Infrared Spectra of γ-Irradiated Poly(acrylic acid)–Polyacrylamide Complex

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ABSTRACT: Samples of polyacrylamide (PAAm), poly(acrylic acid) (PAA), and their complex were γ-irradiated at different doses, namely 48, 96, and 144 KGy. The examination of the infrared spectra of these samples showed that there are no significant observable changes in their spectral features apart from slight changes in the intensities of the absorption bands. The analysis of the absorbances ratios (A 1700 cm^{-1}/A 1450 cm^{-1}) and (A 1650 cm^{-1}/A 1450 cm^{-1}), denoted as R_1 and R_2, respectively, showed that these ratios depend on γ-doses. It was found that in the case of PAA, R_1 assumed linear increase with increasing the dose to 96 KGy and then showed marked decrease. For the complex, R_1 increased slightly by increasing the dose to 96 KGy and then decreased. For PAAm, although irradiation with 48 KGy increases the values of R_2, irradiation with 96 and 144 KGy decreases its value. On the other hand, for the complex, R_2 suggested slight decrease on irradiation with 48 KGy followed by continued increases with increasing the dose up to 144 KGy. The increase in R_1 and R_2 may be due to crosslinking as a result of the formation of free radicals. The decrease in these ratios after irradiation with 96 KGy may be due to degradation. It was concluded that γ-irradiation has a lower effect on the complex (i.e., the complex has a structure which is different from those of PAA and PAAm). © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1619–1623, 2002

Key words: FTIR; γ-radiation; polyacryl amide; polyacrilic acid; polyacrylamide–polyacrilic acid complex

INTRODUCTION

In recent years, considerable research has been devoted to the changes produced in polymers when irradiated in the solid state. The major effects observed can be ascribed to the formation of crosslinks or to the fracture of the main chain, depending on the particular polymer studied. Other changes of a less staking character such as the differences in unsaturation and fracture of the side chains are also found.

Alexander and Charlesby[1] investigated the effect of γ-rays on aqueous solutions of polymers such as poly(acrylic acid) (PAA) and polyacrylamide (PAAm). They showed that PAA and PAAm were degraded in dilute solutions and crosslinked when irradiated as solids.

Henglein[2] stated that PAAm and poly(vinyl pyrolidone) (PVP), which in their aqueous solutions crosslink under γ-irradiation, form a common network when irradiated in the same solvent. He observed that the viscosity of dilute PAAm solutions at first increases and at higher doses decreases again. He assumed that micronetworks throughout small parts of the dissolved polymer are formed and at higher doses further crosslinking occurs within these microgels.
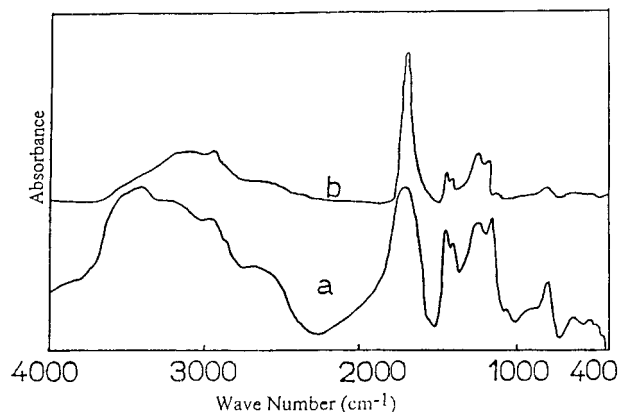
Figure 1   FTIR spectrum of pure PAA (a) disc; (b) film.

On the basis of these considerations, the aim of this work was to characterize the effect of γ-radiation on the molecular structure of the interpolymer complex resulting from the interaction between PAA and PAAm, using Fourier transform infrared spectroscopy.

EXPERIMENTAL

Materials

PAAm was obtained from BDH Chemicals, Pool, U.K.; its molecular weight is over 5,000,000 g/mole. PAA was obtained from Nisso SHOJI Co., Japan (PW-110, lot no. 4029). The two polymers, in the form of white powders, were used as obtained from the manufacturers without further purification.

