These studies point up the dramatic contrast existing in solvent effects. Organic solvents appear remarkably similar in influence, as noted earlier. Yet with polar solutes, water appears to destroy nearly all vestiges of thermal diffusion. The effect is undoubtedly attributable to some aspect of solute–solvent interaction, perhaps the presence or absence of hydrogen bonding. Unfortunately, sufficient data do not exist, particularly in polymer systems, to discern clear solute–solvent trends. While the present study fills a wide gap in the study of solvent and temperature effects, an equally comprehensive study of different solute types is needed to arrive at definitive correlations regarding molecular structure factors in thermal diffusion.

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Aggregation of Polyion Complexes between Synthetic Polyelectrolytes

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ABSTRACT: Dissolving polyion complexes in the aqueous solution aggregate time dependently to a highly ordered fibrous structure. Poly(carboxylic acid)s and integral type polycations with quaternary ammoniums on their chain backbones are used as polyanion and polycation, respectively. The variety of the component poly(carboxylic acid) influences surface condition and diameter of fibrous aggregates and the chain lengths or rigidity of polycations change their basic shapes. Hydrophobic interaction is the main cause for the spontaneous aggregation of polyion complexes.

In biological systems, complicated and specific functionalities are caused by the regular molecular aggregation, for example, folding, renaturation, self-assembly, and so on. In recent years the studies of the higher-ordered structures of biopolymers have been developed remarkably. However, the general rule for molecular aggregation has not been established yet even in biological systems because of the complexity and specificity of biopolymers.

In comparison with biopolymers, synthetic polymers have simple structures. So they would have advantages over confirming and understanding the fundamental phenomena of the complicated reactions in vivo. For this reason, the study about the mechanisms of the complexations between synthetic macromolecules must give important suggestions to design the functions on polymer chains. Some works about the complexation through such secondary binding forces as van der Waals,[1] Coulombic force,[2,3] hydrogen bond,[4,5] and hydrophobic interaction have been reported. Such primary complexes obtained from the contact of synthetic component polymer chains take further aggregation with each other under particular conditions like biological systems.[6,7]

The authors have already reported the primary complexation mechanisms between oppositely charged synthetic polyelectrolytes (polyion complex). The compositions of the complexes are determined mainly by the degree of dissociation of component polyelectrolytes,[8] and each active site reacts cooperatively.[9] Moreover, they reported the phenomenon that the primary complexes begin to show the phase separation time dependently in the form of the highly ordered fibrous structure.[10]

Experimental Section

Materials. Poly(methacrylic acid) (PMAA) and Poly(acrylic acid) (PAA). Purified methacrylic acid and acrylic acid were polymerized with $K_2S_2O_8$ as an initiator in aqueous medium. The monomer concentration was 0.2 mol/l. The reaction products were reprecipitated into methanol–ethyl acetate. The molecular weights of the polymers were calculated from viscosity measurements;[11,12] the number average molecular weights of PMAA and PAA were 6.8×10^4 and 4.9×10^4, respectively.

Poly(L-glutamic acid) (PGA). PGA was prepared by exchanging counterions of a commercial poly(sodium L-glutamate) (M_n = 50 000) before use. An aqueous solution of poly(sodium L-glutamate) (0.5–1.0%) was passed through a column 3 cm in diameter and 30 cm in length, filled with an ion-exchange resin, Dow Chemical IR-120; the pH of the passing solution was 3.3. Then pH of the solution was controlled by the addition of 0.1N NaOH aq. solution.

Polycation. Polycation polymers of integral type with quaternary ammoniums on their chain backbone, poly(*N,N,N′,N′*-tetramethyl-*N-p*-xylylenealkylenediammonium dichloride), $[N^+(CH_3)_2(CH_2)_mN^+(CH_3)_2CH_2PhCH_2{\cdot}Cl^-{}_2]_n$, where m = 2 (2X), m = 3 (3X), and m = 6 (6X), were prepared in the manner similar to our previous paper.[13] Intrinsic viscosities of 2X, 3X, and 6X were 0.4, 0.1, and 0.1, respectively, in KCl aqueous solution (0.1 mol/l.) at 30 ± 0.1 °C.

