Effect of γ-Irradiation and Temperature on the Structure of Metal Chloride Treated Poly(Acrylamide)

M. A. MOHARRAM,* S. M. RABIE, and A. Y. DAGHISTANI

National Research Center and Middle Eastern Regional Center for the Arab Countries, Cairo, Egypt

SYNOPSIS

The gamma-induced changes in the structure of poly(acrylamide) (PAAm) treated with metal chlorides were investigated by following the corresponding variations in their ultraviolet spectra. Careful examination of UV spectra revealed that irradiation of the specimens results in the appearance of an absorption peak at 275 nm whose intensity depends on the applied dose and the nature of the metal ions. This band is ascribed to the formation of the carbonyl group. The results indicate that the dependence of the intensities of the band at 275 nm on the nature of the metal used provides strong evidence for the formation of metal polymer complexes. It was found that the pretreatment of PAAm with the appropriate concentration of $ZnCl_2$, $CoCl_2$, or $NiCl_2$ reduces the effects of heating and the oxidation effects of γ-irradiation. These results show that these metal ions can be used as stabilizers against thermal degradation of PAAm in the temperature range up to 160°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The introduction of metal ions into a polymer, particularly when the metal is linked chemically with a polymer chain, often imparts new or improved properties to the polymer. Many studies have been made on the thermal properties of metal–polymer complexes.[1-4] Burrows et al.[4] studied the thermal degradation of poly(acrylamide) PAAm in the presence of various metal ions using thermogravimetry. They concluded that for main group metal ions the stabilizing effect is inversely proportional to the radius of the metal ions. Transition metal ions, in contrast, show no simple dependence of stabilizing effect on ionic radius, but show instead a dependence upon the ligand field stabilization energy.

The effect of ionizing radiation on the structure of PAAm has also been a subject of interest for several investigators. Burillo et al.[5] studied the gamma ray-induced crosslinking of PAAm in the solid state. They stated that the crosslinking mechanism of PAAm in the solid state appears complex. The crosslinking phenomena probably depends on the shapes of polymer chains in the solid state, that is, whether they are linearly stretched or entangled.

The present study is carried out to investigate the effect of gamma irradiation and temperature on the structure of metal chloride treated PAAm by using a UV spectroscopic technique.

EXPERIMENTAL

The study was carried out on commercial PAAm from laboratory reagents. Mixtures of PAAm aqueous solution and zinc chloride, nickel chloride, cobalt chloride, copper chloride, and ferric chloride (2, 4, 8, and 12 wt %) in water were stirred overnight at room temperature. The mixtures were then treated with potassium hydroxide (1 and 2 equivalent metal-salt) and stirred overnight at room temperature. The treated samples were then cast onto

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 50, 459–468 (1993)
 CCC 0021-8995/93/030459-10

polyethylene sheets and air-dried overnight at ambient temperature, resulting in somewhat wet films. The films were further dried at 70°C for 6 h in an oven.

The samples were then heated to various temperatures up to 180°C in an atmosphere of air for 2 h. PAAm films were exposed to various dosages of γ-radiation namely 2, 5, 8, and 10 mrad from a ^{60}Co source 200,000, dose rate 170,000 rads/h. The UV spectra were recorded on a Bye Unicam spectrophotometer UV pu 8800. The accuracy of the measured values was found to be 4%.

RESULTS

The electronic spectra of films of PAAm before and after treatments with $ZnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $FeCl_2$ with concentrations 2, 4, 8, and 12 wt % (w/w) were recorded and examples of the spectra are shown in Figure 1. The analysis of the recorded spectra revealed that PAAm treated with $ZnCl_2$, $CoCl_2$, and $NiCl_2$ showed a definite peak with a maximum absorption at 220 nm, and PAAm treated with $CuCl_2$ and $FeCl_2$ showed strong absorption around this frequency and had no definite absorption peak. Careful examination of the spectra of $ZnCl_2$, $CoCl_2$, and $NiCl_2$ indicated that the treatment with these metal chlorides produced no shifts in its position and resulted in only a slight change in its absorbances. The absorbances of this band were determined and are given in Table I. Table I indicates that the absorbance of this peak undergoes a slight decrease after treatment with 8 and 12% $ZnCl_2$ and a marked increase after treatment with the same concentrations of $CoCl_2$. Treatment with $NiCl_2$ produced no significant change in the absorbance of this band.

Samples under investigation were then heated to various temperatures over the range 25–180°C. Examples of the electronic spectra are given in Figure 1. It is apparent from this figure that spectra of the samples pretreated with $CoCl_2$ (2, 4, 8, and 12% and $KOH/CoCl_2$ = 1 : 1) and heated above 80°C show, in addition to the absorption band at 220 nm, another absorption peak in the visible region at the frequency 708 nm. It was also observed that the samples pretreated with $NiCl_2$ (8, 12%, and the ratio $KOH/NiCl_2$ = 1 : 2 or 1 : 1 in the case of 12%) and then heated above 80°C exhibit an additional band at 470 nm. On the other band elevating the temperature of the samples treated with $ZnCl_2$, $CuCl_2$,

