Spectroscopic Studies on the Effect of Doping with Iodine on Metal Chloride-Treated Poly(vinyl alcohol)

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SYNOPSIS

The ultraviolet and infrared spectra of films of PVA treated with Co(11), Ni(11), and Cu(11) and then doped with iodine were studied. The spectra of the films preheated in air at temperatures from 25 to 180°C for 2 h were investigated. The obtained data revealed that treatment of PVA with different concentrations of each of the mentioned metal salts causes profound spectral changes. The analysis of UV spectra showed that the intensity of the band at 280 nm decreases with increasing metal concentration. It was also found that doping with iodine results in an appearance of an additional peak at about 360 nm. Careful examination of the infrared spectra indicated that the crystallinity of the samples depends on the concentration of metals and is affected by temperature treatment.

INTRODUCTION

A metal introduced into a polymer, particularly when linked chemically with the polymer chain, as a rule causes improvement of the polymer behavior and often even brings about new performance properties. There are a number of studies[1-7] on the thermal properties of metal–polymer complexes. In the literature, however, one often encounters the statement that polymer–metal complexes are more flame resistant than is the polymeric ligand alone. Many metal–polymer complexes such as those containing Fe(111) or Cu(11), Ti(111), and Zn(11) have been used in dehydrogenation catalysis. These complexes may act as catalysts for dehydrogenation of the hydrocarbon chain during pyrolysis, and graphitic structure may be formed.

These metal chelate parts of the polymer apparently catalyze complete oxidation of the carbon structure and may also produce a shift of the formation of N_2 and CO_2 to lower temperature.

The present study is carried out to investigate the effect of doping with iodine and temperature on the structure of metal salts-treated poly(vinyl alcohol) (PVA) by using ultraviolet (UV) and infrared (IR) spectroscopic techniques.

EXPERIMENTAL

The study was carried out on commercial poly(vinyl alcohol) (PVA) (from Fluka). Mixtures of PVA (10 wt %) aqueous solution and copper chloride, nickel chloride, cobalt chloride, and cobalt sulphate (2, 4, 8, and 16 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 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. The UV spectra were recorded on Beckman spectrophotometer UV 5260, and the IR spectra were recorded on a Beckman spectrophotometer 4250. The obtained absorbances of the infrared absorption bands are the averages of four replicate runs. The accuracy of the measured values was found to be 4%.
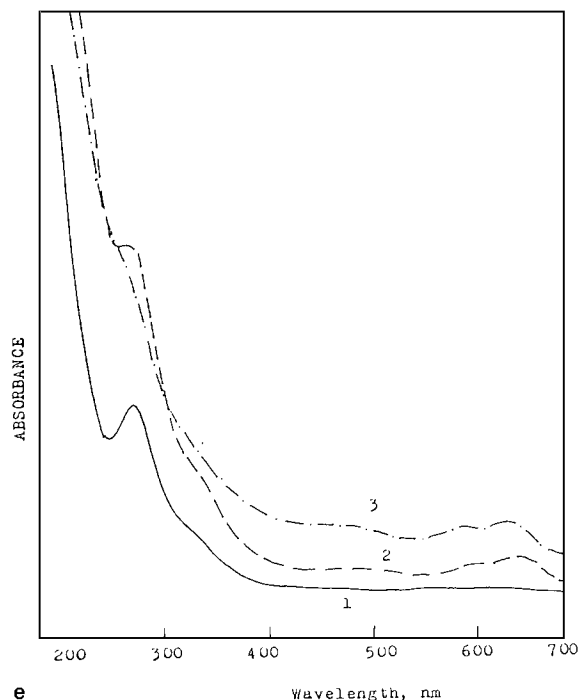
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a