Preparation of Samples

A stock solution from each polymer was prepared by dissolving the polymer in distilled water in a concentration of 1 g/100 mL and each solution was then stirred overnight to ensure complete dissolution. Mixtures from the two polymer solutions with different PAA weight fractions, W_{PAA}, were prepared by mixing the two stock solutions in the appropriate proportions. The total polymer concentration in each mixture was kept constant. These mixtures were stirred overnight. Thin films from these mixtures were prepared by casting a definite volume of each mixture, W_{PAA} ranging from 0 to 1, onto polyethylene dishes, followed by drying in air for about 3 days. The peeled films were then dried in an oven at 90°C for about 6 h.

The pH of these mixtures was then adjusted by adding drops of 10% HCl until precipitation or

phase separation takes place.[3] The dried precipitates were filtrated and washed with distilled water. The samples were then ground in an agate mortar, followed by sieving to a particle size of 100–120 μm, suitable for IR measurements.

γ-Irradiation

Samples of pure PAA, pure PAAm, and the dried precipitate, with W_{PAA} of 0.5 and ionic strength (IS) of 0, were irradiated at room temperature and in an atmosphere of air in ^{60}Co-source Narton control A.S. Gamma unit with a dose rate of 0.33 KGy/h. The radiation doses to which the samples were subjected were selected between 48 and 144 KGy.

IR Measurements

Infrared spectra were recorded on a Perkin–Elmer 1650 FTIR spectrophotometer using the KBr disc technique.

RESULTS AND DISCUSSION

The infrared spectra of samples of PAA, in the form of discs and films, are shown in Figure 1. The spectrum of the film shows the characteristic stretching absorption band of the carbonyl group C=O at 1718 cm^{-1}. Weaker bands associated with scissor and bending vibrations of —CH$_2$— and CH—CO groups are located at 1456 and 1415 cm^{-1}, respectively. The bands at 1248 and 1174 cm^{-1} may be related to the coupling between in-plane OH bending and C—O stretching vibrations of neighboring carboxyl groups.[4,5]

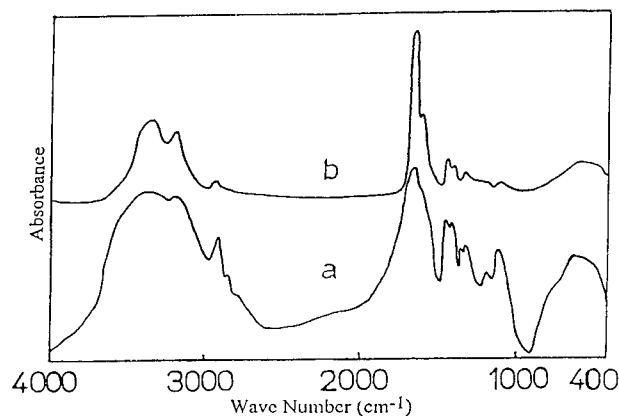Figure 2 represents the IR spectra of PAAm, in the form of film and disc. The bands located at

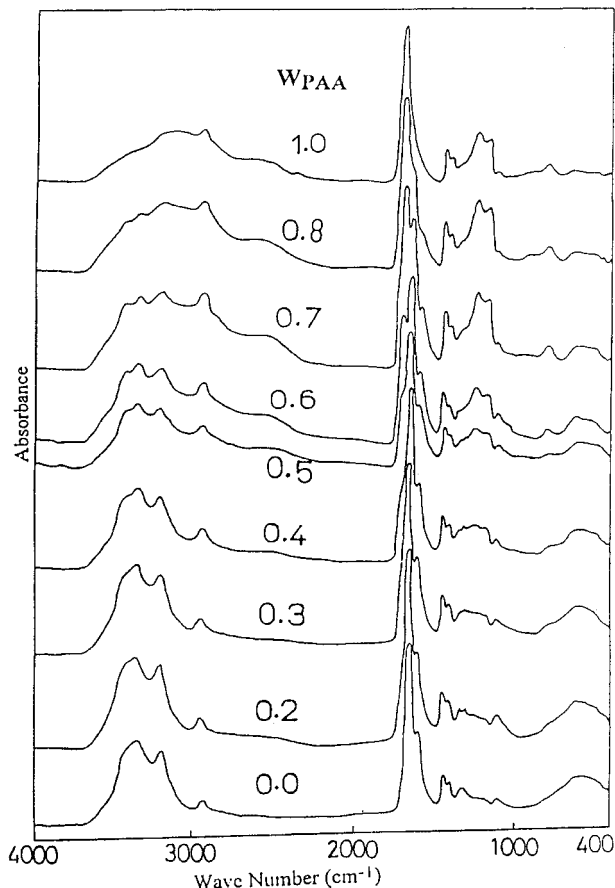**Figure 2**   FTIR spectrum of pure PAAm (a) disc; (b) film.