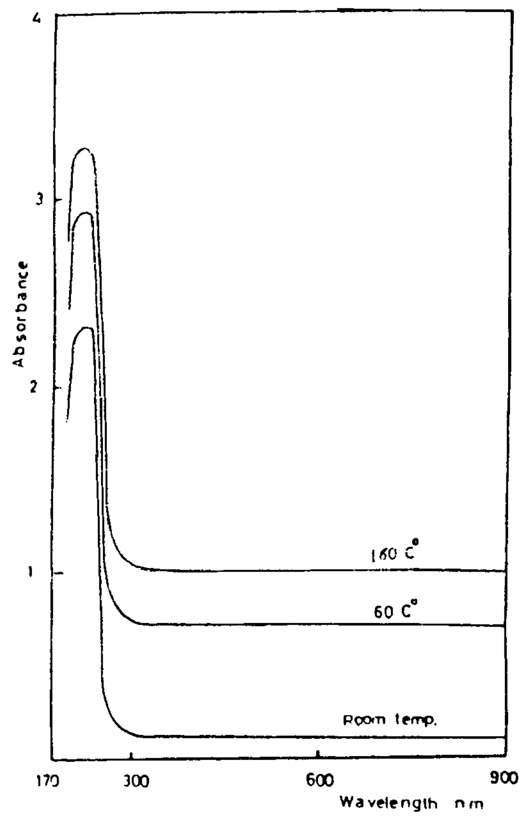

Figure 1(a) Electronic spectra of PAAm before and after heating.

and $FeCl_2$ results in no new bands in the visible region.

Higashi et al.[3] reported an absorption peak in the visible region of the spectra of PAAm treated with $CuCl_2$. This may be because their samples were treated with higher concentrations of $CuCl_2$ (10–35%) than those used in the present study.

The absorbances of the 220-nm band are given in Table II. Table II indicates the following:

1. The absorbances of the 220-nm band in the spectra of PAAm increase with increasing heating temperature up to 160°C.
2. Elevating the heating temperature of samples treated with $ZnCl_2$ and $NiCl_2$ (KOH/metal chloride 1 : 1 or 1 : 2) up to 120°C causes no considerable changes in the absorbances of the 220-nm peak but heating up to 160°C causes slight increases in its absorbances. It can be easily noticed that at any given temperature the value of the absorbances of the

