

Infrared Study of the Complexation of Poly(acrylic acid) with Poly(acrylamide)

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SYNOPSIS

Infrared spectroscopy was used to study the interpolymer complexation of poly(acrylic acid) with polyacrylamide. The spectrum of the interpolymer complex showed characteristic absorption bands which are different from those of the spectra of the individual components, particularly in the O—H and N—H stretching vibration regions. The effects of ionic strength and poly(acrylic acid) weight fractions on the spectral features of the complex were investigated. It was found that hydrogen bonding is the primary mechanism of interaction between the two polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The interactions between poly(acrylic acid) (PAA) and polyacrylamide (PAAm) have been studied in recent years using fluorescence spectroscopy and viscometry.^{1–5} Interpolymer complexes resulting from these interactions possess unique properties which are different from those of the individual components.⁶ The structure, as well as the stability of the complexes, depends on the type of interactions, the solutions conditions, and macromolecular characteristics such as pH, ionic strength, temperature, solvent, molecular weight, and conformation.⁶ The present study was conducted to investigate the PAA–PAAm interpolymer complexation using FTIR spectroscopy.

EXPERIMENTAL

Polyacrylamide (PAAm) was obtained from BDH Chemicals, Pool, England; its molecular weight is over 5,000,000. Poly(acrylic acid) (PAA) was obtained from Nisso Shoji Co., Japan (PW-110 Lot No. 4029). The two polymers were used without any further purification. A solution of each polymer was

prepared by dissolving 1 g in 100 mL of distilled water. Each solution was then stirred overnight to ensure complete dissolution. Mixtures from the two solutions with different PAA weight fractions, W_{PAA} , were prepared. Also, solutions of PAA were prepared in electrolytes of NaCl with various ionic strengths, namely, 0, 0.001, 0.005, and 0.02 M and mixtures of the two polymers were prepared. The pH of the mixtures was then adjusted⁷ by drops of 10% HCl until precipitation or phase separation took place. The precipitate was filtrated and washed with distilled water to remove any soluble salts. The samples were dried in an oven at 90°C for 6 h and then ground to a particle size suitable for IR measurements. The FTIR spectra were recorded on a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique.

RESULTS AND DISCUSSION

The FTIR spectra of films prepared from mixtures of PAA and PAAm solutions with different W_{PAA} are shown in Figure 1. The characteristic absorption bands of PAA are located at frequencies 3413, 2955, 1718, 1450, 1417, 1248, and 1174 cm^{-1} , while those of PAAm are located at frequencies 3350, 3203, 2936, 1670, 1659, 1452, 1420, 1350, and 1324 cm^{-1} . As is seen in Figure 1, the addition of a 0.1–0.3 weight fraction of PAA to PAAm produces no substantial

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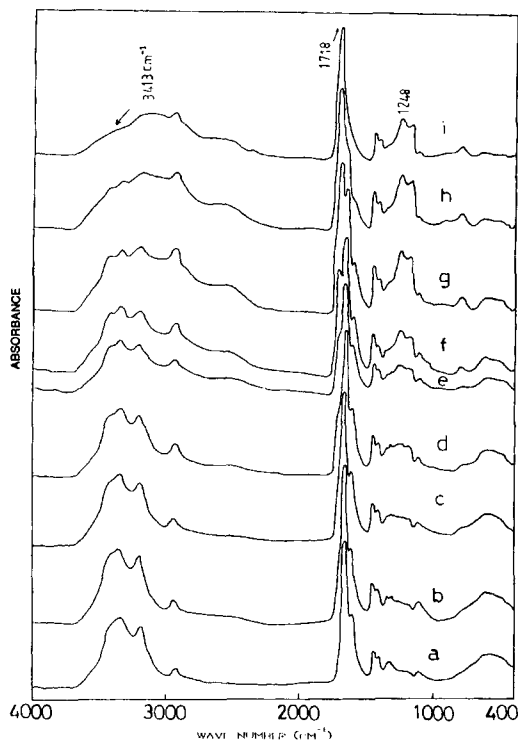


Figure 1 FTIR spectra of mixtures of PAA and PAAM at different W_{PAA} : (a) 0; (b) 0.2; (c) 0.3; (d) 0.4; (e) 0.5; (f) 0.6; (g) 0.7; (h) 0.8; (i) 1.

observable changes in the characteristic spectral features of the latter. Continued increases of the W_{PAA} result in the appearance of the characteristic bands of PAA (3413, 1718, 1248, and 1174 cm^{-1}). When W_{PAA} is increased to 0.7, its characteristic absorption bands predominate and therefore the maximum of its C=O band (1718 cm^{-1}) appears higher than that corresponding to the band of C=O of amide I (1669 cm^{-1}). The spectra of samples containing W_{PAA} of 0.8 and 0.9 show only the characteristic bands of PAA.

