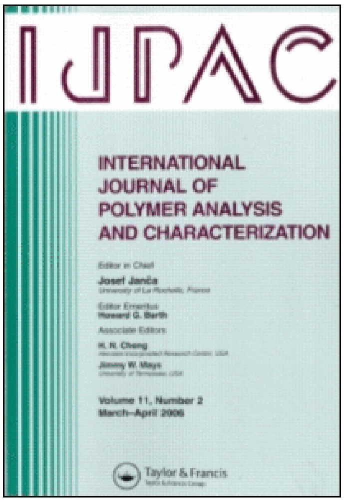

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Polyelectrolyte Complexes on a Dimeric Interface

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Thin films of the polyelectrolyte complexes between poly-2-vinylpyridine (poly-2-methyl-5-vinylpyridine) and sodium polystyrenesulphonate (polyacrylic acid) at benzene-water phase boundary have been synthesized. Polycomplex compositions and their stability to action of solvents, temperature and pH have been determined. The behaviour of polycomplexes in mixed organic solvents is compared to predictions of the Dondos-Patterson theory for viscosity of individual polymers in mixed solvents. It allows us to consider the polymer complexes formed on a dimeric interface as new individual nonpolar polymers.

KEY WORDS polycations, polyanions, polyelectrolyte complexes, interface layer

INTRODUCTION

Polyelectrolyte complexes (PEC) are the products of specific interactions of polyelectrolytes with various low and high molecular weight substances.[1–4] Thin films and membranes based on polyelectrolyte complexes are of great interest. They can be used for separation of liquids and gases, for specific transportation of K^+ and Na^+ ions, for ultrafiltration of biological liquids.[5–7] The preparation of thin films or membranes from PEC is a multistage process consisting of the separation of the precipitate of PEC, its dissolution, casting, evaporation of the solvent and sometimes thermal treatment of the films. Reactions in which PEC are formed and which proceed on a dimeric interface represent a new method of obtaining various types of membranes and thin films and so far have not yet been considered.[8] In the present communication the results of complex formation reaction between polyvinylpyridines and sodium polystyrenesulphonate as well as polyacrylic acid on a dimeric interface are discussed.

EXPERIMENTAL PART

Poly-2-vinylpyridine (P2VP, weight-average molecular weight $M_w = 3,4 \cdot 10^5$), sodium polystyrenesulphonate (PSS, $M_w = 3 \cdot 10^5$) purchased from "Polysciences Inc." (Warrington, USA) and polyacrylic acid (PAA, $M_w = 2,5 \cdot 10^5$) purchased from "Aldrich Chem. Comp. Inc." (Milwakee, USA) were used without purification.

Poly-2-methyl-5-vinylpyridine (P2M5VP) was synthesized by the procedure described in reference.[9] Viscosity-average molecular weight M_V of P2M5VP calculated from the Mark-Houwink-Kuhn equation $[\eta] = 1,8 \cdot 10^{-4} M^{0,83}$ in methanol at 298°K[10] is equal to $7,2 \cdot 10^4$.

Potentiometric measurements were carried out with the digital pH-meter of Radelkis type OP-211/1 (Budapest, Hungary) at room temperature. The viscosity of the solutions was measured in an Ubbelodhe viscometer. The organic solvents were purified according to.[11]

Complex formation reaction on a dimeric interface was performed as follows: to the aqueous solution of water-soluble component the benzene solution of poly-2-vinylpyridine was added gradually so that the surface of the aqueous solution was fully covered by the organic solution. The formation of thin film occurs immediately. The thickness of the films depends on the concentration of the reacting components and varies from 10 to 100 μm. These thin films of the polyelectrolyte complexes were separated and dried to constant weight. For the following investigations the solutions of PEC of necessary concentrations were prepared directly before the measurement.

RESULTS AND DISCUSSION

It is well known[1–4] that polycomplexes can be obtained by mixing of interacting components in solution (or by melting) or by matrix polymerization. The complex formation reaction on an interface layer is a new method for the synthesis of polymer complexes.[8]

Figure 1 represents the potentiometric titration curve of aqueous solution of sodium polystyrenesulphonate by benzene solution of poly-2-vinylpyridine. The gradual increase in pH is connected with the formation of polyelectrolyte complexes and release of NaOH into the water phase. The release of NaOH is stopped when complex formation reaction is completed. The value pK = 6.55 when P2VP = 0 is the pH value of sodium polystyrenesulphonate. The mechanism of PEC formation on a dimeric interface is expected to be similar to the process taking place in solution. The composition of PEC determined from the bend of potentiometric curve is equal to [P2VP]:[PSS] = 1:1. The compositions of PEC formed as thin films on a dimeric interface for other systems are equal to [P2M5VP]:[PSS] = 1:2, [P2VP]:[PAA] = 1:1 respectively.

