

Application of FTIR Spectroscopy for Structural Characterization of Ternary Poly(acrylic acid)–Metal–Poly(vinyl pyrrolidone) Complexes

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ABSTRACT: The FTIR spectroscopic technique was used in the study of ternary polymer–metal complexes containing two polyelectrolytes of opposite charge and metal ions. The structure of the ternary (PAA-Fe³⁺-PVP) complexes was examined by following the changes in their infrared spectra. It was found that the shapes of the absorption bands of the resultant compounds are influenced by the presence of Fe³⁺. According to this result it was suggested that two types of structure which differ in the composition are formed, one of which results from the coordination of Fe³⁺ with PAA-PVP complex and the other is due to the formation of Fe³⁺ polycarboxylate. Comparison between the spectrum of PAA-PVP complex and those of the compounds resulted from the reaction between the two opposite charged electrolytes, PAA and PVP and each of the divalent metal chlorides NiCl₂, CoCl₂, CuCl₂, and ZnCl₂ led to the conclusion that a reaction took place between the divalent transition metal chlorides and the extent of reaction depends on the nature of metal ions and PAA-

PVP complex. The FTIR spectra of the precipitate resulted from the mixtures of PAA-PVP and Ni(NO₃)₂ or Sr(NO₃)₂ were investigated. It was noted that the addition of Ni(NO₃)₂ or Sr(NO₃)₂ to the mixture of the electrolytes of PAA and PVP provoked appreciable changes in the characteristic spectral features of the complex resulting from the interaction of the metal ions with the polymer–polymer complex. The FTIR spectra of the precipitate resulted from the reaction between CeCl₃, ErCl₃, and LaCl₃ were also investigated. It was concluded that a reaction took place between the rare earth metals and the PPC. This means that ternary polymer–metal–polymer complexes were formed. The extent of changes in the spectral features differs from metal to metal according to the nature of metal ions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1888–1893, 2007

Key words: FTIR spectroscopy; poly(acrylic acid); poly(vinyl pyrrolidone); ternary (polymer–metal–polymer) complex

INTRODUCTION

The interpolymer interaction between water soluble polymers has been a subject of interest for a number of investigators over the past two decades.^{1–8} The cooperative interaction between synthetic water-soluble polymers has been a popular research topic because of their importance from both academic and applied viewpoints.

Interpolymer complexes resulting from these interactions possess unique properties, which are different from those of the individual components and find various applications, for example, in dialysis, ultrafiltration, reverse osmosis and production of blood-compatible materials and batteries.

The study of ternary polymer–metal complex containing two polyelectrolytes of opposite charge and metal ions is a new trend in polymer chemistry. This trend is based on the chemistry of inter macromolecu-

lar reactions and coordination chemistry of polymer–metal compounds.^{9–14} Till the present time the formation, structure, and properties of ternary PAA–metal–PVP complexes has not yet been fully investigated.

The main purpose of this study is to investigate more quantitatively the process of the complexation of poly(acrylic acid)–poly(vinyl pyrrolidone) and poly(acrylic acid)–metal–poly(vinyl pyrrolidone) complexes by using Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Polyvinyl pyrrolidone (PVP) was obtained from Sigma Chemical, its average molecular weight was 360,000. Poly(acrylic acid) (PAA) was obtained from Nisso SHOJI, Japan. The polymers were used as received without further treatment. A solution from each polymer: PAA and PVP was prepared by dissolving the polymer in distilled water with the concentration 1 g/100 mL and each solution was then stirred to ensure complete dissolution. Mixtures from the two polymer solutions with different PAA weight fractions (WF_{PAA}), were prepared by mixing

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the two solutions in the appropriate proportions. Just after mixing the two solutions complete precipitation or phase separation took place without any further treatments. The precipitates were then filtered, washed with distilled water and air dried over 3 days at room temperature. The complexes were further dried at 60°C in a drying oven until a constant weight is maintained. The dried samples were then ground in ball mixer mill. The samples were sieved and a suitable particle size was used (between 125–160 μm).

