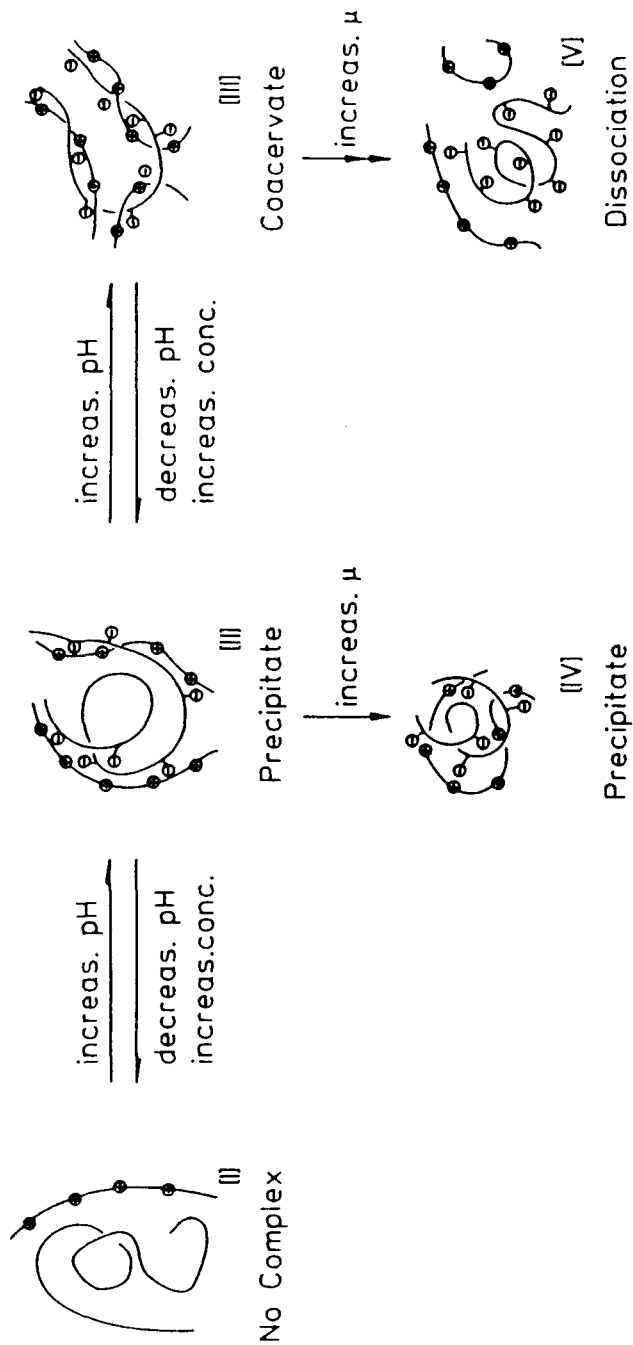


FIG. 6. Schematic representation of the equilibrium for the phase changes of the PMAA-integral type polycation complex.

the complex is obtained as a curdy precipitate. A further increase of ionic strength (IV) leads to a decrease in solubility. Thus the complex yield increases with decreasing solubility, and the complex is obtained as a more compact precipitate. At $\text{pH} > 7.0$, an equimolar complex coacervate is generated because of the complete dissociation of PMAA (III). In this pH range, hydrophobic interaction may be diminished by the considerable hydration. When a large amount of microsals is added to the system beyond $\mu = 0.7$, the complex coacervate is broken (V).

COOPERATIVE PHENOMENA IN COMPLEXATION

In the case of the complexation of a long polyanion chain (l^-) with a short polycation ($l^+ < 1/10l^-$), the subsequent complexation of polycation to the partly complexed polyanion occurs prior to other polyanion chains as represented by Eq. (1). At this time there exists a critical chain length of polycation. To demonstrate such a cooperative interaction experimentally, the relationship between the stability constant of the polyelectrolyte complex of PMAA with quarternize oligoethyleneamines and the chain length of the oligocations was studied [7, 8]. As shown in Fig. 7, the stability constant of the complex increases exponentially and the free energy change in the complex formation increases almost linearly with the degree of polymerization of oligocations (≤ 4). These relationships are described by the equations

