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Interpolymer Complexes: Study of Interaction of Polyvinylpyrrolidone) with *p*-Hydroxybenzoic Acid-Formaldehyde Copolymer in Nonaqueous Media

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INTERPOLYMER COMPLEXES: STUDY OF INTERACTION OF POLY(VINYLPYRROLIDONE) WITH *p*-HYDROXYBENZOIC ACID-FORMALDEHYDE COPOLYMER IN NONAQUEOUS MEDIA

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ABSTRACT

Interactions between poly(vinylpyrrolidone) (PVP) and *p*-hydroxybenzoic acid-formaldehyde copolymer have been studied in methanol solution. The component polymers appear to form interpolymer complexes in distinct stages. The results are interpreted in terms of 1) hydrogen bonding, 2) ion-dipole interaction, 3) tacticity of PVP, and 4) multiple coordinating positions of component polymers.

INTRODUCTION

The potential practical applications of interpolymer complexes and their resemblance to intermacromolecular interactions in biological systems have aroused great interest [1, 2]. Since synthetic polymers have simpler structures than biopolymers, study of interactions between synthetic polymer chains may lead to the understanding of complex reactions in biological sys-

tems. Proton-accepting polymers, e.g., poly(vinylpyrrolidone) (PVP) and poly(ethylene oxide) (PEO), and proton-donating polymers, e.g., poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), typically interact with each other through hydrogen bonding to form interpolymer complexes [3-7].

Some preliminary investigations at this laboratory revealed that phenolic polymers also interact through hydrogen bonding and ion-dipole interactions with nonionic polymers, such as PVP and PEO, to form interpolymer complexes [8, 9]. This encouraged us to extend the studies to a more complex phenolic copolymerization system, e.g., *p*-hydroxybenzoic acid-formaldehyde copolymer (PHBF). Since both the component polymers (i.e., PHBF and PVP) have two coordinating positions each, it is reasonable to expect that interpolymer complexation takes place in distinct steps. Surprisingly enough, we have observed stepwise complex formation between these component polymers by several experimental techniques. In this communication, efforts are made to interpret the mode of complexation in terms of hydrogen bonding, ion-dipole interaction, and tacticity of PVP.

EXPERIMENTAL

p-Hydroxybenzoic Acid-Formaldehyde Copolymer (PHBF)

The preparation of PHBF was described in an earlier communication [9].

Poly(Vinylpyrrolidone) (PVP)

PVP sample was obtained from BDH, Poole, England, and its weight-average molecular weight (\bar{M}_w), determined by viscosity measurements in aqueous solution at 25°C and the equation [10]

$$[\eta] = 6.76 \times 10^{-2} M_w^{0.55}$$

was found to be 3.75×10^4 .

The tacticity of the PVP sample was characterized by ^{13}C -NMR spectra, recorded on a Bruker WP 80 DS, and the spectrum was recorded in the FT mode with proton decoupling.

Solvent

BDH L.R. grade methanol was used as the solvent in all the experimental techniques.

Viscosity

The viscosity of mixed solutions of PHBF (10 unit mol/L) with PVP (1.0 unit mol/L) at various unit molar ratios was determined at $30 \pm 0.05^\circ\text{C}$ by an Ubbelohde viscometer, for which the kinetic energy correction was negligible. The measured time of flow for a given solution was always within 0.02%.

Potentiometric and Conductometric Titrations

The apparent pH and conductance of mixed solutions were measured at various stages of addition of PHBF (10 unit mol/L) to PVP (1.0 unit mol/L). The details of the experimental measurements have been described elsewhere [9].

Transmittance Measurements

The component polymers were mixed in definite unit mole ratios. The percentage transmittance of the mixed solutions were measured after 5 to 10 min at a fixed wavelength of 625 nm by a Perkin-Elmer spectrophotometer (Model 554).

Composition of Interpolymer Complexes

The composition and composition ratios of the interpolymer complexes are expressed everywhere in this article in terms of ratios of repeat unit molar concentrations.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of reduced viscosity, transmittance, pH, and conductance of PVP solutions in methanol with increasing concentration of PHBF in the same solvent. Each of these experimental measurements seems to indicate distinct steps in terms of unit mole ratios of the component polymers. The stoichiometries obtained at the different stages of complexation are summarized in Table 1.

These experimental observations show that PHBF and PVP enter into complex formation. Such stepwise complex formation has also been observed by us for *p*-bromophenol-formaldehyde (PPF)-PVP [8], and PHBF-PEO [9].