The solutions of (PVP) treated with transition metal chlorides FeCl_3 , CoCl_2 , NiCl_2 , CuCl_2 , and ZnCl_2 , rare earth metal chlorides CeCl_3 , LaCl_3 , and ErCl_3 , alkali metal chloride SrCl_2 and $\text{Ni}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ were added to (PAA), which was achieved by dissolving a certain weight of polymer (0.5 g) in fixed volume of distilled water (50 mL) and homogenated by stirring for 2 h. The precipitates were then filtered, washed with distilled water and air dried over 3 days at room temperature. The complexes were further dried at 60°C in dry oven until maintaining constant weight. The dried samples were then ground in the ball mixer/mill. The samples were sieved and the suitable particle size was used. KBr discs were prepared from the powders for FTIR measurements.

RESULTS AND DISCUSSION

In a previous study carried out in our laboratory,¹ the FTIR spectroscopic technique has been used for structural characterization of PAA-PVP complex (PPC). The FTIR spectrum of PAA showed the stretching vibrations of hydroxyl group at 3392–3172 cm^{-1} and the stretching carbonyl group $\text{C}=\text{O}$ at 1711 cm^{-1} . Weaker bands associated with scissor and bending vibrations of $-\text{CH}_2-$ and $\text{CH}-\text{CO}$ groups appeared at 1454 and 1415 cm^{-1} , respectively. The bands at 1245 and 1170 cm^{-1} were attributed to the coupling between in-plane OH bending and $\text{C}-\text{O}$ stretching of neighboring carboxyl groups. The FTIR spectrum of PVP displayed absorption bands at the frequencies 3447 cm^{-1} (absorbed water), 2961 cm^{-1} $\nu(\text{C}-\text{H})$ 1672 and 1657 $\nu(\text{C}=\text{O})$, 1441 and 1379 cm^{-1} (δCH_2), 1294 $\nu(\text{C}-\text{N})$. In addition to other weak bands at lower frequencies. Examination of the spectrum of the complex showed that the frequencies of the absorption bands of the complex are different from those of the bands of the individual components Figure 1. These differences in positions and intensities of the absorption bands were attributed to the formation of interpolymer complex resulting from the interaction between PAA and PVP. The induced changes due to the interpolymer complexation assume that the hydrogen bonding is the primary mechanism of the interaction between the two polymers.

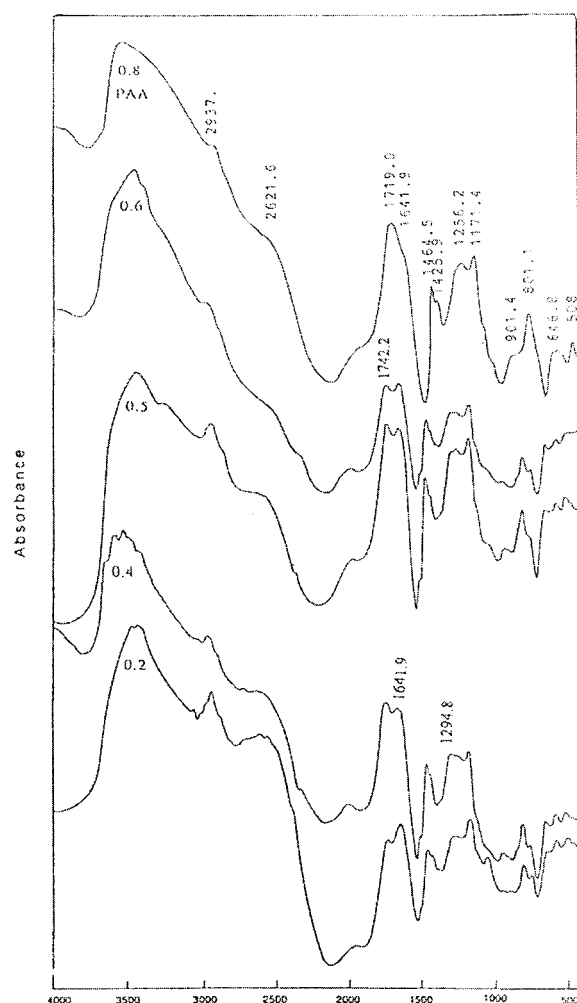


Figure 1 Shows the FTIR spectra of PPCs with different weight fractions of PAA.