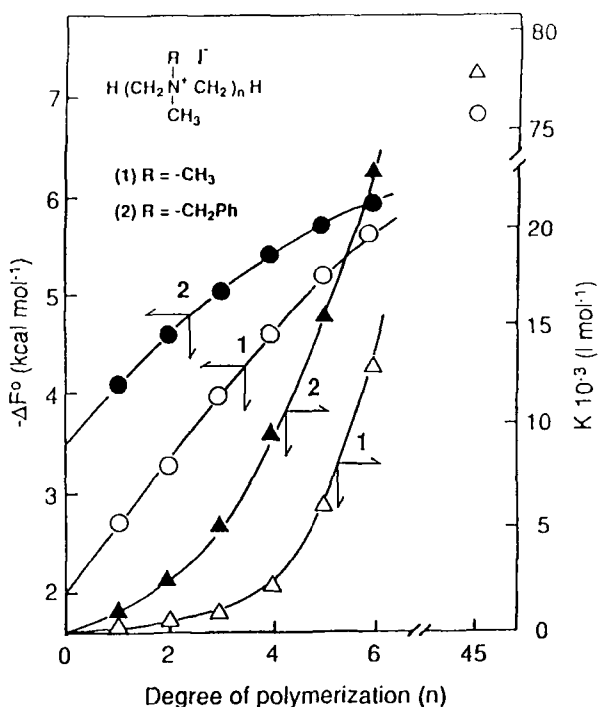


FIG. 7. Cooperativity in the formation of polyelectrolyte complexes between oligocations and PMAA.

TABLE 3. Complex Formation Parameters^a

Complex	<i>A</i>	<i>B</i>	α	β
PMAA-(1)	31.9	1.0	0.63	2.05
PMAA-(2)	49.0	0.8	0.47	3.66

$${}^aK = Ae^{Bn}, -\Delta G^\circ = \alpha n + \beta.$$

$$K = Ae^{Bn} \tag{4}$$

$$-\Delta F^\circ = \alpha n + \beta \tag{5}$$

In Eqs. (4) and (5), *B* represents the basic bonding constant and α is comparable to a cooperative coefficient. The values of *A*, *B*, α , and β are compiled in Table 3. In the range of the chain length of these oligocations, the standard free energy change of complex formation decreases by about 0.6 kcal/mol upon the addition of one cationic residue. The difference of β (about 1.6 kcal/mol) between two different types of cations may be due to the variation of the hydrophobic natures of benzyl and methyl residues. When the total free energy change exceeds the kinetic energies of the polymer chain components, a stable interpolymer complex is formed. Therefore, a stable complex is not formed if the degree of polymerization of the oligocation is below 4.

SUBSTITUTION REACTION [9]

If a polymer (P1) is added to a solution of a polymer complex (P2-P3), and P1 can interact with P2 more strongly than with P3, the substitution reaction of P3 and P1 should take place. In this system, a cooperative interpolymer substitution reaction is

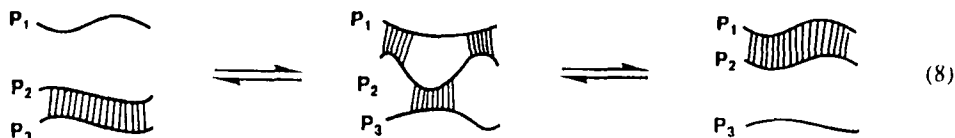


Such substitution reactions may proceed via two types of mechanisms:

(1) An open system:



(2) A closed system:



In an open system, once the complex is formed it dissociates into two components according to the change of environmental factors, and then a different pair of

TABLE 4. Substitution Reaction of the Interpolymer Complexes in the System of PMAA-POE-2X^a

pH	Yield, mg	Elemental analysis				IR, cm ⁻¹	OD ₂₆₉
		C	H	N	C/N		
1.8	58.3	54.3 ₄	7.8 ₁	0	∞	1750	1.9
5.0	59.6	52.1 ₄	7.4 ₃	1.8	29.0		1.4
11.0	98.6	63.8 ₀	9.4 ₅	6.5 ₈	9.7	1400	≈ 0

^aInitial concentration (mg): PMAA = 43.5, POE = 22.0, 2X = 72.8.

component polymers forms another type of complex. In a closed system, before the complex formed is completely distorted, the third component polymer interacts with the complex to form a polymer complex of ternary components, and then the first component polymer is dissociated from the ternary complex. In the closed system, the substitution reaction, especially the releasing process of the first component polymer, might be accelerated when the interaction force between a parent polymer and the third component polymer chain is stronger than that of the two original components.