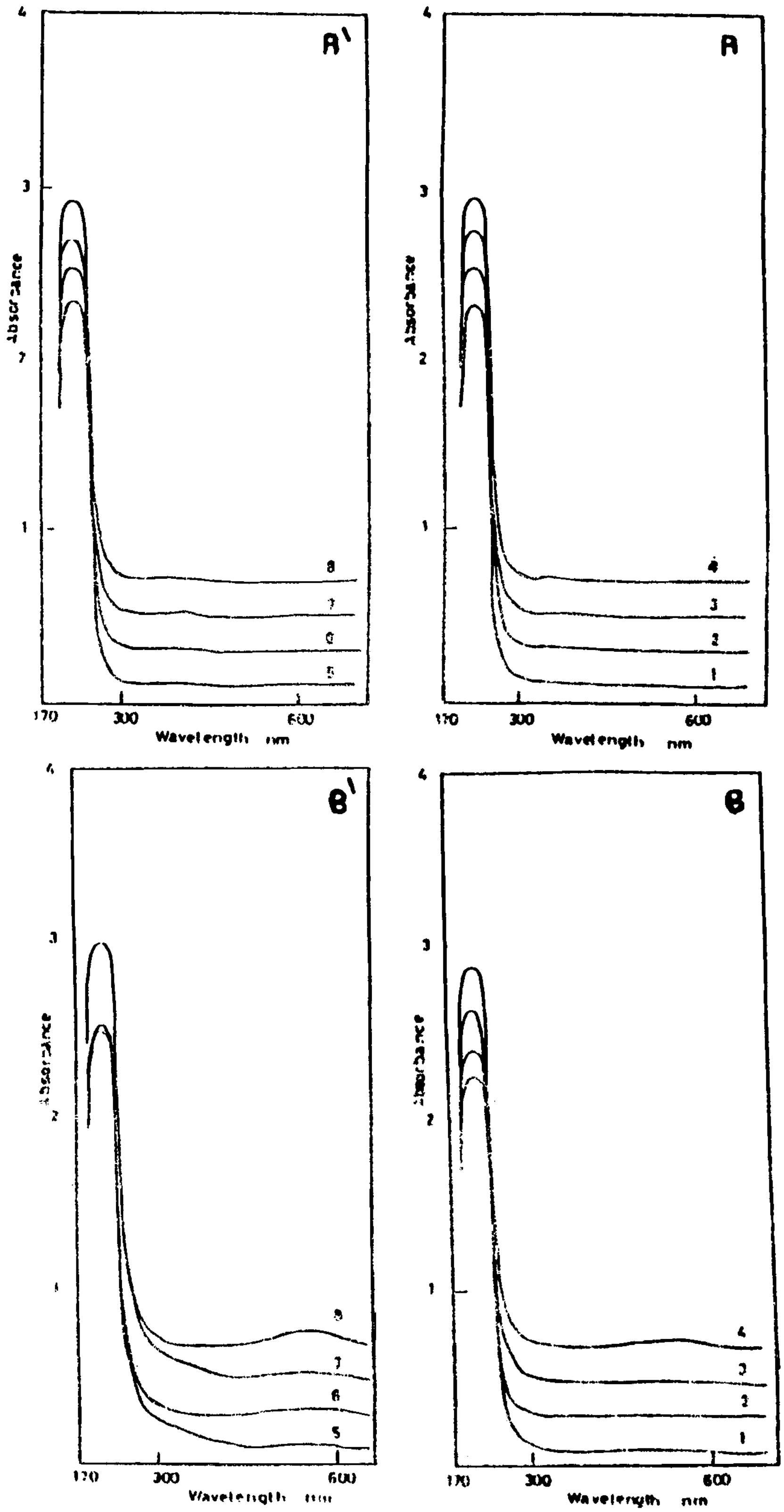

Figure 1(b) Electronic spectra of PAAm treated with different concentrations of $NiCl_2$ (A, A[1]) and $CoCl_2$ (B, B[1]), 2, 4, 8, and 12% [KOH/metal chloride = 1 : 1 (1, 3, 5, 7)] and [KOH/metal chloride = 1 : 2 (2, 4, 6, 8)].

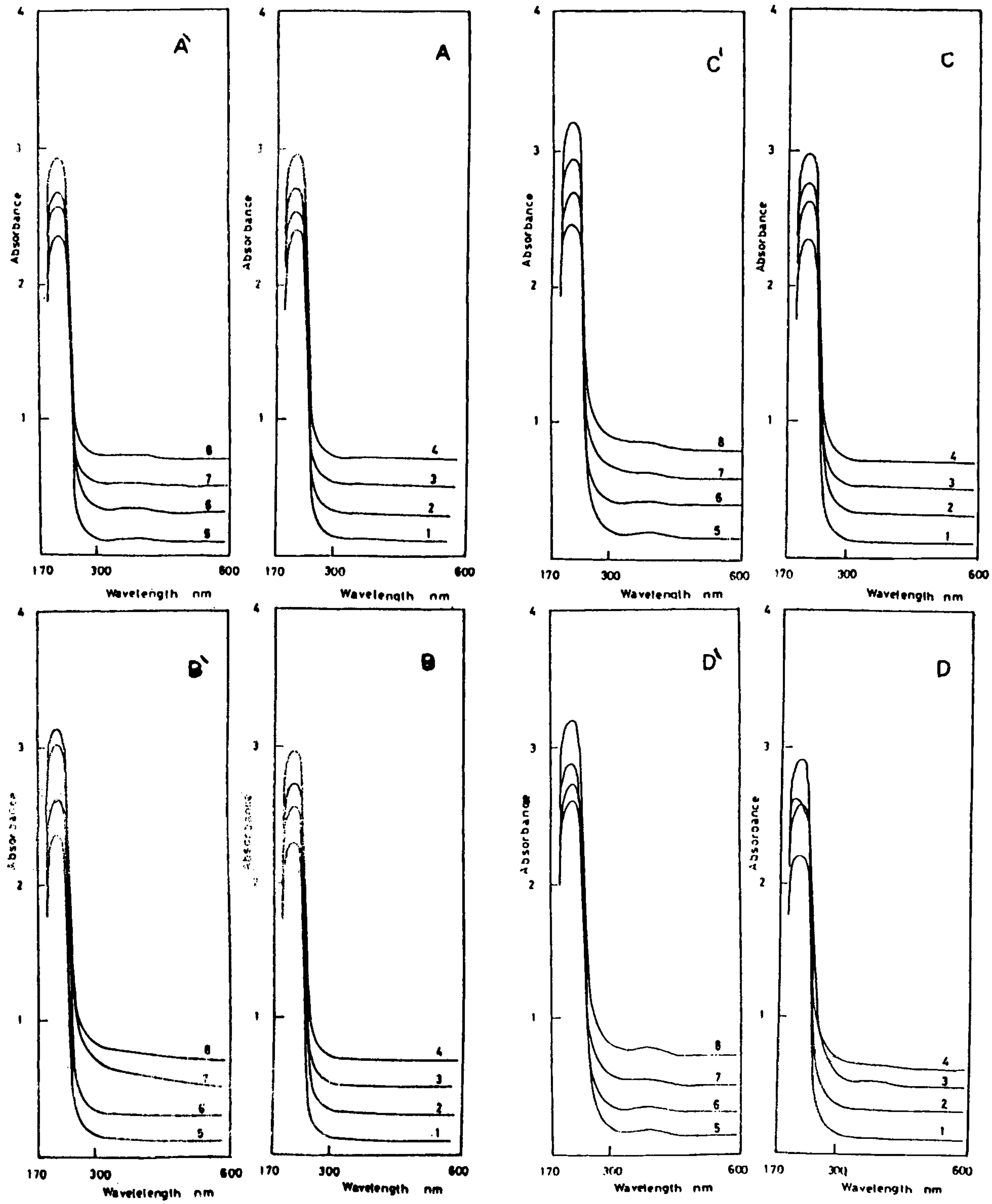

Figure 1 (c) Electronic spectra of PAAm treated with different concentrations of $NiCl_2$ and heated at various temperatures (A = 100°C, B = 120°C, C = 140°C, and D = 160°C).

