

POLYIONIC COMPLEXES DERIVED FROM POLYVINYL ALCOHOL

I. PREPARATION AND THEIR SOLVATION BEHAVIOR*

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ABSTRACT

Polycations and polyanions of polyvinyl alcohol (PVA) with various substitution degrees were prepared by acetalization of PVA with aldehyde derivatives such as p-formylbenzoic acid, glyoxalic acid, p-formyl-benzenesulfonic acid, p-formylpyridine, and p-dimethylaminobenzaldehyde and then neutralized or quaternarized with methyl iodide. The corresponding PVA type polyionic complexes were obtained by mixing the aqueous solutions of these polycations and polyanions. The solvation behaviour of these polyionic complexes were investigated. It was found that the H_2O -DMF-NaSCN solvent system is superior to the H_2O -DMF-NaBr system for these PVA type polyionic complexes.

White precipitate can be obtained by mixing aqueous solutions of oppositely-charged linear polyelectrolytes due to strong electrostatic attraction between these polyions. The aggregates of oppositely-charged macromolecules are called polyelectrolyte complexes (PEC) or polyionic complexes (PIC). Since the earliest study by Bungenberg de Jong^[1] on the interaction of aqueous solutions of water-soluble natural polymers, there have been many reports concerning with the preparation and properties of PIC^[2-10].

Polyionic complexes, unlike ordinary polymers, exhibit some remarkable physicochemical properties, such as neither fusible nor soluble in common solvents, high water absorptivity and high permeability to water molecule and simple water-soluble solutes, good biocompatibility, etc. These PIC have been used as candidate materials for battery separators, electrically conductive and antistatic coatings, dialysis and ultrafiltration membranes, contact lenses, biomembrane ersatzes, blood vessel prostheses and others.

Most researches on polyionic complexes are focused on polystyrene derivatives, such as Ioplex 101, a thoroughly studied PIC which is the product of sodium poly (styrene sulfonate) reacted with poly (vinyl trimethyl ammonium) chloride. In recent years, there have been several articles concerning with the investigation of polyvinyl alcohol derived polyionic complexes^[6-10], but all these researches are only limited in polycations and polyanions of slightly substituted polyvinyl alcohol. Effect of structure of substituents and degree of substitution on properties of formed PIC have not been reported in detail. In this article, the syntheses of polycations and polyanions with various substitution degree by introducing some ionizable groups such as carboxy group, benzoxy group, sulfonic group, pyridinium group, aromatic quaternary ammonium group, etc. onto polyvinyl alcohol chains via acetalization reaction of PVA with glyoxalic acid, p-formylbenzoic acid, p-formylbenzenesulfonic acid, p-formyl-

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pyridine, and *p*-dimethylaminobenzaldehyde, are presented. The PIC formation reactions of the corresponding polycations and polyanions are investigated. In order to find the proper solvent system for the purpose of membrane-casting, the solvation property of these PVA derived PIC are also studied.

EXPERIMENTAL

Materials: polyvinyl alcohol, average *D.P.* 2400–2500, average degree of saponification 98–99%; glyoxalic acid, Merck-Schuchardt; *p*-formylbenzoic acid, Fluka AG; *p*-formylpyridine, Merck-Schuchardt; *p*-dimethylaminobenzaldehyde, Beijing Chemical Plant; were purchased commercially. *p*-Formylbenzenesulfonic acid was synthesized according to literature^[11].

1. Preparation of polyvinyl alcohol derived polycations and polyanions

Preparation of polycations: *p*-Dimethylaminobenzaldehyde, dissolved in 50% sulfonic acid, was added to 2% aqueous solution of PVA. After the reaction was carried out at 80°C for 1.5 hours, the reaction mixture was diluted with water, and then 5% Na₂CO₃ aqueous solution was added to precipitate the product.

The obtained acetalized product was dissolved in dimethylformamide (DMF), excess amount of methyl iodide was added to proceed the quaternarization reaction at room temperature for 30 hours. The yellow quaternary ammonium polycation was separated by precipitating from the reaction mixture in ethyl alcohol-ethyl acetate (1:1) and purified by reprecipitation.

Reaction of *p*-formylpyridine with PVA was the same as that of *p*-dimethylaminobenzaldehyde.

The ionic equivalent weight (*E*) and degree of substitution (*D.S.*) of PVA derived polycations were determined by titration of iodide with HgNO₃ solution using diphenylcarbazide as indicator and calculated according to the equations:

$$E = \frac{W}{N \cdot V} \quad \text{and} \quad D.S. \% = \frac{E_0}{E} \times 100$$

where *N* and *V* were equivalent concentration and volume of standard HgNO₃ used, respectively, *W* is the weight of sample and *E*₀ is the ionic equivalent weight of polycation with 100% substitution.