In the present study aqueous solutions with various concentrations of FeCl_3 were mixed with solution of the mixture of PAA and PVP [50% PAA and 50% PVP]. The concentrations of FeCl_3 were 5, 10, 20, and 30% (w/w) of the total weight of the two polymers of the mixture. Once after mixing the two solutions complete precipitation or phase separation took place without any further treatments. The precipitates were then filtered, washed with distilled water and dried at 60°C in drying oven until maintaining constant weight.

The FTIR spectra of the PPC and PMPC are shown in Figure 2. By comparing these spectra, the following spectral changes are visible.

1. The spectrum of PPC exhibits two absorption peaks at 1742 and 1641 cm^{-1} whose maxima are of nearly equal heights. The shape and the absorbances of these two bands are influenced by the presence of Fe^{3+} . The absorbances of the two bands vary with respect to each other according to the Fe^{3+} concentration from 5 to

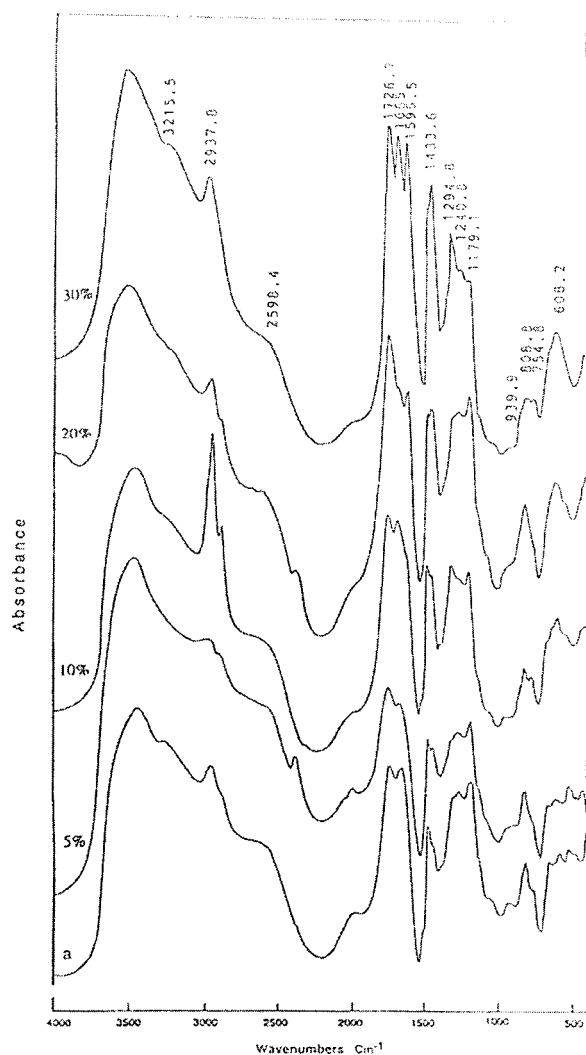


Figure 2 FTIR spectra of PPC of Fe^{3+} [(a) PAA-PVP; (b) Fe^{3+} = 5%; (c) Fe^{3+} = 10%; (d) Fe^{3+} = 20%; and (e) Fe^{3+} = 30%].

20%. The absorbances of the two bands were determined by using the baseline method. A base line was drawn across them from 2300 to 1500 cm^{-1} . It was found that 20% (w/w) concentration of FeCl_3 results in significant increase in this ratio (Table I).

- In addition to the above-mentioned peaks the spectrum of the sample prepared from the mixture containing 10% (w/w) FeCl_3 shows new peak at 1603 cm^{-1} . The intensity of the latter band appears more intense in the condition of 20% (w/w) concentration.
- The spectrum of the sample, resulted from the mixture containing 30% (w/w) FeCl_3 , displays unique spectral features over the absorption region under discussion, which are different from those for the spectra of the samples having 5, 10, and 20% (w/w) FeCl_3 . In the present case the spectrum shows three definite sharp peaks at 1726, 1665, and 1595 cm^{-1} .