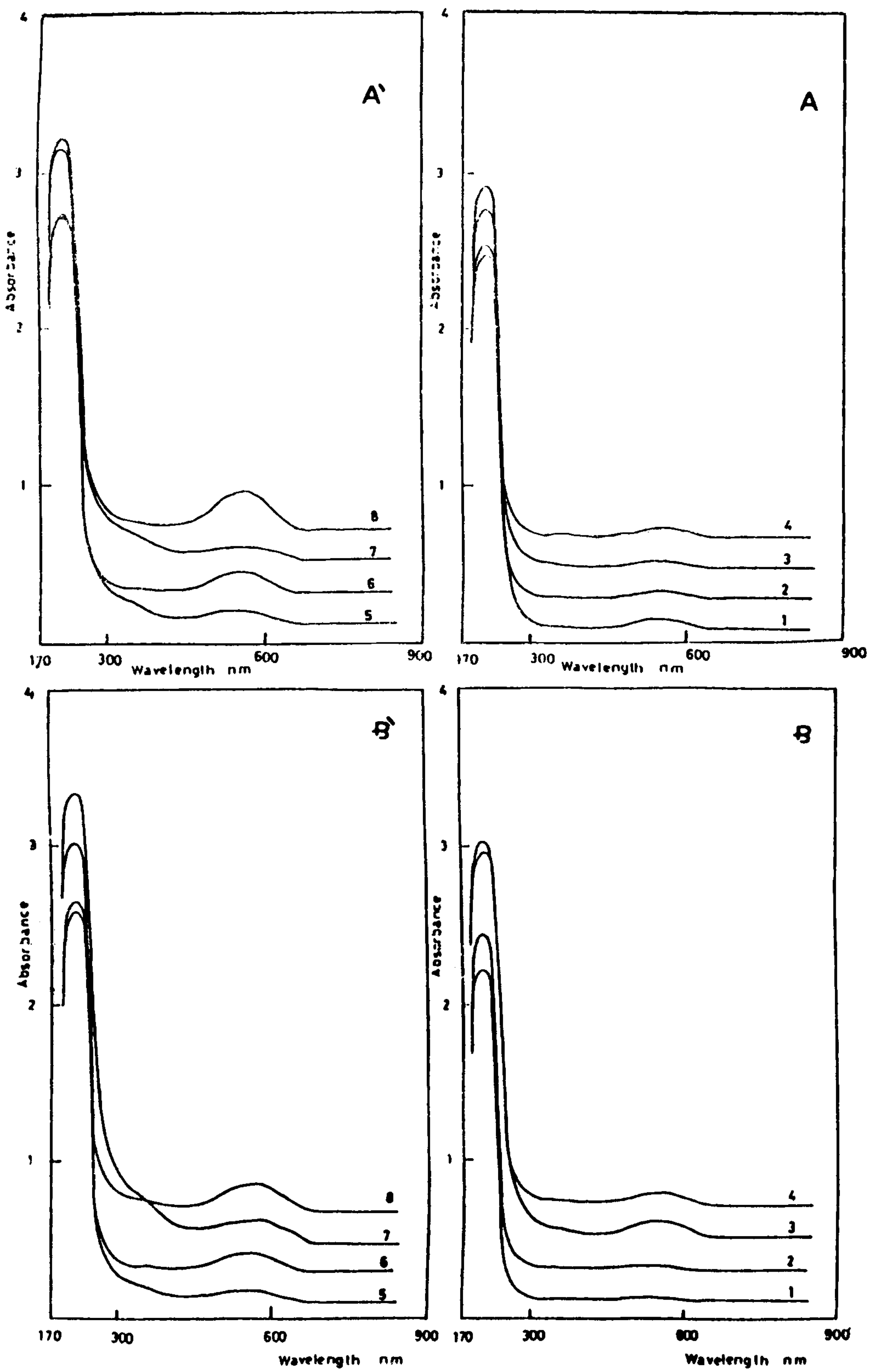

Figure 1 (d) Electronic spectra of PAAm treated with different concentrations of $CoCl_2$ and heated at various temperatures (A = 100°C, B = 120°C, C = 140°C, and D = 160°C).