The degree of complex formation θ for the system P2VP-PAA according to[12,13] was determined from the potentiometric titration curves (Fig. 2). As seen from Figure 2 both the P2VP-PAA complex formation as a thin film on a dimeric interface and the complex formation reaction in solution occur in a narrow interval of pH and resembles the known cooperative conformational transitions in polypeptides, nucleic acids solutions. The cooperative interaction of polyelectrolyte macromolecules is caused by the polymeric nature of these reagents.

Polyelectrolyte complexes formed on a dimeric interface in contrast to complexes formed in solution are dissolved in organic hydrocarbon and aromatic solvents, for instance in benzene. Solubility of PEC in organic solvents is typical only for PEC formed on a dimeric interface and is apparently explained by more hydrophobicity of these complexes due to high degree of conversion.

The intrinsic viscosities of [P2M5VP]:[PSS] = 1:2 complexes were measured in benzene-methanol and benzene-dimethylformamide (DMF) mixtures (Fig. 3, curves 2 and 3), [P2VP]:[PAA] = 1:1 complexes was measured in benzene-methanol mixtures (Fig. 3,

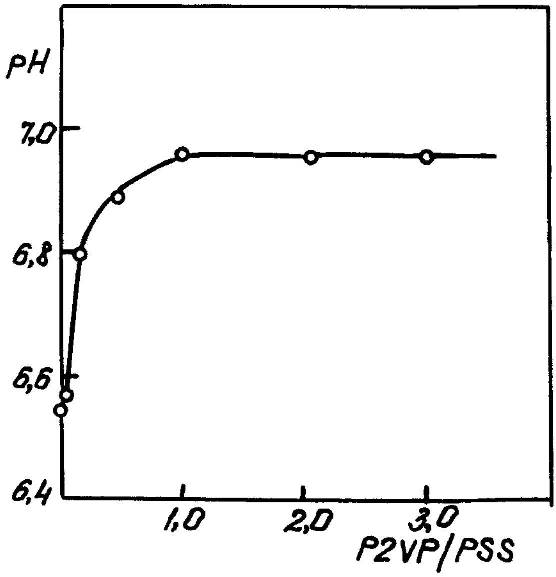

FIGURE 1 Potentiometric titration curve of PSS water solution by P2VP benzene solution. [PSS] = 1 × 10^{-2} mol/l, [P2VP] = 1 × 10^{-1} mol/l.

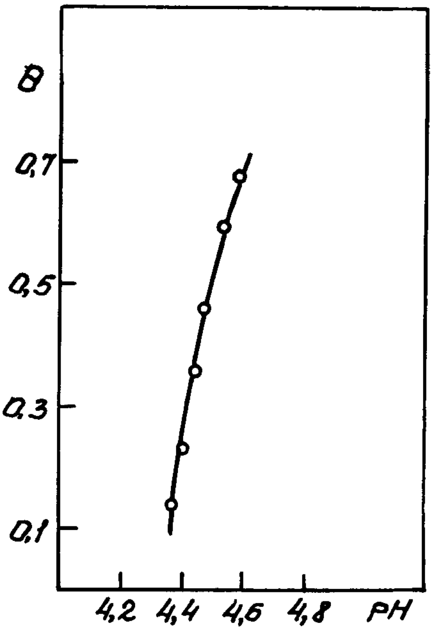

FIGURE 2 Dependence of degree of conversion in complex formation reaction θ on pH for [P2VP]:[PAA] = 1:1 complexes.

curve 1). The addition of organic solvents (CH_3OH or DMF) to benzene solution of PEC leads to the increasing of the intrinsic viscosity of the polycomplexes. The maximum of $[\eta]$ corresponds to the unfolded state of complex particles due to their high solubility. The mixtures of organic solvents are probably thermodynamically the best solvents for complex particles. The properties of polycomplexes in mixed solvents are in good agreement with the predictions of Dondos-Patterson theory.[14] Therefore one can consider the complexes formed on a dimeric interface as individual nonpolar polymers.

It is interesting to study the change of structure of polycomplexes as a function of temperature and pH of the medium. The dependences of reduced viscosity η_{sp}/C of [P2M5VP]:[PSS] = 1:2 complexes on pH in methanol measured at 298°K are shown in Figure 4. The sign of the charge and its magnitude for complex particles are changed at the interval of pH 3,5–8,0. It is possible that in these conditions the structure of polycomplexes is altered. The behaviour of polyelectrolyte complexes as a function of pH is evidence for similarity in the behaviour of polyampholytes and in some cases[15] one can consider PEC as polyampholytes.