Complex Formation and Measurement. Microscopic Observation. The aqueous solution of poly(carboxylic acid) (2.0×10^{-2} unit mol/l.) was added to one of a polycation (2.0×10^{-2} unit mol/l.) (mixing molar ratio, [anionic sites of poly(carboxylic acid)]/[cationic sites of polycation] was equal to 1:1) with stirring. The precipitate immediately after mixing for 5 min was separated from the solution by means of centrifuge (15 000 rpm, 15 min). The supernatant solution was quite clear and no aggregate was observed even by an optical microscope. This supernatant solution was left as it was under nitrogen atmosphere at room temperature. The sample for an optical microscope was taken every 10 or 25 h from 100 to 500 h from this supernatant complex solution (× 125–× 1250, Nikon-SUR-UT). The sample for an electron microscope was prepared by shadowing the same sample as an optical microscope with gold under vacuum on a thin carbon layer. The electron micrographs were taken by a scanning electron microscope (× 1 000–× 20 000, Hitachi-SS2).

Conductivity. The aqueous solution of PMAA (its degree of neutralization (α) was equal to unity, 5.0×10^{-3} unit mol/l.) was added to the one of 2X (5.0×10^{-4} unit mol/l.) or to water. The conductivities of these solutions were measured in a specific cell with a platinum–platinum (black) electrode at 30 °C in nitrogen atmosphere. The water used here had a specific resistance more than 3.5×10^6 ohm cm.

Transmittance. The aqueous solutions of PMAA and 2X (both concentrations were equal to 2.0×10^{-2} unit mol/l.) were mixed with stirring (unit molar ratio, [PMAA]–[2X], was equal to unity). The supernatant solution of centrifuge was titrated by NaCl aqueous solution (1.0 mol/l.). Transmittance of this solution was measured by a photoelectric colorimeter (Shimadzu Spectronic 20) at 420 nm. The limit of error by the difference of wavelength was ±5% at most.

X-Ray Diffraction. X-ray diffraction was taken on the photographic plate mounted perpendicular to the incident beam behind the sample of the aggregate of 2X–PMAA (40 KV, 10 mA, Cu-Target).

Aggregation of Polyelectrolyte. The aqueous solutions of polyelectrolytes (10^{-2} unit mol/l.) were left as they were with micro salts (10^{-1} mol/l.). The microscopic observation was done in the same manner as the one of complex aggregates.

Results

Precipitate of the polyion complex, formed by mixing aqueous solutions of oppositely charged polyelectrolytes at the concentration more than 10^{-1} (unit mol/l.), takes an amorphous structure. Such primary complexes through Coulombic force are formed suddenly and irregularly. At more dilute concentration where the complex precipitate is avoided, the primary complexes are dispersed as small particles in the solution. By means of the centrifuge a part of the complex is separated from the solution. If the supernatant solution, which is clear, is left as it is under nitrogen atmosphere at room temperature, fine fibers are formed time dependently within about 10 days after mixing. Figure 1 shows the time-dependent electron micrographs of the aggregation in the 2X–PMAA system. Within 4 days after mixing the fibrous aggregates are separated from the solution (A) and then they continue to aggregate in all directions to a network structure (B). At last these aggregates can be observed even with the naked eye (C). Many branches are observed clearly on the fine fibers in Figures 1A and 1B. Figure 2 shows magnified photographs of this part by the electron microscope. It is found that they are at right angles to the main chains and that their diameters are all the same as those of the main chains, i.e., 2 μ. Similar phenomena are observed also in the other complex systems or in the only polycation systems. However, the aggregates of poly(carboxylic acid)s hold no branches.