The relation between the absorbance of the C=O stretching vibration of PAAM and W_{PAA} in the mixtures is represented graphically in Figure 2. This figure indicates that the absorbance of C=O of PAAM decreases linearly with increasing the W_{PAA} to 0.6. This result means that no significant reaction or association took place between PAA and PAAM in their mixtures.

Figure 3 represents the spectra of PAAM, PAA, and their W_{PAA} 0.5 mixture and complex. Careful examination of the spectra reveals that the spectrum of the mixture displays absorption bands at frequencies which represent the characteristic absorption bands of the individual components of the mixture. On the other hand, it is clear that the spectrum

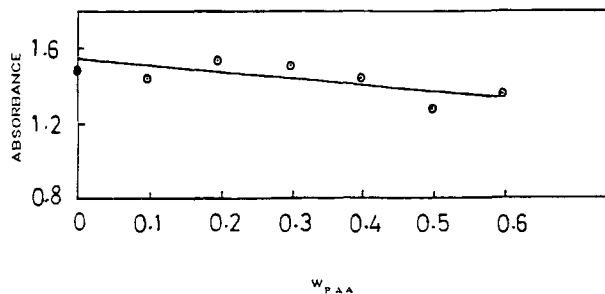


Figure 2 The relation between the absorbance of the C=O absorption band of amide I and W_{PAA} in the polymer mixtures of PAA and PAAM.

of the interpolymer complex shows similar spectral features but the bands appear at shifted positions of 3341, 3216, 2927, 1713, 1648, 1583, 1443, 1410, 1238, and 1168 cm^{-1} and with different intensities. These differences in positions and intensities of the absorption bands are attributed to the formation of an interpolymer complex resulting from the interaction between PAA and PAAM at low pH \sim 2.69 and hydrogen bonding is the primary mechanism of interaction among these polymers.

The present result is in good agreement with the results reported in the literature. Sivadasan et al.² reported that PAAM forms a stable complex with PAA at low pH by using the excimer fluorescence and viscosity techniques. They found that the analysis of the precipitate confirmed that PAAM and PAA formed an equimolar complex at the phase separation pH.

The effect of the PAA weight fraction, W_{PAA} , on the structure of the complex was also investigated. The FTIR spectra of the interpolymer complexes

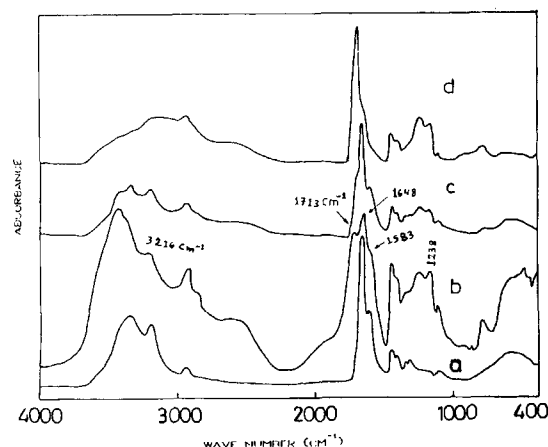


Figure 3 FTIR spectra of (a) pure PAAM "film," (b) W_{PAA} 0.5 complex "KBr disc," (c) W_{PAA} 0.5 mixture "film," (d) pure PAA "film."