Preparation of polyanions: *p*-formylbenzoic acid was dissolved in DMF and then mixed with 4% aqueous solution of PVA. Concentrated H₂SO₄ was used as catalyst and the reaction was proceeded at 80°C for 3 hours. After that, the mixture was poured into large amount of water to separate the product and neutralized with 10% of NaOH solution. The polyanion was precipitated in absolute alcohol-ethyl acetate and purified.

Reactions of *p*-formylbenzenesulfonic acid and glyoxalic acid with PVA were carried out as that of *p*-formylbenzoic acid.

The ionic equivalent weight and degree of substitution of these polyanions were determined by immersing the acetalized products in excess amount of standard NaOH solution for 24 hours and then titrating reversely with standard HCl solution using phenolphthalein as indicator.

2. Formation of polyionic complexes

Reaction of polycations and polyanions: The formation of complexes between polycations and polyanions were studied mainly by turbidimetric method. While polycation aqueous solution of 0.10 mmol/100 ml (about 0.05 g/100 ml) was added to polyanion aqueous solution with the same concentration, the clear solution turned to turbid and the turbidity was measured with Model 72 photoelectric spectrophotometer at 600 nm as a function of the mixing ratio. The turbidity is defined by

$$\tau' = l\tau = \ln I_0 / I = \ln(T)^{-1}$$

where τ and τ' is the turbidity and relative turbidity respectively, l is the thickness of cell, I_0 and I is the intensity of incident and transmitted light respectively, and T is the transmittancy.

Preparation of complexes: Polycation was added slowly to aqueous solution of polyanion with stirring and some white coacervate were precipitated from the solution at the stoichiometric point. After washed thoroughly with water and then dried, transparent amorphous polyionic complex which is extremely hard and brittle was obtained.

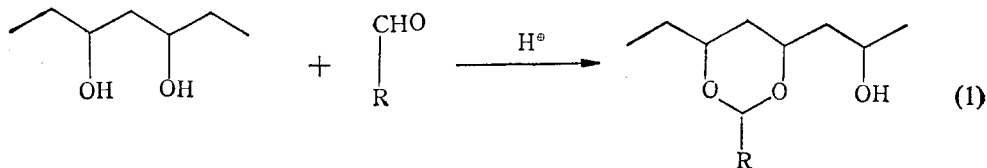
Thermal-analysis of complexes: Polyionic complex sample for thermal-analysis was prepared as mentioned above and polyions blend was prepared by mixing the corresponding polycation and polyanion (1:1) and grinding into powder. The CDR-1 differential scanning calorimeter (DSC) (Shanghai Analytic Instrument Plant) was used.

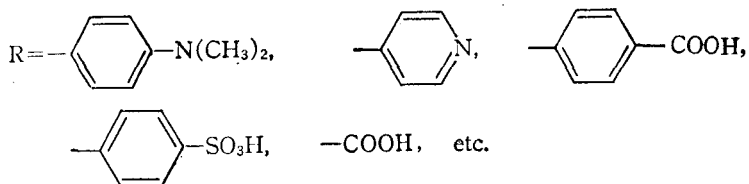
Phase diagrams of polyionic complexes: To a series of organic solvent-water or salt-water mixtures with different compositions, 0.5 ml of 5% aqueous solutions of polycation and polyanion were added, then some white precipitate were formed immediately. The mixture was kept in a thermostat for 15 minutes and then, certain amounts of microsalt or organic solvent were added partially. The points where the solution turned to clear were the boundaries of PIC solubility at these special composition of ternary solvent system.