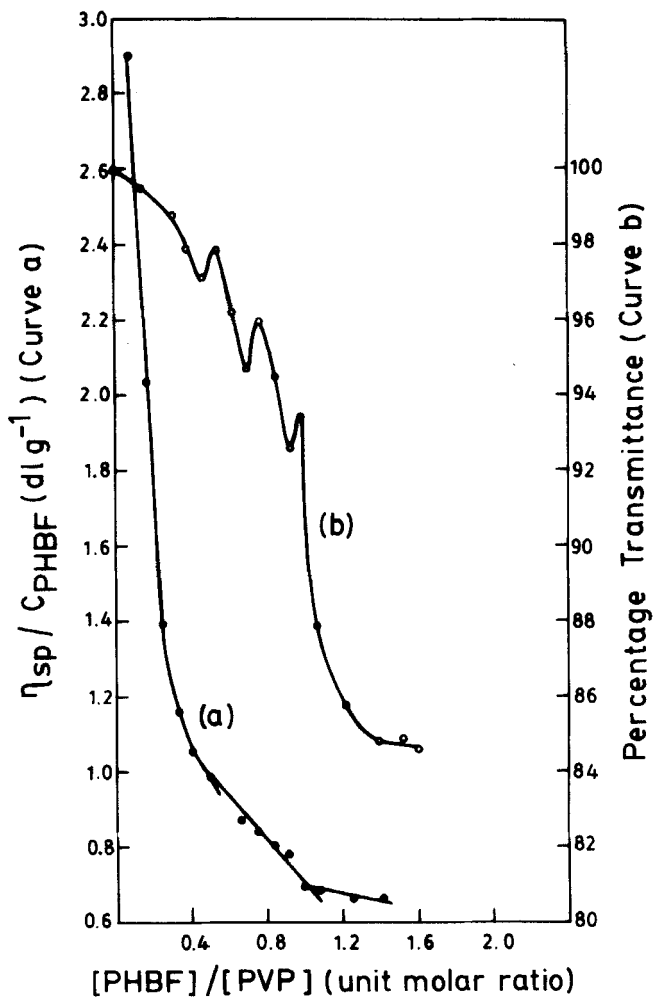


FIG. 1. Variation of reduced viscosity and transmittance with [PHBF]/[PVP] ratio. (a) Reduced viscosity (η_{sp}/C_{PHBF}); (b) turbidity.

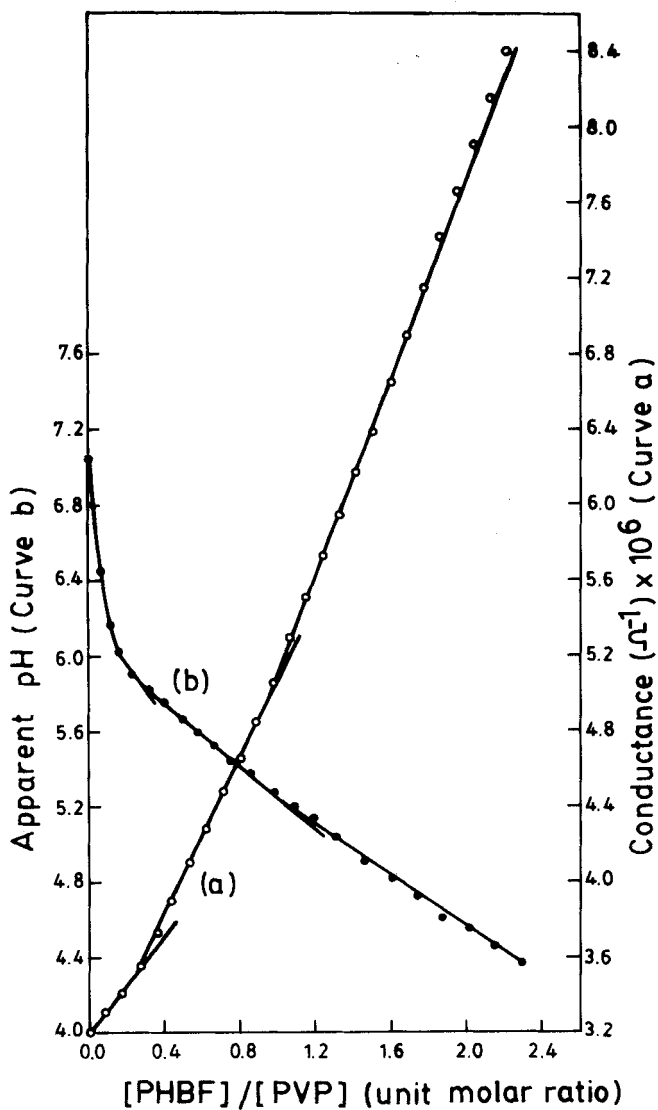


FIG. 2. Variation of conductance and apparent pH with [PHBF]/[PVP] ratio. (a) Conductivity; (b) apparent pH.