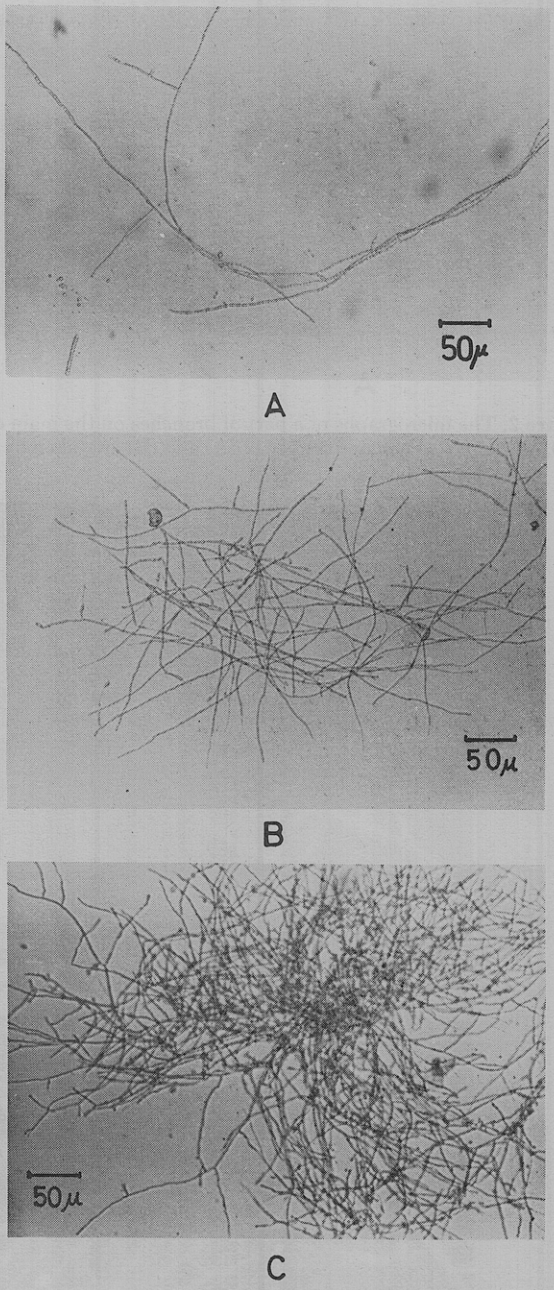

Figure 1. Time dependence of the aggregation process in the PMAA–2X system (A) 4 days, (B) 7 days, and (C) 14 days after mixing, observed by an optical microscope (× 125).

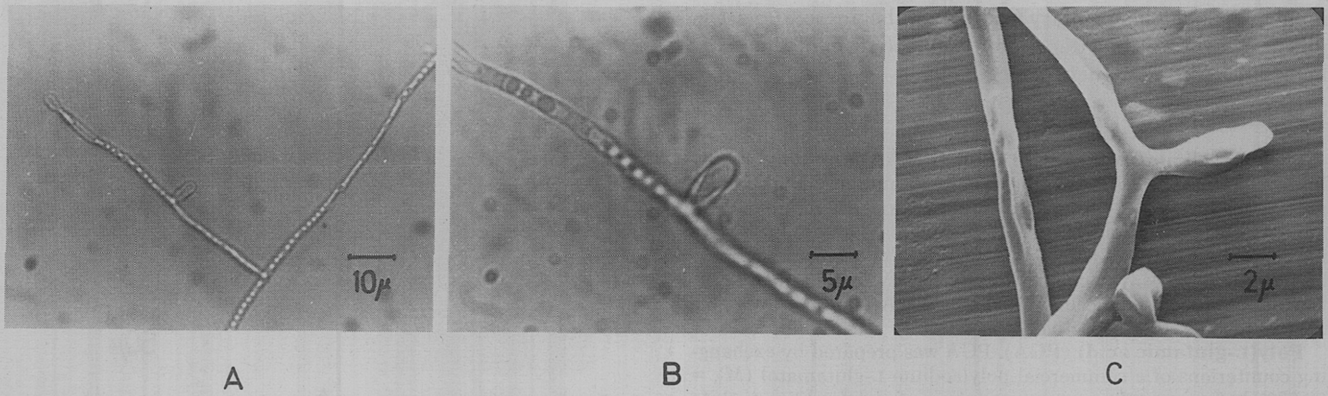

Figure 2. The micrographs of a part of branches on the main chain in the system of PMAA–2X at four days after mixing (A) × 500, (B) × 1250, (C) × 5000. The micrographs of (A) and (B) are taken by an optical microscope and (C) is done by a scanning electron microscope.