TABLE I
The Absorbance Ratio $A_{1742}/A_{1641} \text{ cm}^{-1}$ and the Concentration of FeCl_3 in the Complex of (PAA-PVP)

Concentration of FeCl_3	Absorbance ratio $A_{1742}/A_{1641} \text{ cm}^{-1}$
PAA-PVP	1.01
PAA- Fe^{3+} -PVP (5%)	1.01
PAA- Fe^{3+} -PVP (10%)	1.06
PAA- Fe^{3+} -PVP (20%)	1.28

- Two bands of medium and weak intensities appear in the spectrum of PPV at 1464 and 1433 cm^{-1} , respectively. In the spectrum of the PMPC prepared from the mixture containing 20% (w/w) FeCl_3 two sharp definite peaks whose maxima are of equal heights appear at the same frequencies. In the case of 30% (w/w) FeCl_3 the band at 1433 cm^{-1} predominates and the other band appears as shoulder on its higher frequency side.
- The absorption over the spectral region 1300–1100 cm^{-1} was also markedly influenced by Fe^{3+} . In this region the band at 1294 cm^{-1} appears more intense and sharp in the spectra of samples prepared from mixtures containing 10% (w/w) and 30% (w/w) FeCl_3 than in the spectra of the other samples.

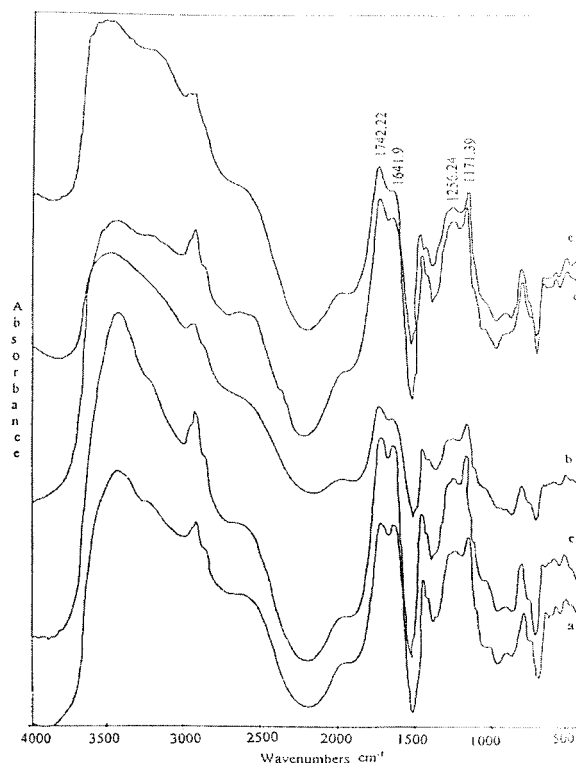


Figure 3 FTIR spectra of PPC, with divalent transition metal chlorides [(a) PPC; (b) (PPC- CoCl_2); (c) (PPC- NiCl_2); (d) (PPC- CuCl_2); and (e) (PPC- ZnCl_2)].

TABLE II
The Absorbance Ratios A 1742/A 1641, A 1456/A 1641, A 1171/A 1641, and A 801/A 1641 cm^{-1} Together with the Ionic Radii of the Metal Ions

Ionic radii	Absorbance ratios			
	A1742/ A1641 (cm^{-1})	A1456/ A1641 (cm^{-1})	A1171/ A1641 (cm^{-1})	A801/ A1641 (cm^{-1})
PAA-PVP	1.01	0.68	0.83	0.39
PAA-NiCl ₂ -PVP (0.69)	1.08	0.72	0.99	0.37
PAA-CoCl ₂ -PVP (0.72)	1.05	0.67	0.91	0.35
PAA-CuCl ₂ -PVP (0.72)	1.14	0.73	0.92	0.42
PAA-ZnCl ₂ -PVP (0.74)	1.14	0.73	0.98	0.44
PAA-SrCl ₂ -PVP (1.12)	0.99	0.67	0.85	0.38

The spectrum of the complex resulted from the reaction between FeCl₃ and PAA exhibits absorption bands at 1726, 1595, and 1456 cm^{-1} . The presence of the band at 1595 cm^{-1} provides strong evidence for the formation of Fe³⁺ polycarboxylate.

Based on the above-mentioned considerations, one can suggest that two types of structure which differ in the composition are formed, one of which results from the coordination of Fe³⁺ with PPC and the other is due to the formation of Fe³⁺ polycarboxylate.