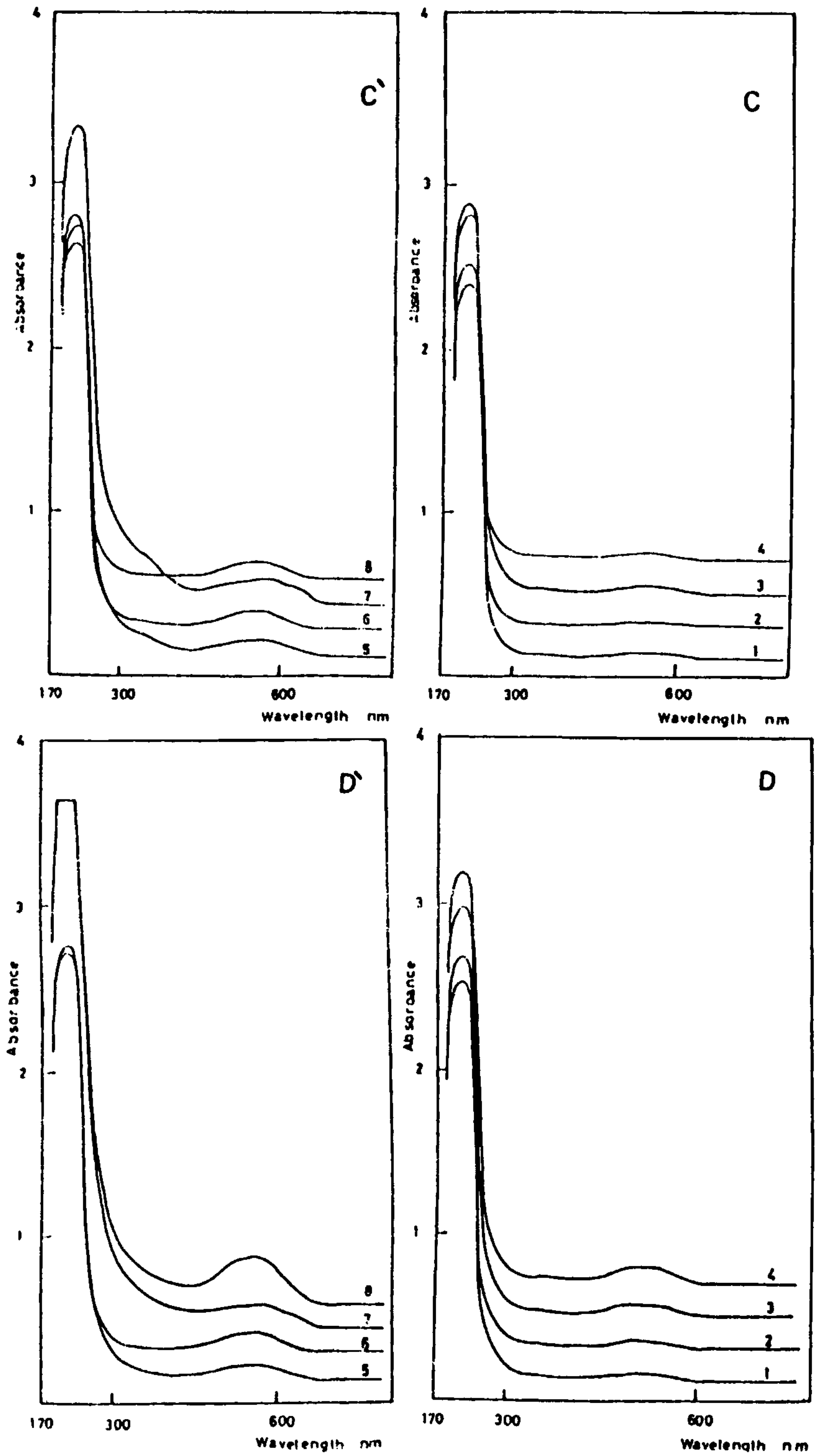

Figure 1 (d) (*Continued from the previous page*)

Table I Absorbances of 220-nm Band of PAAm Treated With Various Concentrations of Metal Chlorides

		KOH : Metal Chloride							
		1 : 1				1 : 2			
Conc. Sample : Absorbances	Untreated A1	2% A1	4% A1	8% A1	12% A1	2% A1	4% A1	8% A1	12% A1
PAA	2.22								
PAA + $ZnCl_2$	—	2.17	2.16	2.09	2.12	2.13	2.17	2.09	2.06
PAA + $NiCl_2$	—	2.19	2.16	2.05	2.18	2.27	2.20	2.23	2.20
PAA + $CoCl_2$	—	2.18	2.16	2.40	2.52	2.16	2.20	2.25	2.32

treated samples are always lower than the corresponding values for the samples before treatments.

3. Heating the samples treated with 2 and 4% $CoCl_2$ up to 140°C produces no marked changes in the absorbances whereas the absorbances for the samples treated with 8 and 12% increase with increasing the temperature up to 160°C. It should be mentioned here that the absorbance of the 220-nm band suggests a slight depression at a certain temperature over the range from 100 to 140°C and the

Table II Absorbances of 220-nm Band of Metal Chloride Treated PAAm After Heating at Various Temperatures

		Concentration of Metal							
		1 : 1				1 : 2			
Metal Temperature (°C)	Untreated A1	2% A1	4% A1	8% A1	12% A1	2% A1	4% A1	8% A1	12% A1
ZnCl, 25	2.22	2.17	2.16	2.09	2.12	2.13	2.17	2.09	2.06
60	2.25	2.18	2.14	2.17	2.18	2.18	2.12	2.12	2.13
80	2.28	2.24	2.18	2.19	2.20	2.12	2.15	2.20	2.16
100	2.33	2.19	2.22	2.20	2.23	2.14	2.18	2.24	2.07
120	2.40	2.14	2.22	2.21	2.33	2.04	2.16	2.21	2.20
140	2.47	2.34	2.38	2.18	2.00	2.34	2.40	2.17	2.00
160	2.52	2.50	2.47	2.45	2.49	2.57	2.29	2.36	2.22
$NiCl_2$ 25	2.22	2.19	2.16	2.05	2.18	2.24	2.25	2.21	2.24
60	2.25	2.09	2.18	2.14	2.18	2.26	2.20	2.25	2.24
80	2.28	2.34	2.21	2.27	2.29	2.38	2.34	2.26	2.36
100	2.33	2.30	2.22	2.26	2.18	2.25	2.27	2.37	2.25
120	2.40	2.20	2.22	2.25	2.35	2.26	2.26	2.32	2.42
140	2.47	2.25	2.27	2.32	2.34	2.33	2.27	2.30	2.40
160	2.52	2.28	2.30	2.48	2.38	2.47	2.23	2.43	2.48
$CoCl_2$ 25	2.22	2.18	2.16	2.20	2.25	2.16	2.20	2.25	2.32
60	2.25	2.22	2.30	2.51	2.56	2.22	2.34	2.39	2.57
80	2.28	2.44	2.34	2.25	2.54	2.23	2.30	2.38	2.56
100	2.33	2.40	2.29	2.58	2.62	2.25	2.23	2.42	2.50
120	2.40	2.12	2.44	2.49	2.54	2.18	2.31	2.35	2.66
140	2.47	2.30	2.28	2.52	2.37	2.22	2.17	2.45	2.73
160	2.52	2.40	2.46	2.57	—	2.37	2.48	2.45	—