Figure 3 FTIR spectra of films of PAA–PAAm mixtures at different W_{PAA}.

Figure 4 The relationship between the absorbance of the C=O stretching vibration of amide I. A ν C=O (amide I), and W_{PAA} in the PAA–PAAm mixtures.

3350, 3203, 1670, and 1616 cm^{-1} are ascribed to the asymmetric and symmetric NH$_2$ stretching vibrations, amide I (ν C=O + ν CN), and amide II (δ NH + ν CN),[6,7] respectively.

Figure 3 illustrates the IR spectra of the films of the PAA–PAAm mixtures containing different values of W_{PAA} of the polymers. As seen in this figure, the addition of PAA up to W_{PAA} of 0.3 to PAAm produces no substantial observable changes in the characteristic spectral features of the latter. Continued increase of W_{PAA} results in the appearance of the characteristic absorption bands of PAA. When W_{PAA} is increased to 0.7, the characteristic absorption bands of PAA predominate, and therefore, the peak 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 relationship between the absorbances of C=O stretching vibration of PAAm in the PAA–PAAm mixtures and W_{PAA} is illustrated in Figure
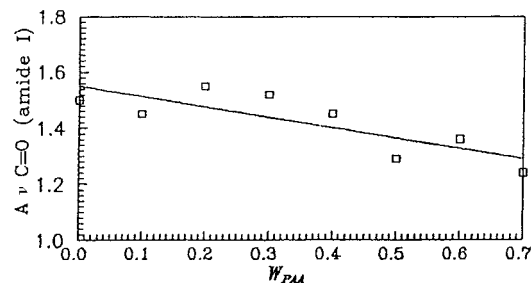
4. This figure indicates that the absorbance of C=O of PAAm decreases linearly with increasing W_{PAA} up to 0.7. This result means that no significant interaction or complexation took place between PAA and PAAm in their mixtures under the conditions studied in the experiments.

Figure 5 represents the IR spectrum of the precipitate resulting from the PAA–PAAm system (W_{PAA} 0.5), after adjusting the conditions, as in the experimental part, together with those of the films of PAA, PAAm, and the PAA–PAAm mixture (W_{PAA} 0.5). The frequencies of the absorption bands of these samples are given in Table I. Careful examination of the spectra and the table 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.

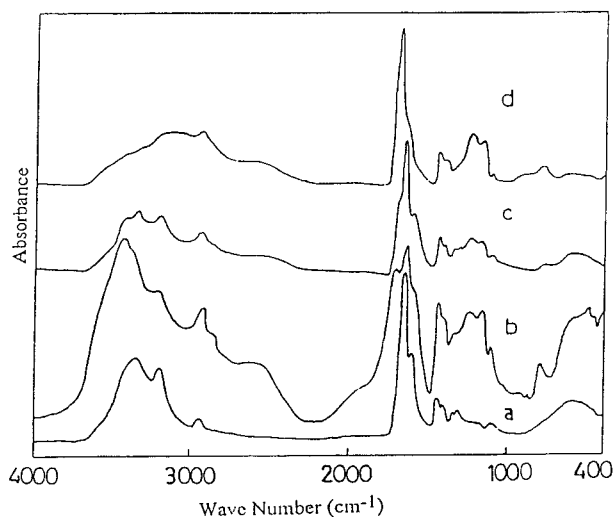On the other hand, it is clear that the spectrum of the precipitate (interpolymer complex) shows

Figure 5 FTIR spectra of (a) pure PAAm; (b) PAA–PAAm complex; (c) PAA–PAAm mixture film; and (d) pure PAA film.

Table I The Frequencies of the Absorption Bands of the Complex (W_{PAA} 0.5) Compared with those of PAA, PAAm, and the Mixture (W_{PAA} 0.5)

Frequency (cm^{-1})			
PAAm	Mixture	Complex	PAA
—	3413	3441	3000–3450
3350	3350	—	—
3203	3202	3216	—
2936	2940	2927	2955
—	1713	1713	1718
1670	1663	1648	—
1616	1608	1583	—
1454	1451	1443	1456
1420	1420	1410	1415
1350	—	—	—
1324	—	—	—
—	1250	1238	1248
—	1173	1168	1174

similar spectral features but the bands appear at shifted positions 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 solutions at low pH (2.69). Hydrogen bonding is the primary mechanism of interaction among these polymers.

