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INTERPOLYMER COMPLEXES OF A NEW TYPE
Three-component interpolymer complexes involving a monobasic low molar mass mediator

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Abstract

A new type of three-component interpolymer complexes (3IPCM) formed by two similarly charged polyelectrolytes and an oppositely charged low molar mass compound was studied by DSC, NMR and X-ray methods. The low molar mass monobasic compounds in these complexes act as mediators. This type of complexes differs from earlier-obtained 3IPCM, which contained a dibasic low molar mass mediator.

The present 3IPCM were obtained from two polymers (polyacrylic acid and sodium polyphosphate) and bases such as 4-vinylpyridine and 2-methyl-5-vinylpyridine.

Keywords: DSC, optical densities, thermal stability, three-component interpolymer complexes

Introduction

We recently discovered a new class of interpolymer complexes: three-component interpolymer complexes (3IPCM) involving a low molar mass mediator [1, 2]. These complexes are totally different from earlier-described polyelectrolytes (PEC), the main components of which are chains of two oppositely charged polymers [3]. The present 3IPCM are formed by two similarly charged macromolecules contact with a low molar mass organic component of opposite charge, which acts as a mediator. Mediators are usually dibasic components. In the present work an attempt was made to establish whether monobasic compounds, and in particular 4-vinylpyridine (4VP) and 2-methyl-5-vinylpyridine (2M5VP), could serve as mediators in the formation of 3IPCM by polyanions such as sodium polyphosphate (NaPP) and polyacrylic acid (PAA).

Experimental

2M5VP and 4VP from Reachim (Russia) were used without further purification.

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The 3IPCM were obtained by the interaction of aqueous solutions of NaPP and 4VP or 2M5VP with an aqueous solution of PAA at $pH<5.0$. The complexes precipitate at once from aqueous solution.

A 50% solution of PAA in dioxane was prepared as described previously [4]. The molar mass M was measured viscosimetrically in 0.5 N NaCl solution, $[\eta]=1.05\cdot10^{-3}\cdot M^{0.54}$, where $[\eta]$ is the intrinsic viscosity.

NaPP was obtained by condensation of $NaH_2PO_4\cdot2H_2O$ through fusion at 800°C for 15 h. M was calculated via the relationship $[\eta]=1.76\cdot10^{-5}M$ [5]; $[\eta_S]$ was measured in 0.035 N NaBr solution.

DSC curves were obtained with a Mettler DSC-30 instrument (Switzerland) over the temperature range 25–300°C at a heating rate of 2 K min^{-1} [6]. The temperature and energy scales of the DSC were calibrated with gallium, *p*-nitrotoluene, dimethyl terephthalate, indium, tin and lead.

Optical density of solutions was determined with a PEC-56 photoelectrocolorimeter (Russia).

NMR spectra were measured in a mixture of D_2O and DCl (volume ratio 1:1) with DSS as standard at 80°C, with a Tesla-70 instrument.

X-ray analysis of 3IPCM samples was performed with Rigaku D_{max}-RC equipment (CuK, Ni filter).

Carbon, hydrogen and nitrogen were determined with a Carlo Erba EA1108 automatic analyser. Phosphorus in the combustion products of the samples was determined colorimetrically [7].

Results and discussion

Both monobasic low molar mass compounds (2M5VP and 4VP) reacted with aqueous solutions of NaPP and PAA at $pH=2.5$ to yield water-insoluble products. NMR and elemental analysis revealed the compositions PAA:4VP:NaPP =4.1:1:1.5 and PAA:2M5VP:NaPP=5.1:1:2.6. It remained to clarify whether the products are true 3IPCM, i.e. solid interpolymer compounds, rather than compounds of the monobasic low mass molar mass salts and one of the reacting polyacids, or a mixture of the two salts.

to answer this question, the dependence of the optical density D of solutions on pH was investigated for each system studied, in the pH region in which the products exist in a water-insoluble form.

Let us consider what water-insoluble compounds can be formed in the systems containing NaPP, PAA and 2M5VP or NaPP, PAA and 4VP. Besides 3IPCM, they can be salts of 2M5VP or 4VP with one of the polyacids, or a mixture of such salts. It is evident from the data in Fig. 1(a,b) that in solutions containing all three original components the water-insoluble product precipitates in the pH region from 1.5 to 3.9 for 2M5VP and from 1.0 to 3.4 for 4VP. It is also clear that PAA salts with both monobasic compounds precipitate from