Figure 3 shows the FTIR spectra of the compounds resulted from the reaction between the two oppositely charged polyelectrolytes, PAA and PVP and each of the divalent transition metal chlorides NiCl₂, CoCl₂, CuCl₂, and ZnCl₂.

Comparison between the spectrum of PPC and those of the compounds resulted from the reaction between PAA-PVP and each of the divalent metal chlorides showed that the existence of the metal chlorides resulted in no significant changes in the spectral features of the PPC, apart from slight changes in the intensities of the absorption bands. It was found that while the spectrum of PPC displays two peaks of nearly equal maxima at 1742 and 1641 cm^{-1} , the spectra of the samples containing 10% (w/w) of each mentioned chlorides show the same peaks but the maximum of the 1742 cm^{-1} band appears higher than that of the 1641 cm^{-1} band.

The absorbance ratios A1742/A1641, A1456/A1641, A1171/A1641 cm^{-1} , and A801/A1641 cm^{-1} were calculated and are given in Table II together with the ionic radii of the metal ions. It could be seen from this table that, for the divalent metal chlorides the absorbance ratios are slightly influenced by the nature of the metal ions.

The above-mentioned observations lead to the conclusion that the formation of ternary polymer-metal-polymer complex is a result of the coordination of the metals to the polymer-polymer complex.

It seems very important to mention that the PAA-SrCl₂ PVP systems give rise to spectrum whose spectral features are similar to those of the spectrum of PVP-transition metal chlorides-PAA system.

The FTIR spectra of the precipitates resulted from the mixtures of PVP-PAA and Ni(NO₃)₂ and Sr(NO₃)₂ are given in Figure 4. It was found that the addition of Ni(NO₃)₂ or Sr(NO₃)₂ to the mixture of the electrolytes of PAA and PVP causes changes in the characteristic spectral features of the complex resulting from the interpolymer interaction of the two polymers. The most striking changes are:

1. Marked decrease in the intensity of the band at 1742 cm^{-1} with respect to the intensity of the band at 1641 cm^{-1} .
2. Remarkable increase in the intensity of the absorption bands at 1387, 1171, and 1032 cm^{-1} .

The absorbance ratios 1742/1641, 1456/1641, 1171/1641, and 801/1641 cm^{-1} were determined and are given in Table III. It was observed that values of these ratios are different from the corresponding values in the case of PPC.

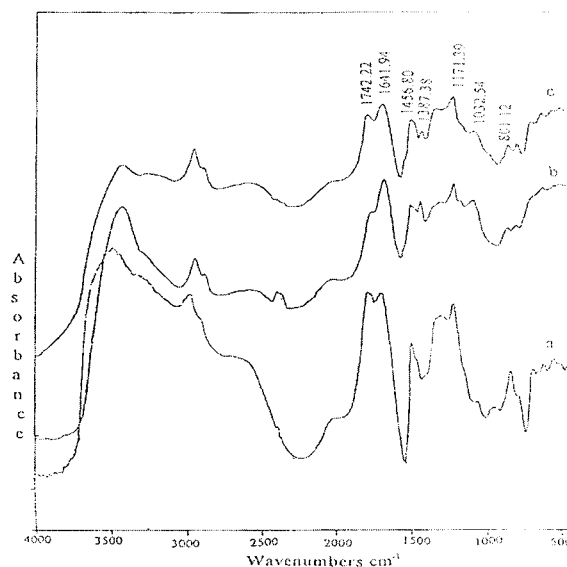


Figure 4 FTIR spectra of the (a) PAA-PVP; (b) PAA-Ni(NO₃)₂-PVP; and (c) PAA-Sr(NO₃)₂-PVP complexes.

TABLE III
The Absorbance Ratios of PPC with Metal Nitrates

Metal nitrate	Absorbance ratios			
	A1742/ A1641 (cm ⁻¹)	A1456/ A1641 (cm ⁻¹)	A1171/ A1641 (cm ⁻¹)	A801/ A1641 (cm ⁻¹)
PAA-PVP	1.01	0.68	0.83	0.39
PAA-Ni(NO ₃) ₂ -PVP	0.66	0.6	0.73	0.08
PAA-Sr(NO ₃) ₂ -PVP	0.89	0.7	0.89	0.19

It was noticed also that Ni(NO₃)₂ causes greater changes in the spectra of PPC than Sr(NO₃)₂.