RESULTS AND DISCUSSION

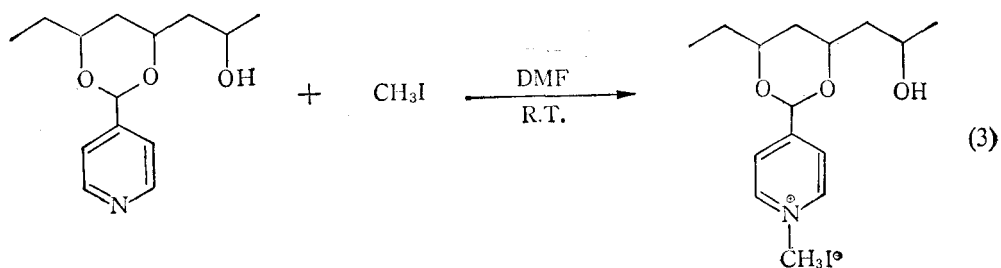
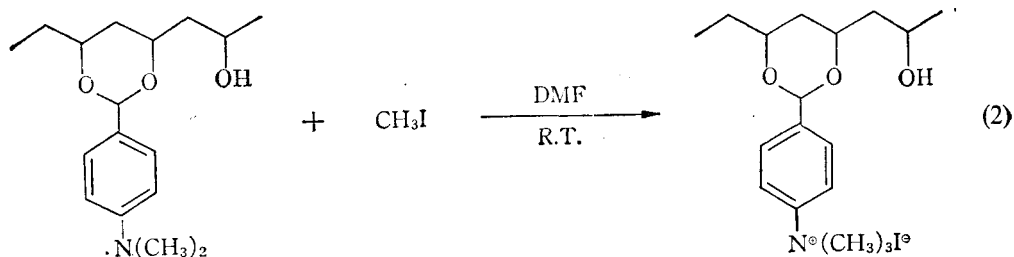
1. Syntheses of polycations and polyanions

Polyvinyl alcohol, as a polyhydroxy compound, exhibits the same reactivity towards some reactions as common hydroxy compounds do. As the acetalization reaction is easy to be controlled, the use of acetalization of PVA to prepare a series of PVA derivatives with different substituent structure and various degree of substitution were explored. The acetalization reaction was carried out in aqueous solution with inorganic acid as catalyst:

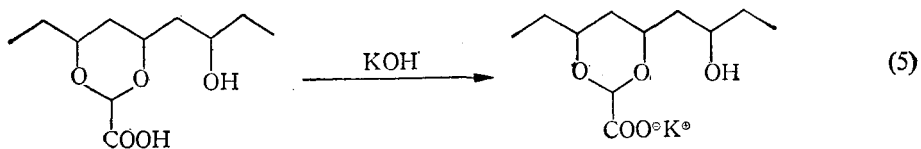
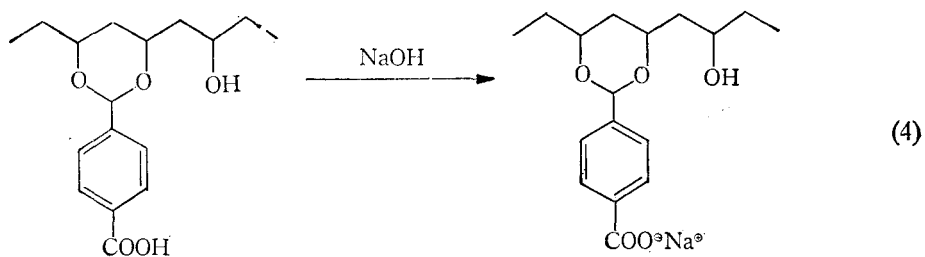




then, the aromatic tertiary amino group and the pyridyl group bearing acetalized products were quaternarized by methyl iodide in DMF at room temperature:



The carboxy group bearing acetalized products were neutralized:



The ionic equivalent weight and degree of substitution of all these polycations and polyanions were determined by titration. Table 1 shows the chemical structure, degree of substitution

Table 1 Chemical structure, degree of substitution and equivalent weight of PVA derived polyions

Derivative of PVA	Chemical structure	D.S. of PC or PA (mole-%)	Equivalent weight of PC or PA (g/eq)
Polycation: PC-I ₁		35	1031
PC-I ₂		46	781
PC-II ₁		27	1204
PC-II ₂		36	901
PC-II ₃		48	662
PC-II ₄		50	641
PC-II ₅		64	498
Polyanion: PA-I ₁		25	880
PA-I ₂		47	471
PA-II ₁		27	943
PA-II ₂		31	820
PA-II ₃		41	600
PA-III		34	424

and ionic equivalent weight of these PVA derived polyions.

2. Reaction of polycation and polyanion

Mixing aqueous solutions of polycations and polyanions, white, water-insoluble products, namely polyionic complexes were obtained due to electrostatic interaction of these oppositely-charged macromolecules. These formed products, after thoroughly washing, drying, were transparent, hard and brittle. The structures of these PIC are shown in Fig. 1. If the reaction of polycation with polyanion was controlled carefully, the formed complex only suspended in the reaction solution as microparticles without aggregating, so the turbidity of the system would change as the complex formation reaction went on. Fig. 2 and Fig. 3

show the relationship of turbidity with the mixing composition of polycation and polyanion in the complex formation reaction. It can be seen that these two systems all exhibit maximum values of turbidity at the equivalent points. This demonstrates that the complex formation is stoichiometric.