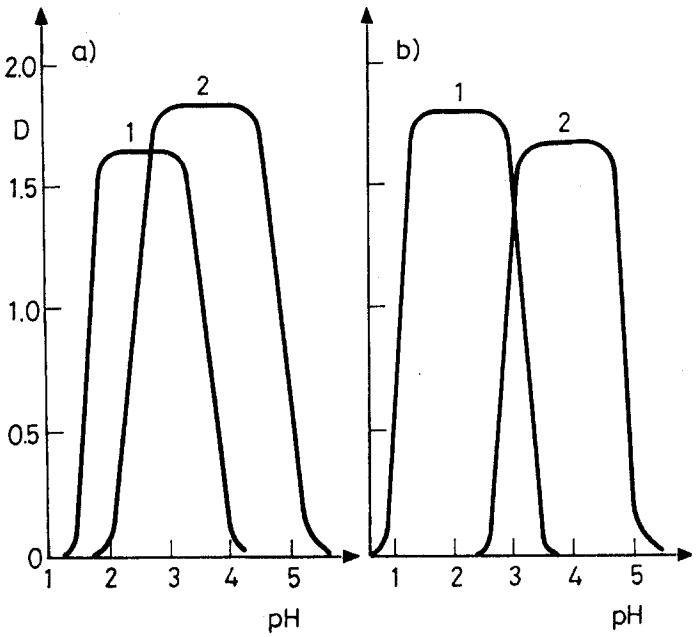

Fig. 1 Dependence of optic density *D* on *pH*: a) 1 PAA-2M5VP-NaPP; 2 PAA-2M5VP; b) 2 PAA-4VP-NaPP; 2 PAA-4VP

aqueous solutions at $pH<5.0$. Salts of 2M5VP and 4VP with NaPP appear to be water-soluble throughout the whole investigated interval of *pH* (*pH* 0.5 to 10.0). While the elemental analysis and NMR data suggest three original components in the precipitating product, it should be accepted that the precipitate can not be a salt of a base with PAA. It is rather a three-component interpolymer complex. The *pH* ranges for precipitation of polymer reaction products involving NaPP, PAA and a base differ markedly from those *pH* regions where the salt of the corresponding bases and PAA precipitate. This favors the fact that the product precipitating spontaneously from NaPP, PAA and 4VP solutions is not a mixture of the corresponding polymer salts, but rather an interpolymer complex. However, the existence of a *pH* region where simultaneous precipitation of 3IPCM and polymer salts is possible demands additional comparative research of the reaction products of NaPP, PAA and 2M5VP or 4VP, and the salts of these bases with PAA.

These studies were conducted by DSC and X-ray methods. Many methods used to study soluble polymers are not applicable for the study of water-insoluble 3IPCM. In this case, DSC is of special value. The fact of complex formation was demonstrated by comparing DSC curves of PAA and NaPP with those for the base product and corresponding model compounds. The differences in the form of the DSC curves and the phase transition temperatures indicate that

the interaction of the two polyacids and the low molar mass base results in a three-component interpolymer complex different from both model mixtures formed by each polyacid with the low molar mass mediator and the mixture of these acids with the corresponding low molar mass base. Figure 2 depicts DSC curves of the interaction products of PAA, NaPP and 2M5VP or NaPP, PAA and 4VP, and the corresponding model compounds: salts of 2M5VP and 4VP with PAA and PPH. One can clearly see the difference in thermal behavior of the reaction products of all three components and the salts of each monobasic mediator (2M5VP and 4VP) with PAA and NaPP.

It is evident that the complex is not a mixture of three components, but is an individual compound with a definite temperature corresponding to a one phase transition. The endothermic peak in the DSC curves presumably relates to melting of the complex structure followed by decomposition at various tempera-