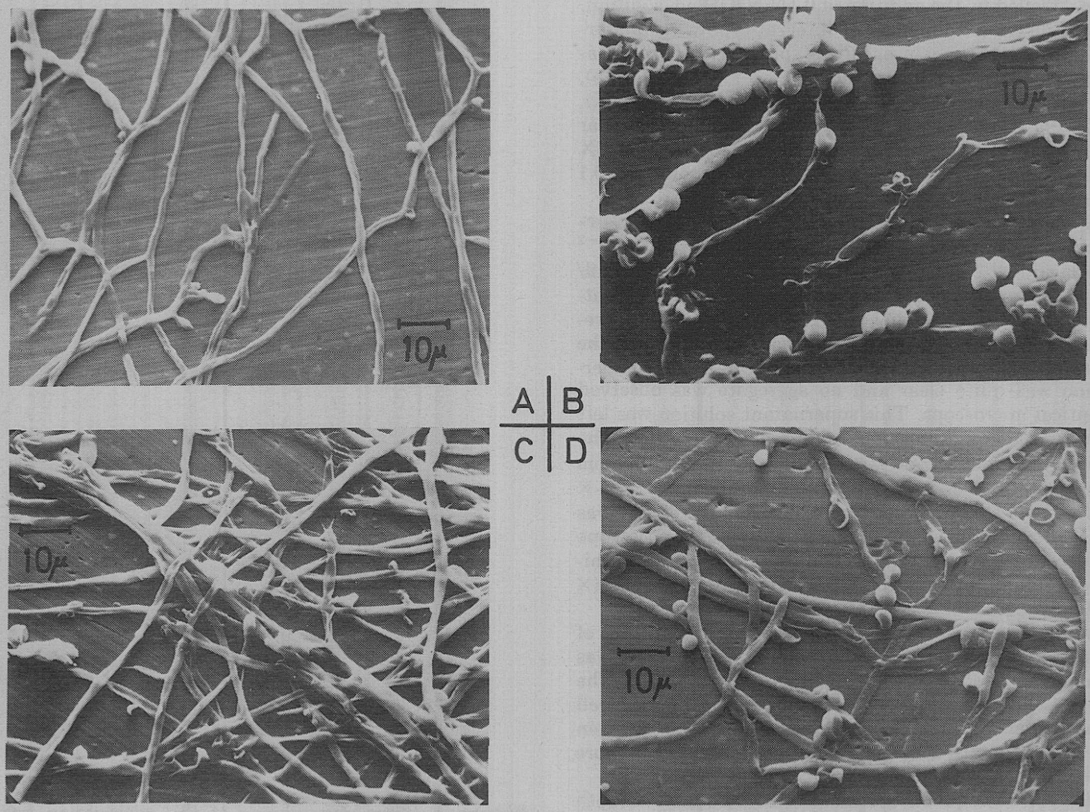

Figure 3. Electron micrographs of various kinds of aggregates (A) PMAA–2X, (B) PMAA–3X, (C) PMAA–6X, and (D) PGA–3X, at 7 days after mixing, taken by a scanning electron microscope (× 1000).

Figure 3 shows the electron micrographs of the final products in various systems, PMAA–2X, PMAA–3X, PMAA–6X, and PGA–3X. The globular aggregates besides fibrous ones are not observed in the 2X–PMAA system. The diameters of these fibrous and globular aggregates are shown in Table I. The diameter of the globular aggregate is 5.0 μ in all systems. On the other hand, the diameters of fibrous aggregates of PMAA– and PGA–polycation complexes are 2.0 and 2.7 μ, respectively. Namely, it is found that the diameters of the globules are not influenced by a kind of component polymers but the ones of fibers are controlled only by the component polyanions.

Figure 4 shows the micrographs of the complex aggregates of PGA–3X (× 1250 or × 5000). The surface of the complex is burried with many small projections, though in other systems the surfaces are smooth having no concern with the component polycations. So it is cleared up that the surface condition is changed by the kind of component polyanions.