temperature at which the depression appears depends on the nature of the metal ion, the concentration of metal chlorides and the ratio of KOH to metal chloride.

The ultraviolet spectra of films of PAAm before and after exposure to various dosages of γ-radiation namely 2, 5, 8, and 10 mrad are represented in Figure 2 and 3. As can be seen from these figures, this exposure results in the appearance of an absorption peak at 275 nm whose intensity varies with the applied dose. This band may be ascribed to the formation of the carbonyl group:saturated aldehydes that usually produces an absorption band in the region 275–290 nm. Rao and Murthy[6] proposed the existence of carbonyl-free radicals probably with aldehyde functional groups in γ-irradiated PVA.

The absorbances of the two bands, 220 nm (A_1) and 275 nm (A_2), and the ratio A_2/A_1 were determined. The variations of A_2/A_1 with the applied dosages are illustrated graphically in Figure 4. It appears from Figure 4 that A_2/A_1 increases with continued increasing of γ-doses up to 8 mrad and then assumes a slight decrease on exposure to 10 mrad.

The samples treated with metal chlorides were also irradiated with the mentioned dosages of γ-radiation and examples of the spectra are shown in Figure 3. The absorbances A_1, A_2, and A_2/A_1 were determined and A_2/A_1 is plotted against the dosage for each concentration of metal chlorides in Figure 4. It appears from Figure 4 that the absorbances of the samples treated with metal chlorides and neutralized with KOH, with a ratio of KOH to metal chloride at 1 : 2, increase with increasing dosage up to 8 mrad and then assume a decrease on exposure to 10 mrad. The absorbances of the samples treated with metal chloride and neutralized with KOH, with the ratio KOH to metal chloride at 1 : 1, increases with continued increasing of γ dosages.

It is clear from Figure 4 that the pretreatment of PAAm irradiated with 2 mrad by 2, 4, 8, and 12% $ZnCl_2$ causes no changes in the absorbances of the 275-nm band. The pretreatment of the samples irradiated with 5 and 8 mrad by 2% $ZnCl_2$ causes marked and slight changes in the absorbances of this band, respectively. Also the pretreatment of the samples with 4, 8, and 12% $ZnCl_2$ results in the same reduction in the absorbance of the 275-nm band in the samples irradiated with 5 mrad, whereas the absorbance of this band in the samples irradiated with 8 mrad increases with increasing concentration of $ZnCl_2$ from 4 to 12%. Moreover the absorption of the 275-nm peak in the samples irradiated with 10 mrad increases with increasing $ZnCl_2$ concentration up to 8% and then decreases with increasing concentration to 12%.

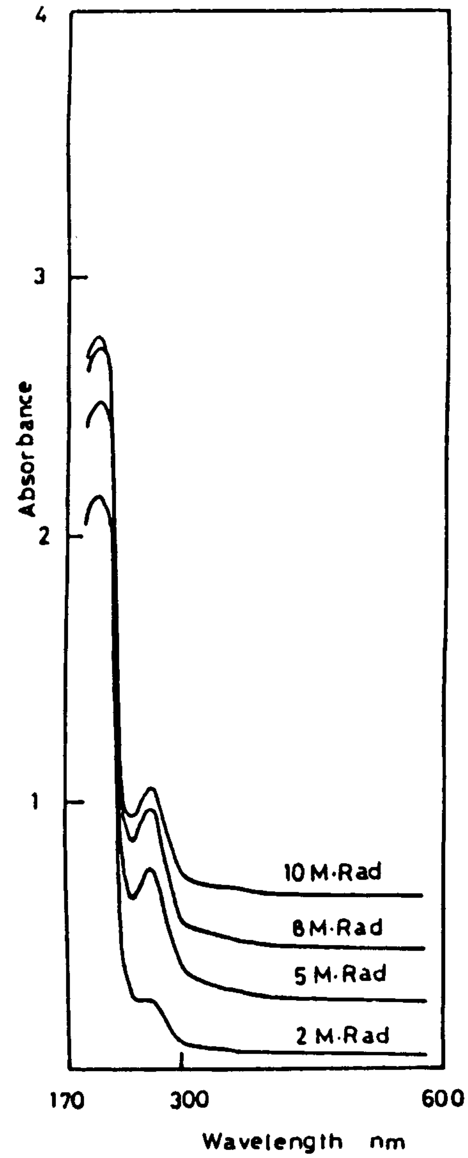

Figure 2 UV spectra of PAAm before and after exposure to different doses.