The foregoing data demonstrate the formation of ternary polymer-metal-polymer complex as a result of the coordination of the metals to the polymer-polymer complex.

The FTIR spectra of the precipitates resulted from the reaction between CeCl₃, ErCl₃, and LaCl₃ are represented in Figure 5. This figure indicates the following:

1. CeCl₃ causes slight changes in the intensities of the absorption bands of PPC. It is clear that the addition of CeCl₃ decreases the intensity of the band at 1641 cm⁻¹ with respect to that of the band at 1742 cm⁻¹. Also the intensities of the two bands at 1294, 747 cm⁻¹ have become more intense.
2. ErCl₃ causes considerable changes in the characteristic spectral features of PPC. It is obvious that the band at 1641 cm⁻¹ has become less intense than the band at 1742 cm⁻¹ and a weak band appears at 1549 cm⁻¹. Also the two peaks appearing at 1456 cm⁻¹ and at 1402 cm⁻¹ became sharper. Moreover, the band at 747 cm⁻¹ became shoulder.
3. LaCl₃ results in marked decrease in the intensity of the band at 1742 cm⁻¹ as compared with that at 1634 cm⁻¹. On the other hand, a new shoulder appeared at 1540 cm⁻¹ and a sharp strong band appeared at 1163 cm⁻¹.

Examination of the spectra in the Figure 5 reveals that each spectrum is characterized by its own spectral features, which are differed from those of the spectrum of PPC.

On the basis of the above observations, one can come to the conclusion that a reaction took place between the rare earth metal chlorides and the PPC. This means that a ternary polymer-metal-polymer complexes were formed. The extent of changes in the spectral features differs from metal to metal according to the nature of metal ions.

CONCLUSIONS

The obtained data demonstrate that FTIR techniques have become most important tools for the characterization of the physical and chemical natures of the ternary (polymer-metal-polymer) nature. It can be concluded that in the case of PAA-PVP-metal systems, it was observed that precipitations were formed in these systems and these precipitations were attributed to the formation of ternary metal-polymer complexes as a result of the co interaction of metal cations with the PPCs. The behavior of change of the absorbances ratios with the metal cation concentrations depends on the nature of the cation (ionic radius and valency) and on its concentration.

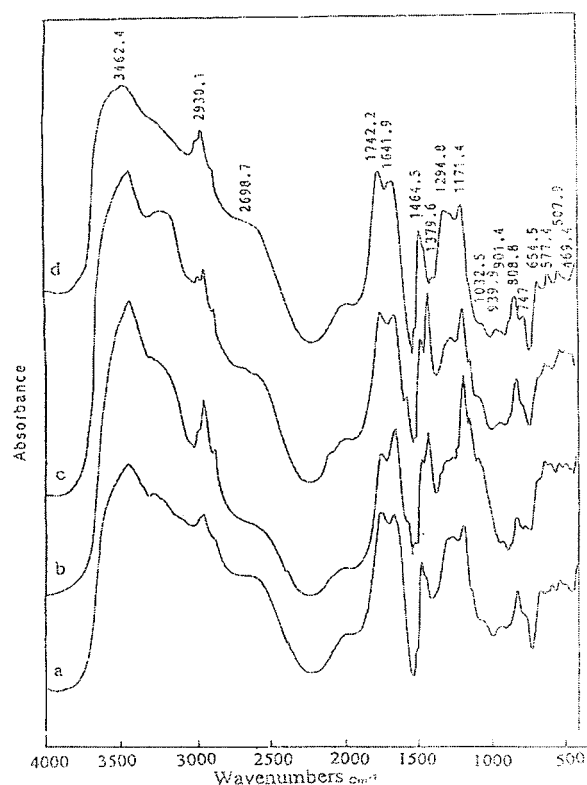


Figure 5 FTIR spectra of PPC with rare earth metal chlorides [(a) PPC; (b) PPC-LaCl₃; and (d) PPC-CeCl₃].

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