Table I
Relation between Distinctive Features of Aggregates and Component Polyelectrolytes

Polyanion	Poly-cation	Diameter, μ Fiber	Diameter, μ Globule	Surface condition
PMAA	2X	2.0		Smooth
PMAA	3X	2.0	5.0	Smooth
PMAA	6X	2.0	5.0	Smooth
PGA	2X	2.7		Many projections on the surface
PGA	3X	2.7	5.0	
PGA	6X	2.7	5.0	
PMAA		2.5	5.0	Smooth

Such aggregation phenomena are observed in the system of only one of the component polyelectrolytes but under quite different conditions from the complex systems as shown in Table II. Though complex aggregates are obtained within about 4 days after mixing without micro salts, it takes a much longer time for the aggregates of poly-

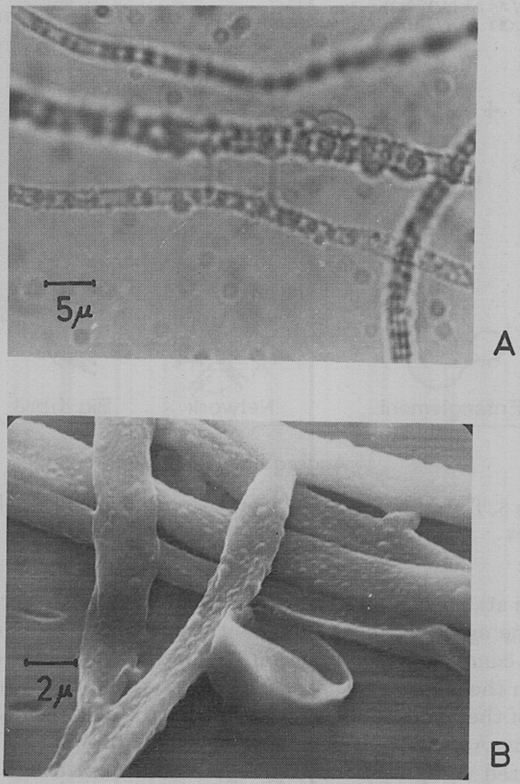

Figure 4. The surface condition of the aggregate in the system of PGA–3X: (A) × 125 by an optical microscope, (B) × 5000 by a scanning electron microscope.

Table II
Fibrous Aggregates of Polyelectrolytes

Polyanion	Poly-cation	Concentration, unit mol/l.	[NaCl]/[ionic site]	Time
PMAA		2.0×10^{-2}	10	1 week
PGA		2.0×10^{-2}	10	2 weeks
	2X	2.0×10^{-2}	10	4 weeks
PMAA	2X	2.0×10^{-2}	0	4 days

Table III
Elementary Analysis of the Complex Aggregates in the PMAA–2X System

Sample	C, %	H, %	N, %
Primary complex			
Calcd[a]	60.09	8.59	2.60
Found	59.98	8.26	2.55
Final product			
Calcd[b]	67.50	8.21	7.02
Found	67.25	8.30	6.92

[a] Composition is 5:1. [b] Composition is 1:1.

electrolytes to be obtained, i.e., more than a week, in the existence of micro salts. This result coincides well with the dissociation states of them, that is, 2X and poly(carboxylic acid) are a strong and a weak polyelectrolyte, respectively.

The final aggregates of the complexes are insoluble and their compositions are 1:1 as a unit molar ratio as shown in Table III. Furthermore, the final product is believed to be packed comparably densely and regularly by the results of x-ray diffraction as shown in Figure 5 and Table IV. Though PMAA is an amorphous polymer and 2X is a crystalline polymer with the lattice spacing (*d*) more than 2.2 Å, the complex aggregate shows more diffraction patterns and its *d* is less than 2.2 Å.

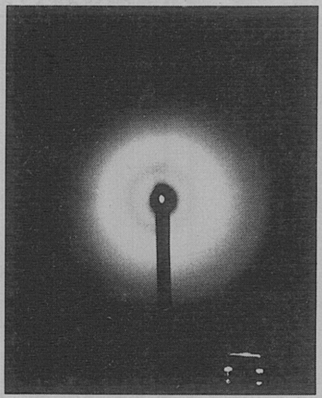

Figure 5. X-ray diffraction pattern on photographic plates about the final aggregation product of PMAA–2X.