CONCLUSION

The foregoing data lead to the conclusion that the dependence of the intensities of the bands at 220 nm and 275 nm on the nature of the metal used either before or after heating and γ-irradiation provides strong evidence for the formation of metal

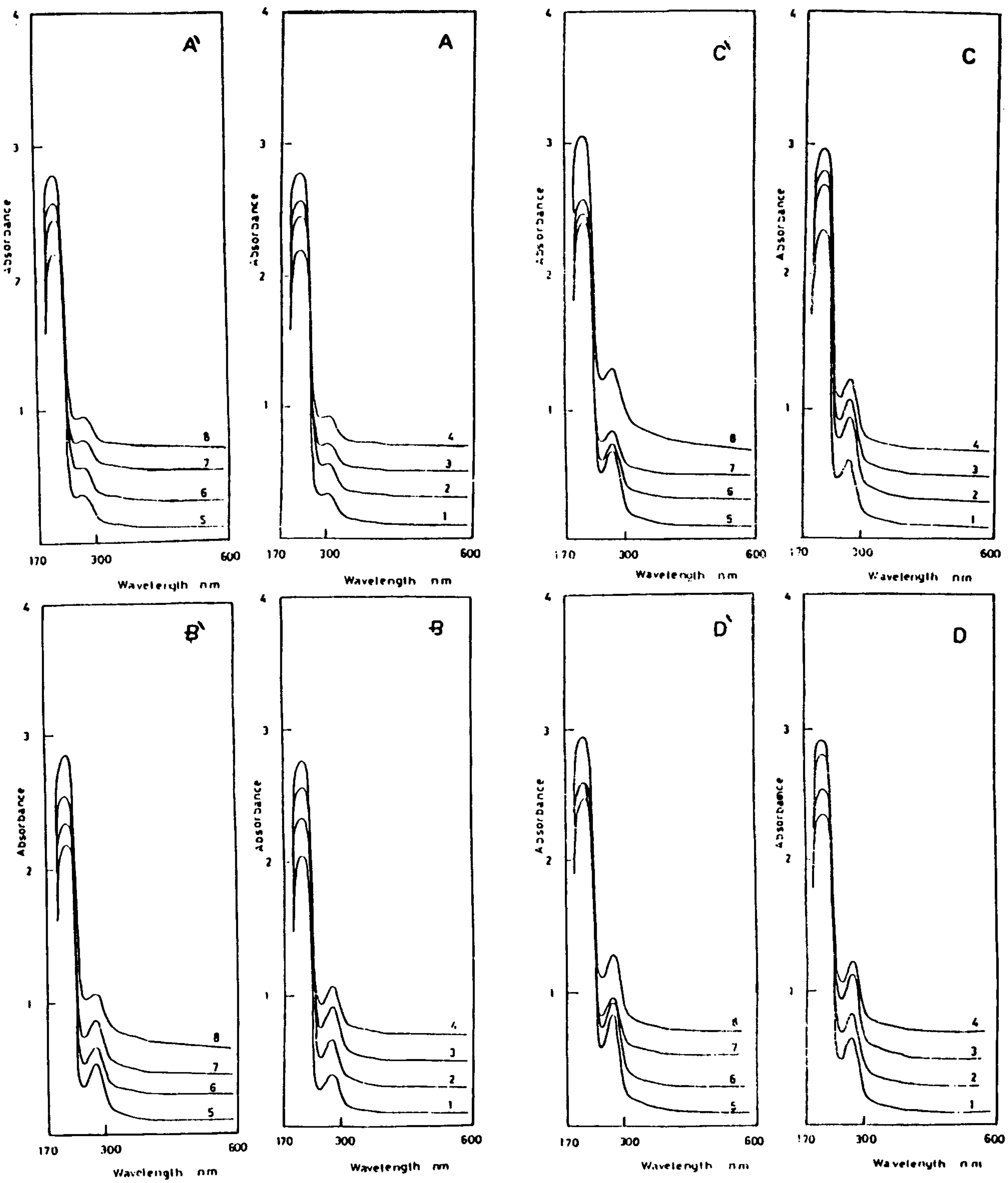

Figure 3 UV spectra of $ZnCl_2$ treated PAAm γ-irradiated with different doses (A = 2 mrad, B = 5 mrad, C = 8 mrad, and D = 10 mrad).