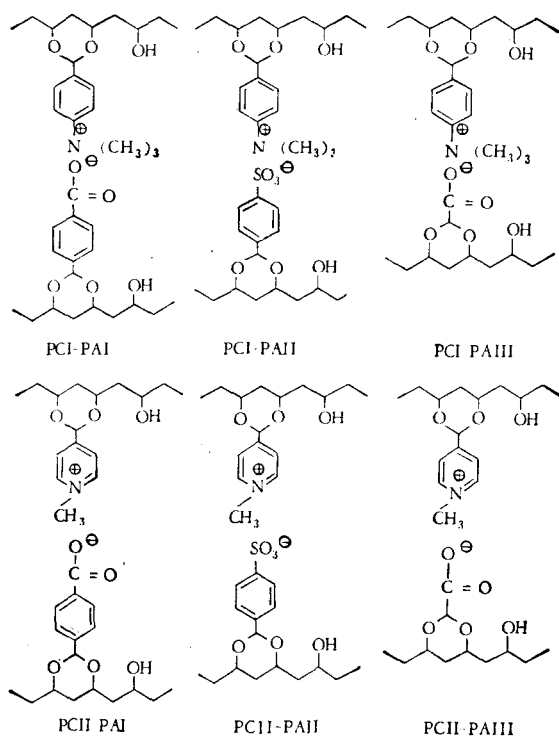


Fig. 1 Structures of PIC derived from PVA

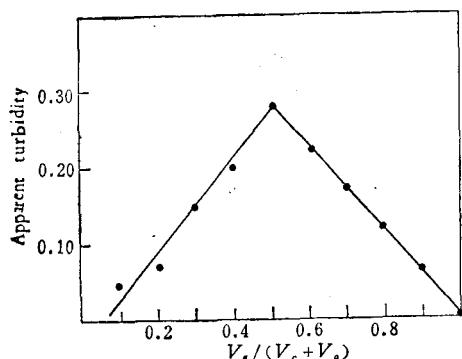


Fig. 2 Apparent turbidity plotted against mixing ratio
Polycation: PC-I₂. Polyanion: PA-I₂.
Concentration: [PC]=[PA]=0.1 meg/100 ml.
Mixing condition: PC solution was added to
PA solution and then the mixture was stirred
for 5 minutes.

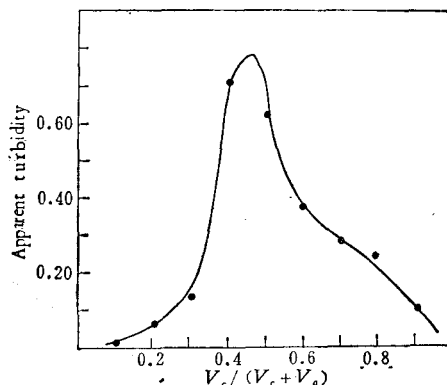


Fig. 3 Apparent turbidity plotted against mixing ratio
Polycation: PC-II₂. Polyanion: PA-I₂.
Concentration: [PC]=[PA]=0.1 meg/100 ml.
Mixing condition: PA solution was added to
PC solution without stirring.

3. Properties of polyionic complexes derived from PVA

As the complex is formed, some original properties, such as solubility, fusibility, etc., of the polyions no longer exist, instead, the product becomes insoluble in common solvents, thermoresistant and exhibit some properties of network polymers.

Thermal-analysis of polyionic complex: Fig. 4 shows the differential scanning calorimeter (DSC) thermograms of PVA derived PIC and the mechanical mixture of the corresponding polycation and polyanion. There are appreciable differences between the thermograms of the complex and blend. The mechanical mixture had three endothermic peaks at about 85°C, 205°C, and 380°C, respectively, and had a broaden exothermic peak at about 340°C. However, in the thermogram of the corresponding complex, the endothermic peak at about 85°C disappeared, instead, the complex had two endothermic peaks at about 180°C and 300°C, respectively, and a broaden exothermic peak at about 360°C. From this, it can be concluded that the PIC formed by the reaction of PVA derived polyions in aqueous solution were not simply mechanical mixtures, but new products due to chemical bonding between these oppositely-charged macromolecules.