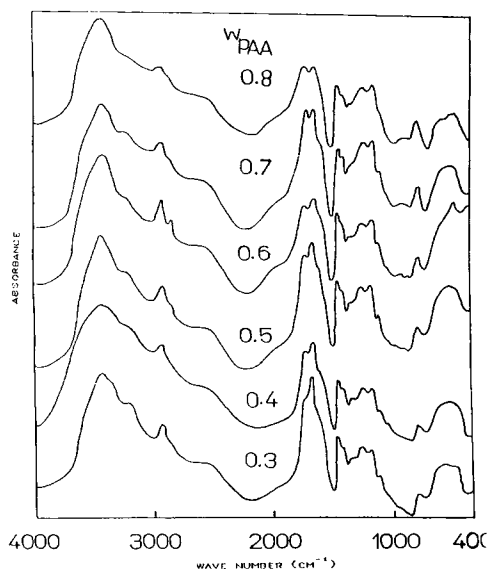


Figure 4 FTIR spectra of the complexes formed between PAA and PAAm at different W_{PAA} .

resulted from solutions containing different W_{PAA} are shown in Figure 4. Analysis of the spectra provides strong evidence that the intensity of the absorption band of the carboxylic group (1713 cm^{-1}) increases as W_{PAA} is increased. To prove this result quantitatively, the absorbance ratio, R , of the $\text{C}=\text{O}$ stretching vibration of the carboxylic group (1713 cm^{-1}) and that of amide I (1648 cm^{-1}), $A_{1713\text{ cm}^{-1}}/A_{1648\text{ cm}^{-1}}$, was determined. The relation between R and W_{PAA} is represented in Figure 5. The figure indicates that R increases by increasing W_{PAA} to 0.4 and then suggests constant values over the W_{PAA} range of 0.4–0.6. Increasing W_{PAA} to 0.7 and 0.8 results in a considerable increase in this ratio. Staikos et al.^{1,3} reported that when the total polymer concentration in the PAA–PAAm mixture solution is kept constant and the reduced viscosity ratio is plotted against the PAA weight fraction, W_{PAA} , a

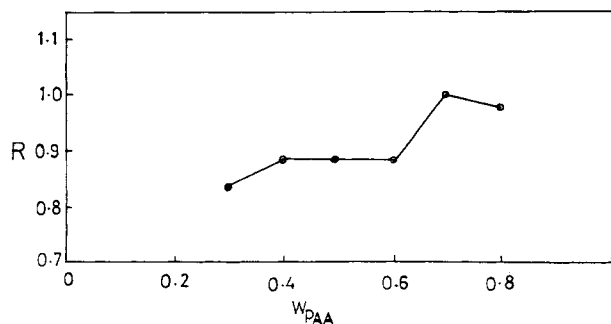


Figure 5 Relationship between R ($A_{\nu\text{C}=\text{O}\text{ acid}}/A_{\nu\text{C}=\text{O}\text{ amide I}}$) and W_{PAA} .

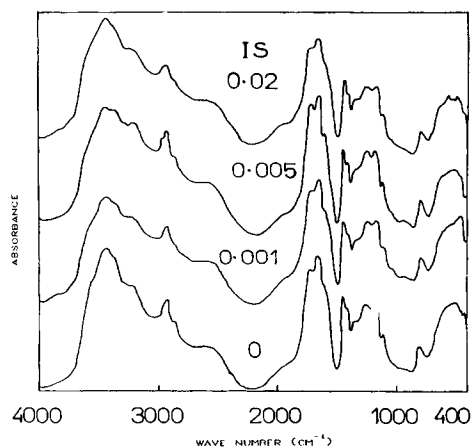


Figure 6 FTIR spectra of the complex W_{PAA} of 0.5 at different ionic strengths ($IS = 0, 0.001, 0.005,$ and $0.02M$ NaCl).

smooth positive deviation from linearity until $W_{PAA} = 0.2$ is observed, followed by a smooth negative deviation. The positive deviation of the experimental curve with respect to the calculated curve implies a gel-like interpolymer association of the polymer mixture poor in PAA ($W_{PAA} < 0.2$), while the negative deviation implies the formation of a compact complex when the polymer mixture is rich in PAA ($W_{PAA} > 0.2$). Sivadasan et al.² stated that PAAm forms a stable complex with PAA at low pH values. The segmental mobility of the polymer chain varies with PAA concentration and becomes constant only at very high concentrations. For mixtures of high concentration ratios, the local concentration of PAA