TABLE 1. Stoichiometries of PHBF-PVP Complexes

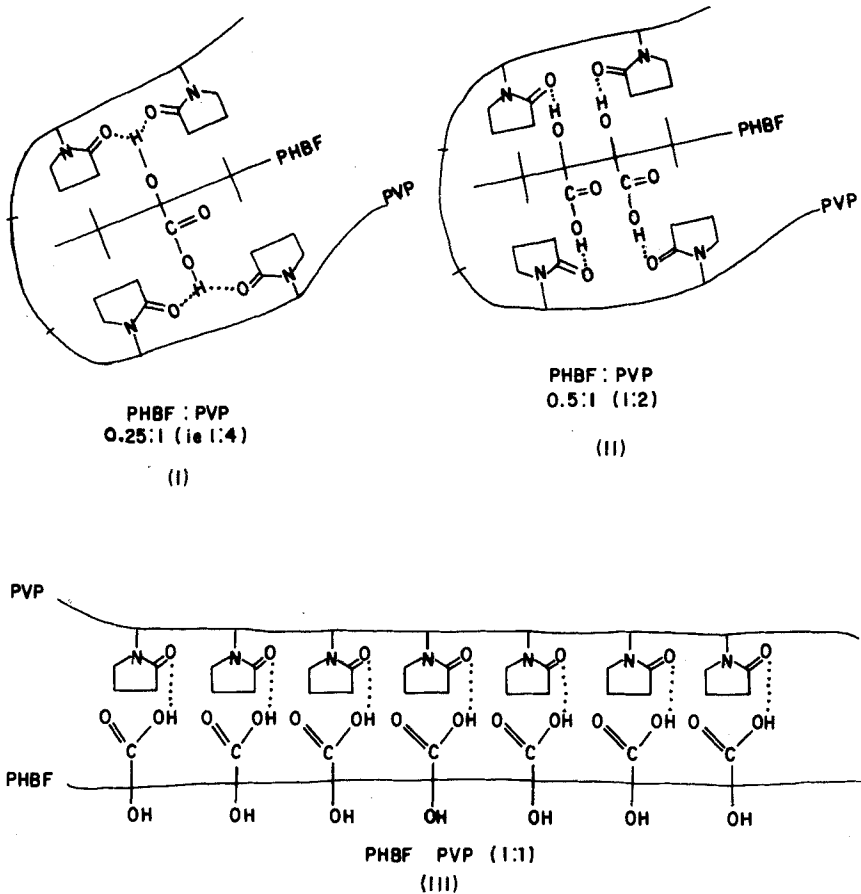
Physical property	[PHBF]/[PVP]
Reduced viscosity	0.5:1, 1:1
Transmittance	0.5:1, 0.75:1, 1:1
Conductance	0.25:1, 1:1
Apparent pH	0.25:1, 1:1

Of course, in those systems only one of the component polymers had two coordinating positions (i.e., PVP and PHBF). Since both the component polymers in the present system have two coordinating positions, one would expect a more complicated type of interaction.

The mode of interaction between the component polymers at various stoichiometries may possibly be explained on the basis of Scheme 1.

It is known that, when a polydisperse oligomer is complexed with a matrix polymer, the higher molecular weight fractions of the oligomer are selectively complexed with the matrix. In this case the complexed polymer molecule may consist of flexible (free) and rigid (complexed) sections. This implies that there are two parts of the matrix in the solution, one part being almost completely filled with the oligomer and the other part being more or less free. This type of complexation between an oligomer and matrix polymer is known as "all-or-none" complexation. However, the distribution of oligomer on the matrix polymer can be completely random, depending upon the initial conformation of the matrix polymer in each particular solvent. Kabanov and co-workers [11] reported from their sedimentation studies that, in aqueous solutions of mixtures of PMAA and PEO or PMAA and PVP, the oligomers are distributed on the matrix chains according to the all-or-none principle. However, in the methanol-water solvent system (methanol about 30 vol%), the oligomers are statistically distributed on the matrix chains. Of course, only after a certain critical degree of filling is reached does the distribution become nonstatistical.

In our system the matrix polymer (PVP) in pure methanol could possibly be in a specific conformation that may favor random distribution of PHBF on the matrix chains. Due to complexation, the matrix molecules are highly compact, and the intramolecular mobility decreases. The fall in reduced viscosity at different stages of complexation may be attributed to this effect. These interpretations, of course, need further confirmation by independent methods.



SCHEME 1.

On comparing the IR spectra of the interpolymer complexes isolated at different stoichiometries with those of the pure components (i.e., PHBF and PVP), it was observed that the -C=O absorption for the complexes was at 1640 cm^{-1} , whereas it was at 1660 and 1625 cm^{-1} , respectively for pure PHBF and PVP. This indicates the probable involvement of carboxyl group (of PHBF) and carbonyl group (of PVP) in the complex formation. Of course, one cannot rule out the possibility of involvement of OH groups of PHBF in the complex formation [9].