The present result is in good agreement with the results reported in literature. Sivadasan et al.[8] reported that PAA forms a stable complex with PAAm at low pH by using excimer fluorescence and viscosity techniques. They found that analysis of the precipitate confirmed that pyrene-labeled PAAm and PAA formed an equimolar complex at the phase-separation pH.

Pradip and Somasundaran[3] stated that PAA interacts with poly(ethylene oxide) (PEO) and PVP in aqueous solutions through hydrogen bonding and that the interactions between PAA and PVP were stronger than those between PAA and PEO because of the stronger hydrogen-bonding capability of the pyrrollidone group in the PAA–PVP system.

Samples of PAA, PAAm, and their W_{PAA} 0.5 complex were exposed, in the solid state, to various doses of γ-radiation at the levels 0, 48, 96, and 144 KGy and dose rate of 0.33 KGy/h.

The FTIR spectra of these samples were recorded and are shown in Figure 6. Careful examination of these spectra shows that there is no significant observable changes in the spectral fea-

tures of the absorption bands apart from slight changes in the intensities of these bands.

The absorbances of the bands at frequencies 1700, 1650, and 1450 cm^{-1}, corresponding to $\nu C{=}O$ (acid), $\nu C{=}O$ (amide I), and $\delta C{-}H$, respectively, of the complex were determined and the absorbances ratios R_1 = [A 1700 cm^{-1}/A 1450 cm^{-1}] and R_2 = [A 1650 cm^{-1}/A 1450 cm^{-1}] were calculated. These ratios are plotted against the dose of γ-radiation, as shown in Figures 7 and 8.
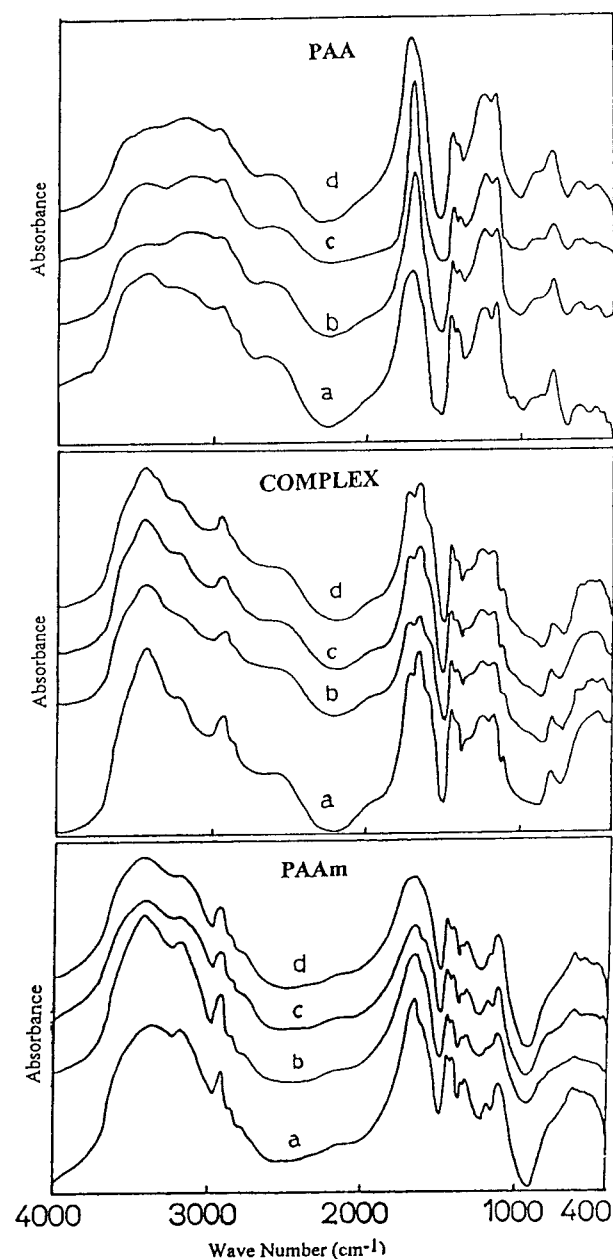

Figure 6 FTIR spectra of PAAm, PAA, and their complex at different doses of γ-radiation (a) 0, (b) 48, (c) 96, and (d) 144 KGy.