The results of the substitution reaction of the 2X-POE-PMAA system are shown in Table 4 and Fig. 8. The POE-PMAA complex and the 2X-PMAA com-

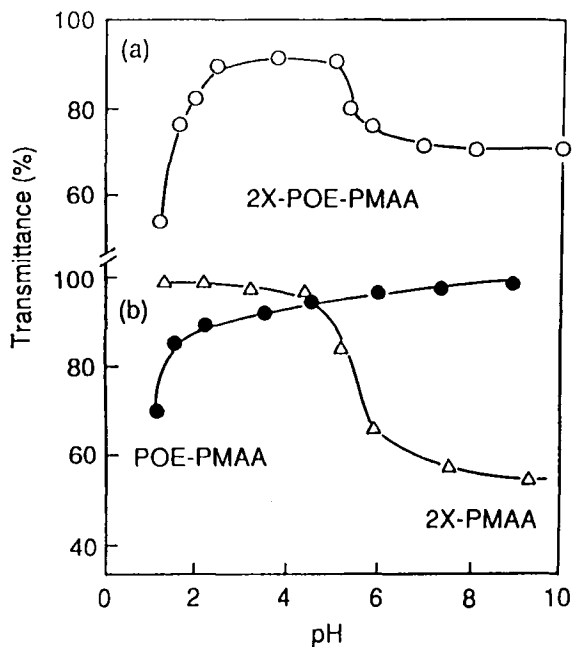
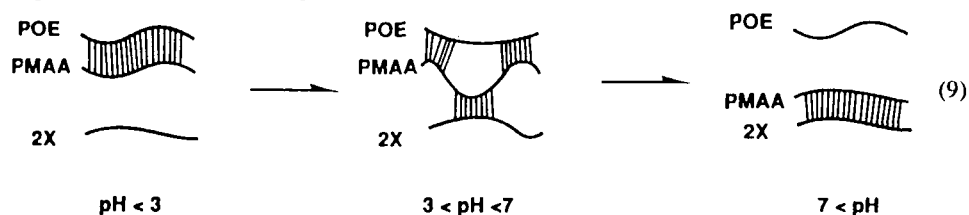


FIG. 8. Substitution reactions in the 2X-POE-PMAA system at different pHs.

plex are preferably formed in low and high pH region, respectively, as shown in Fig. 8(b), but in the intermediate pH region the 2X-POE-PMAA ternary polymer complex is formed (proved in Table 4), except that the precipitate yield is low [see Fig. 8(a)]. That is, in the 2X-POE-PMAA system a substitution reaction takes place through a closed system. The low yield of the ternary polymer complex is explained by the following scheme:



That is, a part of the nonbonding surplus component polymer chain makes the complex itself hydrophobic, and the ternary polymer complex is very soluble in an aqueous solution. As a result, studies of substitution reactions are expected to clarify the polymer effects of synthetic polymers and the fundamental phenomenon of the specific reaction of polymers in biological systems.

SUPERMOLECULAR STRUCTURE

The precipitate of the polyelectrolyte complex formed by mixing aqueous solutions of oppositely charged polyelectrolytes at concentrations higher than 10^{-1} (mol/L per repeating unit) assumes a poor crystalline structure. Such primary com-