The stepwise interaction of PVP with PHBF could perhaps also be explained on the basis of the tacticity of PVP. Cheng and coworkers [12] studied the tacticity of PVP on the basis of ^{13}C -NMR spectra, and concluded that it contained almost equal proportions of isotactic and syndiotactic configurations. The ^{13}C -NMR spectra of our PVP sample was found to be identical in all respects with that of Cheng and coworkers, which indicates the presence of equal proportions of isotactic and syndiotactic configurations in our sample as well. If this is true, the isotactic chains should be in a more favored position to interact with PHBF. Since 1 unit mole of PVP contains roughly 0.5 unit mole each of isotactic and syndiotactic chains, isotactic chains can interact with two coordinating positions of PVP in two distinct stages up to 0.5 unit mole of PHBF, and subsequently the syndiotactic chains probably react with the remaining 0.5 unit mole of PHBF.

It is known that the configurational environment of a polymer molecule during complexation influences the stoichiometry and mode of complexation [6, 7]. Solvent and the presence of an excess concentration of either of the components are some of the factors which may change the environment. With this in mind, we studied the complexation by adding the components in the reverse order (i.e., by adding PVP to PHBF). Figure 3 shows the variations of pH and conductance in such a system, and the stoichiometries are summarized in Table 2.

Two stoichiometries, i.e., 1:4 and 1:2 [PVP]/[PHBF], are found to be different from 1:1 in the reverse addition. It may be assumed that, at high oligomer concentrations (i.e., reverse addition of components), the matrix macromolecules are completely filled with oligomers whereas, at low oligomer concentrations, a conformational transition of the matrix polymer chains takes place. This assumption is confirmed by depolarization data on luminescence [1]. Thus, with the reverse addition, one can expect nonstatistical distribution of the oligomer on the matrix chains, and the additional stoichiometries of interpolymer complexes could possibly be attributed to it.

It may be concluded that, as a result of interaction of an oligomer with a matrix polymer, the complexed molecules possibly consist of two sections, i.e., flexible (free) and rigid (complexed) sections. However, in methanol solution, which destroys hydrophobic interaction, the bound oligomer molecules (i.e., PHBF) are probably randomly distributed on the matrix polymer chains (i.e., PVP).

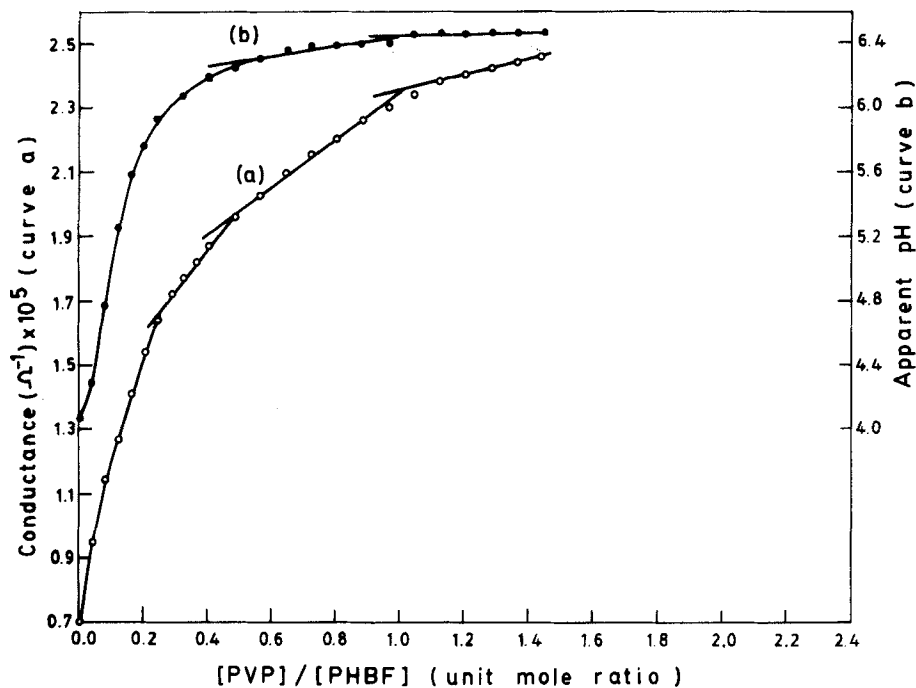


FIG. 3. Variation of conductance and apparent pH with [PVP]/[PHBF] ratio. (1) Conductivity; (b) apparent pH.

TABLE 2 Stoichiometries of PHBF-PVP Complexes in the Reverse Addition of Components

Physical property	[PVP]/[PHBF]
Conductance	0.25:1, 0.5:1, 1:1
Apparent pH	0.5:1, 1:1

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