It is apparent from Figure 7 that γ-irradiation of PAA causes rapid increases in the value of R_1 by increasing the dose up to 96 KGy. Continued increase of the dose above 96 KGy results in a sharp decrease in this ratio. For the complex, R_1 increases slightly with increasing the dose up to 96 KGy, followed by a slight decrease to 144 KGy.

Figure 8 shows that the value of R_2, for PAAm, increases on the irradiation by 48 KGy and then decreases as the dose is increased to 144 KGy. On the other hand, this value, for the complex, decreases slightly on irradiation by 48 KGy and then increases gradually at 96 KGy, followed by a slight decrease by increasing the dose to 144 KGy.

It is probable that the increase in R_1 and R_2 is due to crosslinking taking place as a result of γ-irradiation. Alexander and Charlesby[1] stated that PAA and PAAm crosslink when they are irradiated in the solid state. This can be explained[9] by observing that γ-radiation brings about the formation of free radicals that recombine with each other to form macromolecules, bringing about the elimination of hydrogen and increasing the degree of unsaturation of molecules. Therefore, the number of C—H groups could be decreased. Also, because the irradiation was carried out in an atmosphere of air (i.e., in the presence of O_2), oxidation can take place, and hence, the number of C=O could be increased. From this discussion, R_1 and R_2 are increased. After a dose of 96 KGy, the values of these ratios are decreased. This can be ascribed to the decrease in crosslinking as a result of the break up of carbonyl groups at high doses.

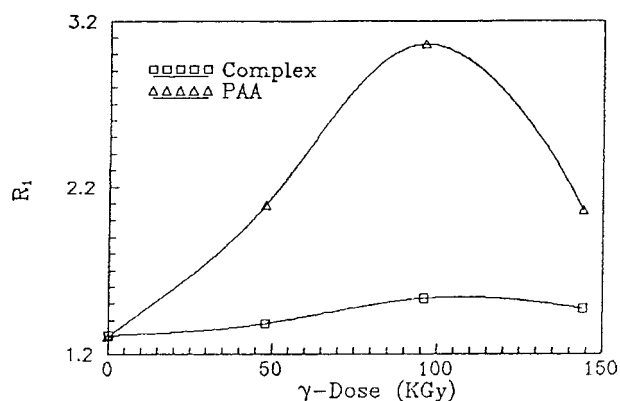From Figures 7 and 8, it is obvious that the response of the PAA–PAAm complex to the effect

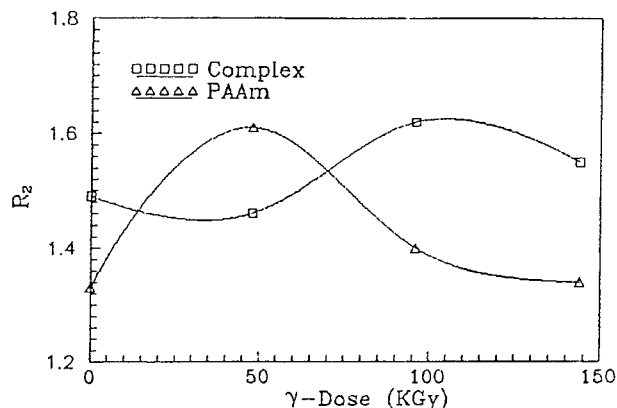**Figure 8** Variation of the absorbances ratio, R_2, in the PAA–PAAm complex with the γ-dose.

of γ-irradiation is lower than that of PAA and PAAm alone (i.e., it is more stable under the effect of γ-irradiation).

Kuzleznev and Shershnev[9] stated that the resistance of polymers to irradiation grows when they contain aromatic rings in their structures, which is associated with the considerable dissipation of energy in aromatic structure. This phenomena is called the sponge effect and substances that protect polymers from the undesirable effect of radiation are called antirads.

On the basis of these considerations, it can be concluded that the structure of the complex formed from the interpolymer complexation between PAA and PAAm is different from that of either PAA and PAAm and is stable with respect to the γ-irradiation effect.

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Figure 7 Variation of the absorbances ratio, R_1, in the PAA–PAAm complex with the γ-dose.