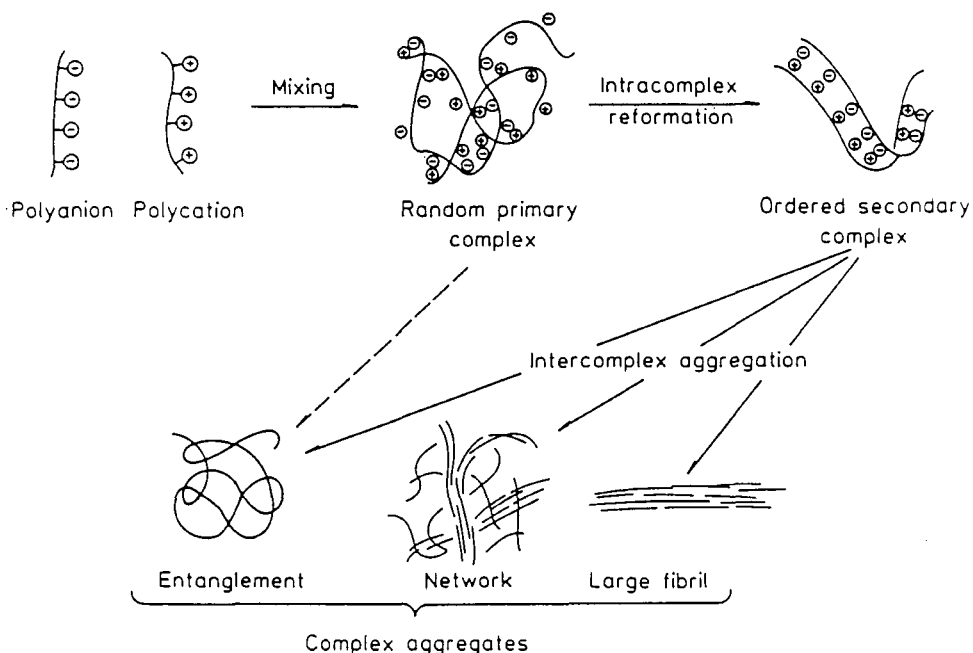


FIG. 9. Schematic representation of the aggregation of polyelectrolyte complexes.

plexes linked by Coulomb forces are formed instantaneously and irregularly [10, 11]. At lower concentrations where the complexes do not precipitate, the primary complexes exist as small particles in solution. By means of centrifugation, part of the complex is separated from the solution. If the supernatant solution, which is clear, is kept under a nitrogen atmosphere at room temperature, fine fibers are formed within about 10 days after mixing, while complex aggregates are obtained within about 4 days after mixing the aqueous solutions in the absence of microsals. In the presence of microsals (0.2 mol/L), the separation of the aggregates takes much longer time, e.g., more than a week. This salt effect coincides well with the dissociation states of the polyelectrolytes, i.e., the aggregation of polyelectrolytes starts when the electrostatic repulsion is sufficiently weakened. Furthermore, the aggregation of the polyelectrolyte complex is accelerated by heating and stirring.

The formation process of polyelectrolyte complexes may be divided into three main classes (Fig. 9):

1. Primary complex formation
2. Formation process within intracomplexes
3. Intercomplex aggregation process

The first step is realized through secondary binding forces such as Coulomb forces immediately after mixing oppositely charged polyelectrolyte solutions. This reaction is very rapid. The second step proceeds within the order of an hour and involves the formation of new bonds and/or the correction of the distortions of the polymer chains. The third step involves the aggregation of secondary complexes, mainly through hydrophobic interactions. Such an aggregation is influenced by many factors, e.g., the structure of the polymer components and the complexation conditions. The final aggregates of the polyelectrolyte complexes are insoluble in ordinary solvents, and the molar ratio of the repeating units of the polymer components in the aggregates is almost unity.

Several studies on the supermolecular structure of aggregated interpolymer

TABLE 5. Formation of Higher-Order Aggregates of Polymer Complexes Composed of Synthetic Polymers^a

Polymer complex	Morphology
P4VP-DNA ^b	Fibrous (partially spherical)
PLL-PMAA	Curdy, fibrous
P4VP-PSS	Fibrous
(template polymerization)	
2X-PMAA	Fibrous (network)
2X } (PMAA	Fibrous (network)
3X } (PGA	
6X }	
PVBMA-PMAA	Needle-like
PLL-PAA	Globular

^aPLL = poly(L-lysine). PGA = poly(L-glutamic acid).

^bNo synthetic deoxyribonucleic acid.

complexes performed by optical and electron microscopies have been reported [12–16]. The results obtained are summarized in Table 5. From the results of x-ray analysis and polarized light microscopy, it is suggested that the assembly forms a certain high-order (supermolecular) structure. Moreover, it should be noted that solvent effects are also clearly observed. The polyelectrolyte complex prepared immediately after mixing the polyelectrolyte components in water is completely amorphous whereas the one obtained in methanol at 64.5°C exhibits a fibrous structure with optical activity. Therefore, the supermolecular structure is affected by the type of polymer components used.

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