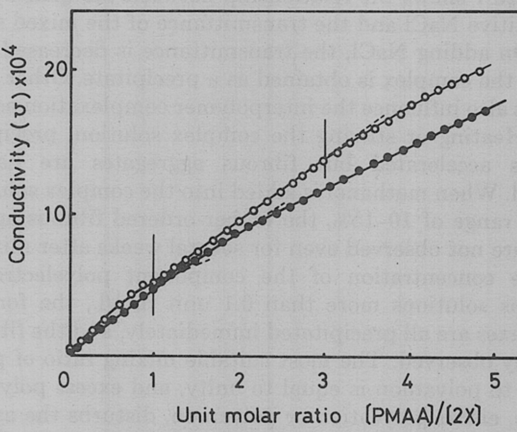

Figure 6. The conductive titration of the PMAA aqueous solution. The aqueous solution of PMAA is added to the one of 2X (○), and to water (●).

Table IV
Lattice Spacings (Å) of the Aggregates

	Aggregates		
Complex	PMAA	2X	2X[a]
1.21	1.21	1.23	
1.34	1.32	1.34	
1.54		1.52	
1.79	1.74		
2.13			2.21
2.46	2.40	2.40	
			2.89
			3.22
			4.75
			6.62

[a] The purified powder reprecipitated into methanol–ethyl acetate.

In order to discuss the aggregation mechanism of polyion complex, it is important to clarify the properties of the primary complex. Figure 6 shows the conductive titration of an aqueous solution of polycation by that of polyanion. In comparison with the conductive change of PMAA solution ($\alpha = 1$), the complex solution shows larger conductivity in a whole unit molar ratio because of the released micro ions on complexation. However, at an equivalent point, [PMAA]/[2X] = 1, micro ions are not released temporarily but beyond this point, on adding PMAA, the conductivity of the complex solution becomes larger again until the unit molar ratio is equal to three. On further adding of PMAA aqueous solution, the conductive change is parallel to that of PMAA.

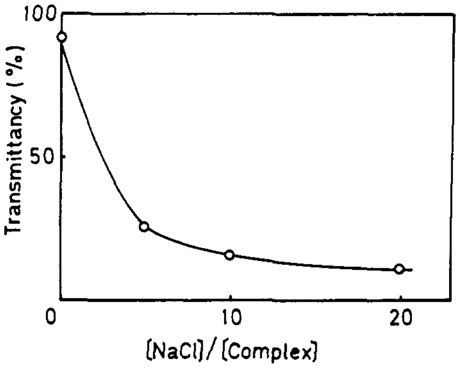

Figure 7. Relation between transmittance and the quantity of added NaCl to the mixing aqueous solution of PMAA with 2X.

Figure 7 shows the relationship between the quantity of an additive NaCl and the transmittance of the mixed solution. On adding NaCl, the transmittance is decreased and at last the complex is obtained as a precipitate. Other conditions also influence the interpolymer complexation as follows. Heating or stirring the complex solution, precipitation is accelerated but fibrous aggregates are hardly formed. When methanol is added into the complex solution in the range of 10–15%, the higher-ordered fibrous aggregates are not observed even for several weeks after mixing. At the concentration of the component polyelectrolyte aqueous solutions more than 0.1 unit mol/l., the formed complexes are all precipitated immediately, and the fiber is scarcely observed. The most suitable mixing ratio of polycation to polyanion is equal to unity, and excess polyelectrolyte, either polycation or polyanion, disturbs the aggregation. These results indicate that the primary complexes easily aggregate each other according to the increase of the collision number and/or their hydrophobicity.