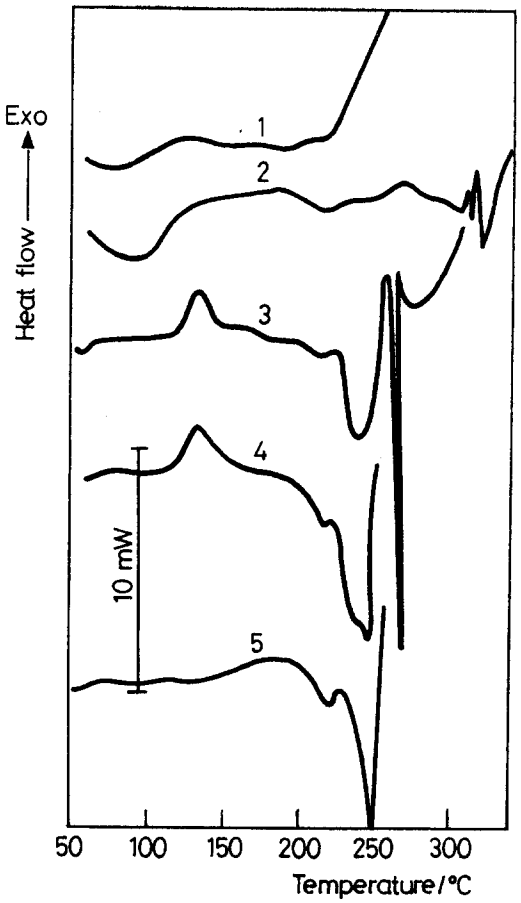

Fig. 2 DSC curves: 1 PAA-4VP, 2 NaPP-4VP, 3 PAA-4VP-NaPP, 4 PAA-2M5VP-NaPP, 5 PAA-2M5VP

tures. This justifies the difference in packing of the mediator molecules in the complex. It can be supposed that the complex structure is sensitive to minor changes in the structure of the low molar mass mediator. The presence of a low-volume substituent in 2M5VP, in contrast with 4VP, where such a substituent is absent, leads to differing DSC temperature curves.

Evidence suggesting a scheme of similar complex structures can be obtained from X-ray structural analysis data on the 3IPCM with monobasic mediators and also from the *D vs. pH* dependence data for each 3IPCM. It is clearly seen from the data (Fig. 1) that the formation of water-insoluble 3IPCM accompanied by a sharp increase in *D* of the solution, depending on the *pH* of the medium, occurs with a negligible *pH* change in both the acidic and close to neutral region. That is, the system markedly changes its state in a rather narrow range of change of one of the parameters of the external medium: *pH*. This behavior is typical for cooperative systems, including some will-known two-component interpolymer complexes. Apparently, 3IPCM should be treated as a cooperative system as well.

It follows from the above that complex formation takes place involving stable contacts between two polyacids with an organized succession of links of low molar mass mediators rather than single base molecules. This is clear because single molecules of monobasic compound are not able to create a similar system

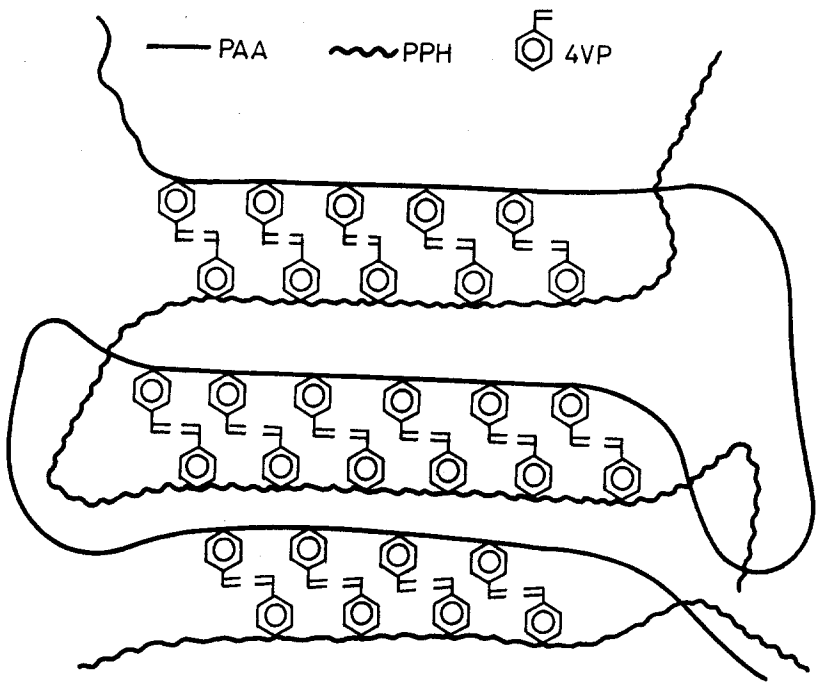

Fig. 3 Structure scheme of theree component interpolymer complex by monobasic low molar mass mediator – 4VP

of contacts due to the charge which each molecule bears. It is presumed then that the molecules of these bases must be organized so that charge-bearing atoms should be directed to both polyacids. Since the molecules of all the studied bases contain aromatic rings (2M5VP and 4VP contain hydrophobic groups) and tend to associate in aqueous solution, the 3IPCM structure based on NaPP can be represented schematically as follows (Fig. 3).

This supposition is confirmed by the X-ray data, where 3IPCM with 2M5VP and 4VP display intensive reflexes d=23.7 Å and d=25.2 Å. Such distances are in good agreement with a 3IPCM structure if d is treated as the diameter of a double-line 3IPCM structure.

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