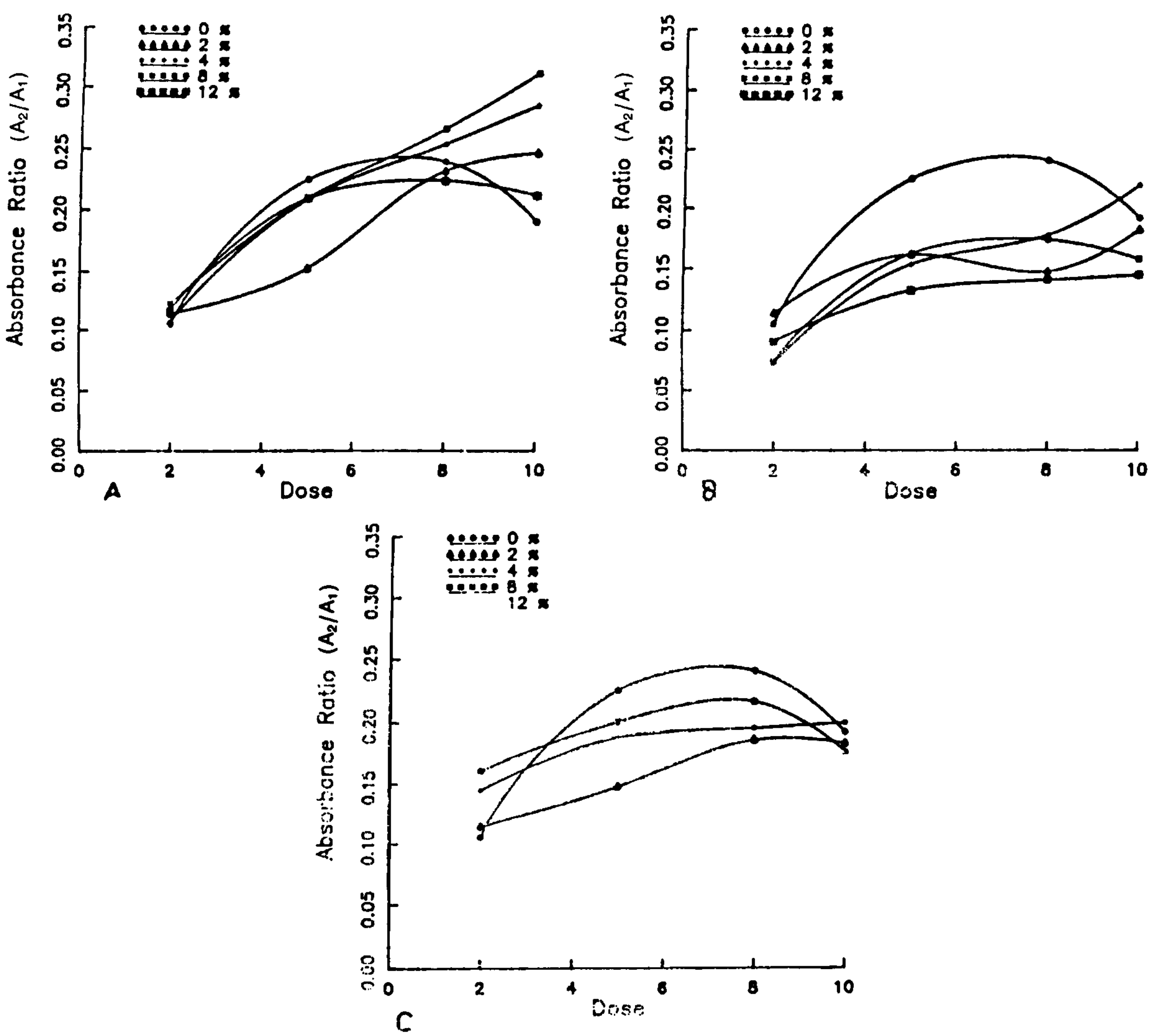

Figure 4 The relationships between the absorbances ratio A_2/A_1 and the γ-doses for PAAm treated with different concentrations of metal chlorides (KOH/metal chloride = 1 : 1) (A = $ZnCl_2$, B = $NiCl_2$, and C = $CoCl_2$).

polymer complexes (metal-polymer chelate). The pretreatment of PAAm with the appropriate concentration of the metal chlorides ($ZnCl_2$, $CoCl_2$, $NiCl_2$) reduces the effects of heating and the oxidation effects of γ-irradiation. This means that these metal ions can be used as stabilizers against thermal degradation of PAAm in the temperature range up to 160°C. The temperature- or γ-irradiation-induced changes in the intensities of the bands at 220 nm and 275 nm depend on the nature and concentration of metal ions as well as the ratio of KOH to metal chloride and the applied dosages. It is premature at present to draw a definite relationship between the physical properties of the metal ions and the temperature or γ-induced changes in the intensities of the absorption bands.

REFERENCES

1. P. H. McCluskey, R. L. Snyder, and R. A. Condrate, *J. Solid State Chem.*, **83,** 332–339 (1989).
2. M. A. Moharram, S. M. Rabie, and W. S. El-Hamouly, *J. Appl. Polym. Sci.*, **42,** 3025–3035 (1991).
3. F. Higashi, C. Sucho, and H. Kakinoki, *J. Polym. Sci., Polym. Chem.*, **15,** 2303–2309 (1977).
4. H. D. Burrows, H. A. Ellis, and S. I. Utah, *Polymer,* **22,** December (1981).
5. Guillemina Burillo and Takeshi Ogawa, *J. Polym. Sci., Polym. Lett.*, **21,** 615–620 (1983).
6. B. S. Rao and M. R. Murthy, *J. Polym. Sci. B., Polym. Phys.*, **25,** 1897 (1987).

Received October 31, 1992
Accepted December 21, 1992