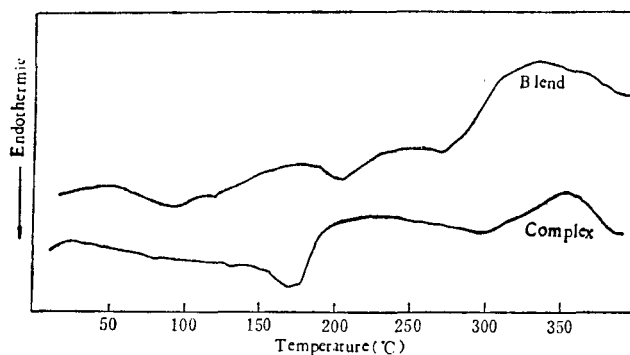


Fig. 4 The thermograms (DSC) of complex and blend of poly (vinyl alcohol) derivatives
Complex: $\text{PCl}_2\text{-PAI}_2$. Blend: $\text{PC-I}_2 + \text{PA-I}_2$.
Experiment conditions: reference: Al_2O_3 , heating rate: 10°C/min . In air.

Solvation property of complex: Linear polyvinyl alcohol and its polyion derivatives prepared by acetalization are water-soluble, but the complexes of these polyions are insoluble in water and other common organic solvents. Like other polyionic complexes such as the complex formed by the interaction of sodium poly (styrene sulfonate) and poly (vinyl benzyl trimethyl ammonium) chloride, PVA derived complexes could only be soluble in so called ternary shielding solvent system comprising water, a water-miscible organic solvent and a strongly ionized simple electrolyte. Furthermore, the shielding solvation ability of the ternary solvent system could be good displayed only when the ternary mixture were at a proper composition. In mixing 0.1% aqueous solutions of polycation and polyanion, some white coacervate were formed. But when adding some polar organic solvent such as DMF and small molecular salt such as NaBr to the polyions aqueous solution, there were no precipitate formed during the mixing of the oppositely-charged macromolecule solutions. In otherway, if only organic solvent or only small molecular salt was added, some precipitate could still be formed. This

showed that the existence of polar organic solvent and small molecular salt in the polyions aqueous solution could inhibit the formation of PVA-type PIC. For PVA derived PIC, the water miscible organic solvent of the ternary solvent system such as dimethylformamide (DMF), dimethylsulfoxide (DMSO) or methylpyrrolidone, the strongly ionizable simple electrolyte such as NaCl, NaBr, NaSCN, etc., could be used. Fig. 5 and Fig. 6 are triangular phase diagrams of complex formed from polycation PC-I₂ and polyanion PA-I₂ in H₂O-DMF-NaBr and H₂O-DMF-NaSCN ternary solvent system respectively. In the diagrams, AB plots are solubility curves of NaBr or NaSCN in H₂O-DMF solution, and the shadow areas are the soluble fields of PIC, in which the complex can be dissolved as homogeneous clear solution. From these triangular phase diagrams, it can be seen that the soluble area of PIC in NaSCN system which have not been reported in literature is larger than that of in NaBr system. Another advantage of the former ternary system is the solubility of NaSCN in H₂O-DMF solution is larger than that of NaBr system. PVA derived PIC membranes can be obtained easily by casting-impregnating method through these solvent systems.

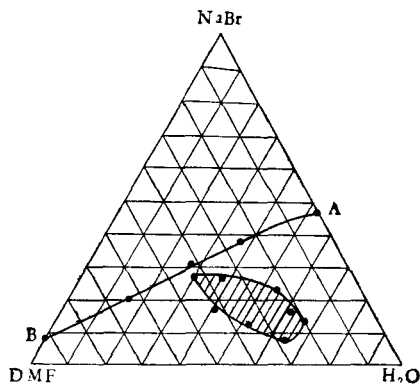


Fig. 5 Phase diagram of polyionic complex in H₂O-DMF-NaBr system
Polycation: PC-I₂;
Polyanion: PA-I₂; Temperature: 30°C.

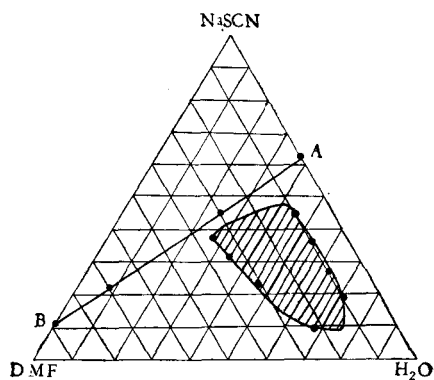


Fig. 6 Phase diagram of polyionic complex in H₂O-DMF-NaSCN system
Polycation: PC-I₂;
Polyanion: PA-I₂; Temperature: 30°C.

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