Discussion

The first step of aggregation is believed to be bindings through Coulombic force among polycations and polyanions (primary complex). If hydrophobicity of the complex is made stronger by adding micro salts or heating the solution, such primary complexes are precipitated immediately and irregularly. The degree of neutralization of PMAA in the experiment of the spontaneous aggregation is equal to zero, so the dissociation of PMAA is restrained within several percent. In this condition, since the complex composition of the primary complex is equal to about 5:1,[8] undissociated carboxylic groups appeared to make the complex more hydrophilic. However, the composition of the final aggregate is equal to unity. Namely undissociated carboxylic groups, which are not related to the bindings with polycation at first, are gradually dissociated. These new dissociations form new bindings in the complexes and the interaction between a pair of polycation and polyanion is made stronger until the composition of the complex is equal to unity. In this way, the complex has more hydrophobic character because of neutralization of the net charge. At this time the aggregation of the complex appears to start. This process is the intra-complex reformation; in this process, the formation of new bindings and/or correction of the distortions in complexes could occur. But even when the composition of the complex is equal to unity, the complex is in a cationic atmosphere[14] from the result that excess polyanion is still able to interact with complexes already formed as shown in Figure 7. The importance of the electrostatic repulsion is suggested by the results that the aggregations of polyelectrolytes are related to their dissociation states and that the existence of micro salts accelerates the aggregation. On the contrary, the hydrophobicity of the complex is also important.[15] On the whole, the complex in the solution seems to be standing on a delicate balance of the hydrophobic attraction and the electrostatic repulsion. According to the increase of hydrophobicity, the dispersed complexes may aggregate with each other time dependently in the same direction in side by side and/or head to tail.

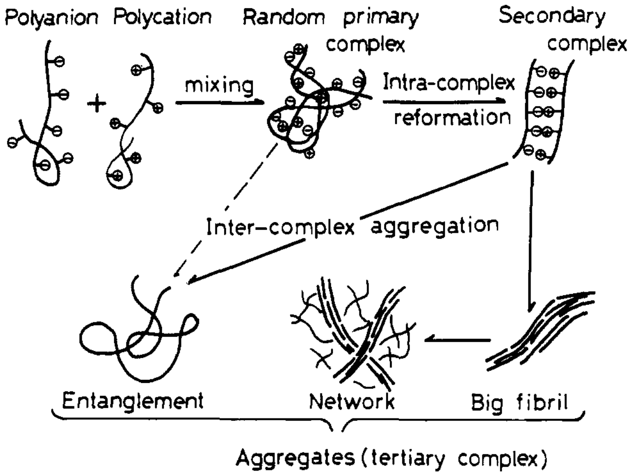

Figure 8. The schematic diagram of the formation of interpolymer complex

The terminations of the fibrous aggregates are composed of many fine whiskers, and then they are folded by the strong hydrophobicity of the main chain resulting in a circle as shown in Figures 1 and 2. Moreover, the distortions that appear in aggregation seem to be compensated partially by the part of loop-out. These loop-out parts are actually observed by electron micrographs (Figure 2). It is considered that the primary complexes are aggregated on these loop-out parts to form the branches on the main chain.

Though only a fibrous complex aggregate is obtained in the PMAA–2X or PGA–2X systems, the globular one besides the fibrous one is obtained in 3X and 6X systems. While molecular weight of PMAA is about 6.8 × 10^4, viscosities of polycations are about 0.1 for 3X and 6X, and 0.4 for 2X. Namely, the shapes of the aggregates are determined mainly by the chain length of the component polyelectrolytes; for example, the polycation with the longer chain length forms the fibrous complex aggregates with PMAA and the one with the shorter chain length does the globular one (Figure 3). Comparing with the PMAA chain, the chain lengths of polycations are shorter but polycations have more rigidity because of the electrostatic repulsion among cationic sites and the existence of the xylylene residues in their main chains. In order to get all carboxylic groups on one PMAA chain a larger number of polycation chains is necessary, so the complexes have many turns corresponding to joints, which appear to allow the aggregation in intra-complex. In the case of the polycation with longer chain length, 2X, the aggregation in intra-complex takes place more difficultly because of the decrease of turns and the increase of the rigidity of the complex.