The increasing of temperature over the interval 288–333°K causes the unfolding of complex particles in both methanol and benzene solution (Fig. 5). In benzene the viscos-

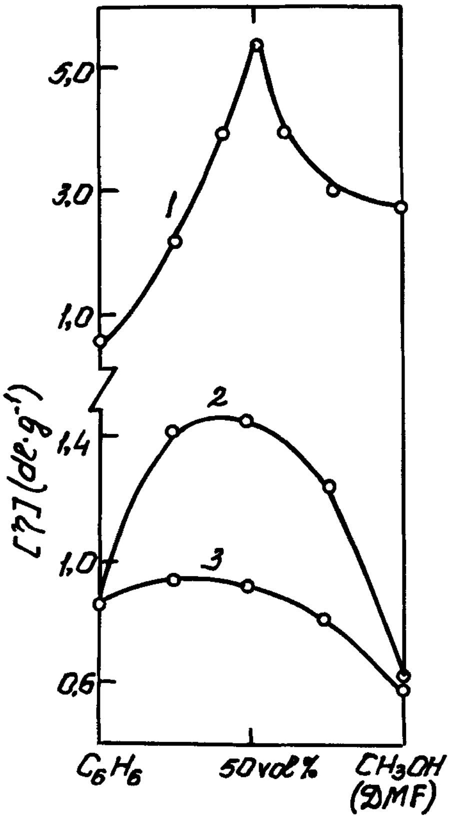

FIGURE 3 Dependence of intrinsic viscosity of P2VP-PAA (1) and P2M5VP-PSS (2,3) complexes on composition of benzene-methanol (1,2), benzene-DMF (3) mixtures.

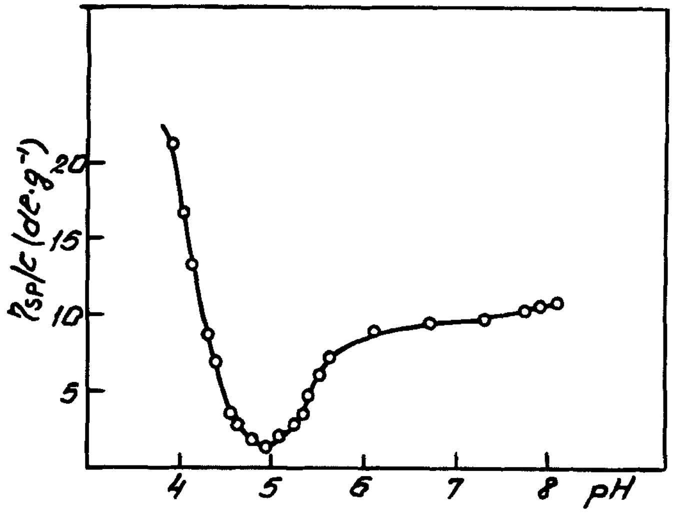

FIGURE 4 Dependence of reduced viscosity η_{sp}/C of [P2M5VP]:[PSS] = 1:2 complexes on pH.

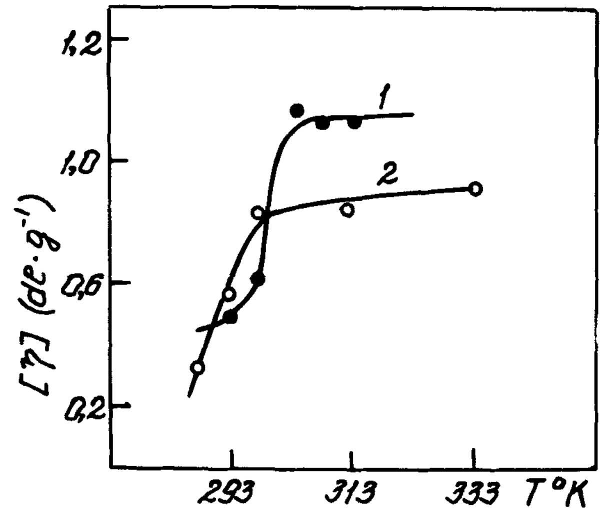

FIGURE 5 Temperature dependence of intrinsic viscosity of [P2M5VP]:[PSS] = 1:2 complexes in methanol (1) and benzene (2).

ity does not practically change upon the increasing of temperature over 298°K, while in methanol the viscosity increases considerably as compared with its value at 298°K. The values of intrinsic viscosities in methanol at increasing of temperature approach the magnitudes corresponding to the thermodinamically best benzene-methanol mixtures (Fig. 3, curve 2). These results show that the partial destruction of polycomplex structure occurs in methanol on increasing temperature.

Thin films of polyelectrolyte complexes between poly-2-vinylpyridine (poly-2-methyl-5-vinylpyridine) and sodium polystyrenesulphonate (polyacrylic acid) were synthesized by carrying out a complex formation reaction on a dimeric interface. PEC are sensitive to the nature of organic solvents, pH medium and temperature. Behaviour of the polyelectrolyte complexes synthesized on a dimeric interface allows us to consider them as new nonpolar polymers.

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