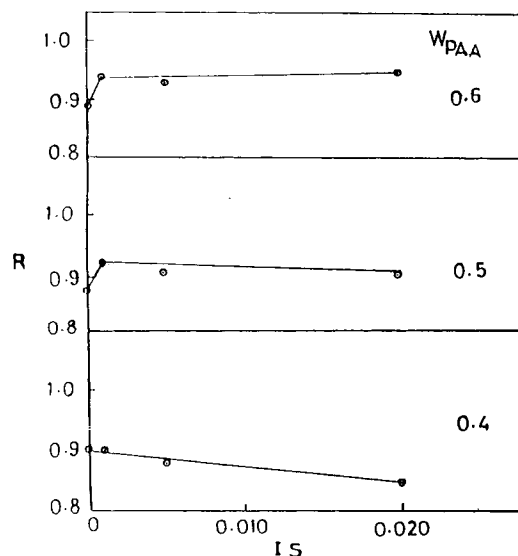


Figure 7 Relationship between R [$(A_{\nu\text{C}=\text{O}\text{ acid}}/A_{\nu\text{C}=\text{O}\text{ amide I}})$] and IS at different W_{PAA} .

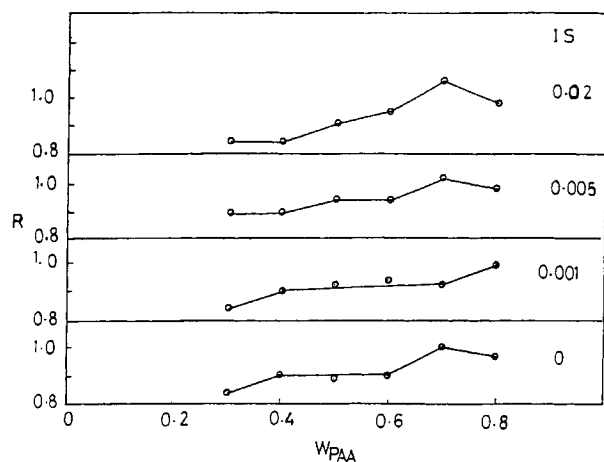


Figure 8 Relationship between $R(A \nu C=O \text{ acid}/A \nu C=O \text{ amide I})$ and W_{PAA} (PAA weight fraction) at different IS.

molecules around the PAAm chains is high and possibly most of these molecules participate in hydrogen bonding with PAAm to form a rather crosslinked structure.

It could be pointed out that the absorbance ratio, R , can be taken as a measure of the number of hydrogen-bond linkages. It appears from Figure 5 that this ratio varies with the PAA weight fraction and becomes constant over the W_{PAA} range of 0.4–0.6. This ratio increases at higher W_{PAA} . This result may be explained on the basis that for mixtures of high W_{PAA} most of PAA molecules participate in hydrogen bonding with PAAm molecules forming a rather crosslinked structure.

The infrared spectra of solutions of different ionic strength (IS) and different W_{PAA} were recorded and an example is shown in Figure 6. Figure 7 illustrates the relationship between the ratio R and IS for W_{PAA} of 0.4, 0.5, and 0.6. It is apparent from this relation that R for a W_{PAA} of 0.4 decreases linearly as IS is increased up to 0.02. For a W_{PAA} of 0.5, R suggests an initial increase and then decreases slightly with IS. Finally, the characteristic features of the curve of $W_{PAA} = 0.6$ are a rapid initial increase followed by a slight increase. This relationship proves that R depends on both IS and W_{PAA} . Figure 8 shows the relationship between R and W_{PAA} for different IS. This relation also provides confirmation that R de-

pends on both W_{PAA} and IS. It has been reported^{1–3} that precipitation occurs in the mixture composition region of $0.4 < W_{PAA} < 0.8$ when the concentration of NaCl is 0.1 M and that the ionic strength affects both the dissociation of PAA and ion–dipole interactions which favor the complex formation. The analysis of the data represented in Figure 8 leads to the conclusion that for the mixture containing W_{PAA} of more than 0.4–0.8 the increase of IS, in general, increases the number of hydrogen-bond linkages between PAA and PAAm as indicated by the increase of R with increasing IS.

CONCLUSION

The foregoing data lead to the conclusion that PAA interacts with PAAm at low pH ~ 2.69 , resulting in an interpolymer complex, and that hydrogen bonding is the primary mechanism of interaction among these polymers. The absorbances ratio of the C=O bands corresponding to the absorption of the carboxylic and amide I groups may be taken as a measure of the number of the hydrogen-bond linkages between the carboxylic and amide groups. The structure of the complex depends on the weight fraction of the PAA in the mixture and the ionic strength of the PAA electrolyte.

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