It is clear that the complexation processes are divided into three main classes: i.e., (1) primary complexation, (2) reformation of intra-complex, and (3) aggregation of inter-complex as shown in Figure 8. The first step is realized through such secondary binding forces as Coulombic force and hydrogen bonds. The second step occurs according to the formation of new bindings and/or correction of the distortions in complexes. The third step is developed by the aggregation of the complexes through hydrophobic interaction. Primary complexes are dispersed in the solution because of their cationic atmosphere immediately after reaction, but they are gradually rich in hydrophobicity in accordance with the progress of the reformation of intra-complex, and then because of moving equilibrium of electrostatic repulsion with hydrophobic attraction the complexes aggregate gradually and regularly to a fibrous structure. Such aggregation is influenced by many factors, for example, the structure of the component polyelectrolytes (chain length, hydrophobicity, rigidity, and so on) and the complexation conditions (solvent, ionic strength, temperature, etc.).

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Bulk Properties of Synthetic Polymer–Inorganic Salt Systems. IV. Role of the Polymeric Substrate

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ABSTRACT: The equilibrium melting behavior and the kinetics of crystallization of mixtures of a synthetic polymer with LiCl (composition range 0–10 w/w) were determined using differential scanning calorimetry. Polymers investigated were: nylon 4, nylon 6, nylon 66, nylon 11, poly(ethylene terephthalate) (PET), polyoxymethylene (POM), polyethylene (PE). Preparation of the mixtures was achieved by several methods, including polymerization in the presence of the salt. The choice of the most efficient method for mixing the two components is a crytical one when polymer–salt compatibility is poor. On increasing the number of CH_2 groups per polymer unit in the nylon series, the melting point depression due to LiCl decreases. The depression is almost a negligible one in the case of nylon 11 which is able to dissolve only about 1% LiCl. Simultaneously with the decrease of the melting temperature depression, an effect of LiCl in reducing crystallization rate is observed. In the case of PET, no melting point depression due to LiCl is observed, and the salt has a noticeable effect in increasing crystallization rate. Upon further decreasing the polarity of the chain, the effect of LiCl on increasing crystallization rate decreases until, for PE, all salt effects vanish. In a case in which the decomposition temperature of the polymer was close to its melting temperature, LiCl was able to depress the latter without affecting the former.

We have recently reported the effect of inorganic salts on the melting behavior[1] and on the crystallization kinetics[2] of nylon 6 in the absence of water or any conventional liquid diluent. It was shown that some salts, notably LiCl and LiBr, can intimately mix with nylon 6 causing a large reduction of the thermodynamic melting temperature and of the crystallization rate of the pure polymer. Other salts, notably KCl, are incompatible with nylon 6 and are unable to affect its melting temperature. The ranking of various salts for their ability to interact with undiluted nylon 6 is similar to the order of various ions for interacting with biopolymers in the presence of water.[3-5] A general mechanism for direct interaction (i.e., binding[6]) between ions such as Li^+ or Br^- and polar groups of the disordered polymer seems to be involved.[1-6]

In addition to the interest connected with the detailed mechanism of salt interaction, undiluted polymer–salt mixtures have now attracted attention for the possibility that they offer to control some processing parameters such as processing temperature, melt viscosity, and rate of crystallization.[7-10] Use of salt additives may, in principle, be advantageous for processing high melting or thermally unstable polymers.[8-10]

Although the effect of various salts for a given polymer substrate (nylon 6) was adequately investigated,[1,2,7] much less is known concerning the effect of a given salt on different polymers. In this work we analyze the melting and the crystallization behavior of several polymers mostly in the presence of LiCl. The purpose is that of establishing how the compatibility of LiCl is affected by an alteration of number and type of polar groups along the polymer chain. Polymers investigated include members of the nylon series: poly(pyrrolidone), poly(ϵ-caprolactam), poly(hexamethylene adipamide), and poly(ω-aminoundecanoic acid) (nylon 4, nylon 6, nylon 66, nylon 11) where the ratio of methylene to amide group can be analyzed, and polymers such as poly(ethylene terephthalate), polyoxymethylene, and, also, polyethylene.

Preliminary attempts to investigate the above systems revealed that the occurrence of polymer–salt interaction is dependent upon the manner in which the polymer–salt mixture is formed. Accordingly, the efficiency of various mixing processes, including direct polymerization in the presence of LiCl, was considered in detail.

Experimental Section

Materials. Preparation of Polymer–Salt Mixtures. Nylon 4. Sample Ny4, TiO_2 free, was kindly supplied by the ALRAC Corp.,