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c

d
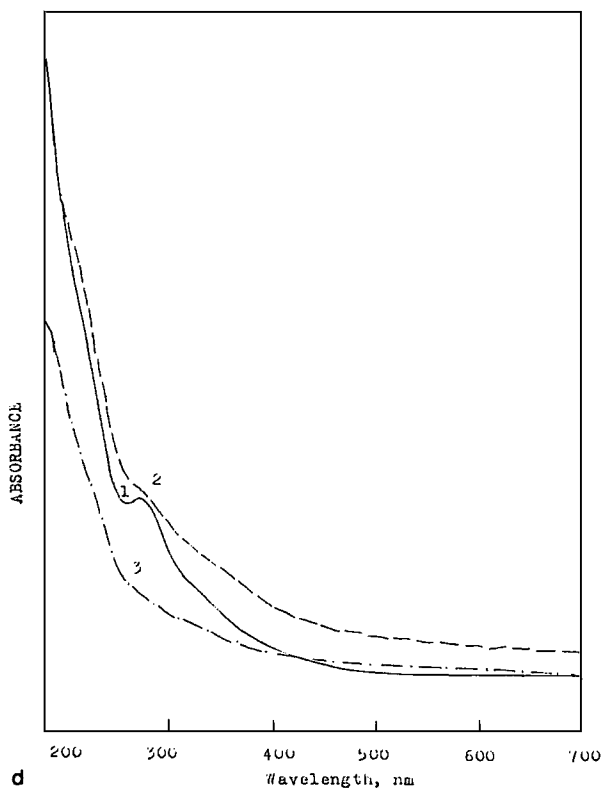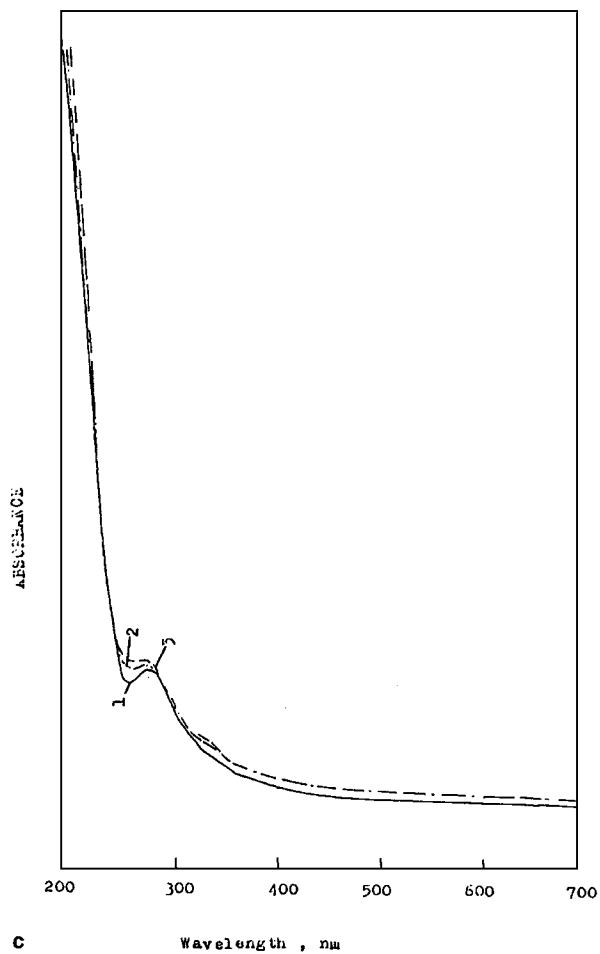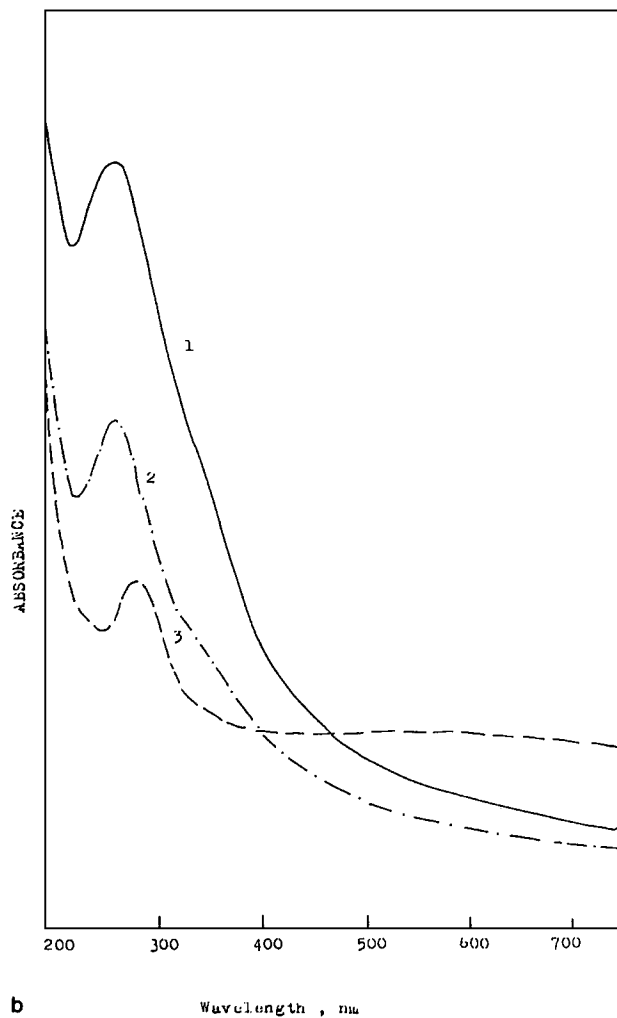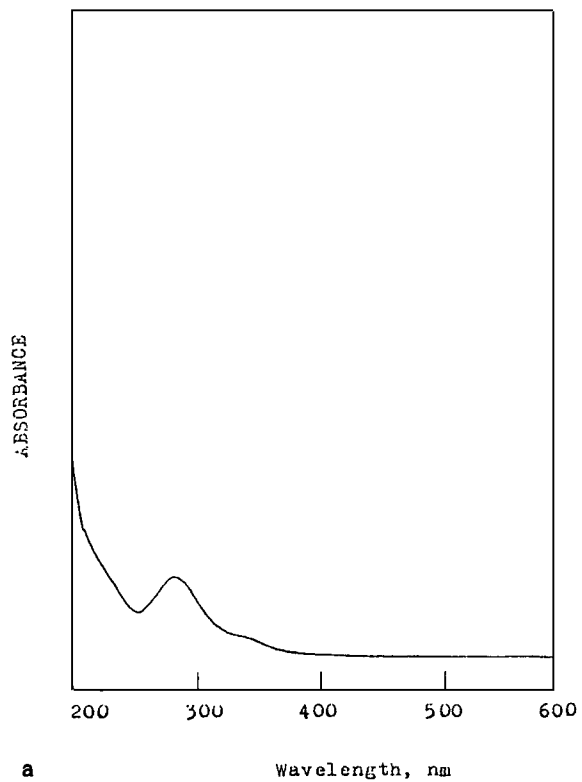
Figure 1 (a) Electronic spectrum of PVA. (b) Electronic spectra of PVA treated with (1) 4% $CuCl_2$; (2) 8% $CuCl_2$; (3) 16% $CuCl_2$ ($KOH/CuCl_2$ 1 : 1). (c) Electronic spectra of PVA treated with (1) 4% $NiCl_2$; (2) 8% $NiCl_2$; (3) 16% $NiCl_2$ ($KOH/NiCl_2$ 1 : 1). (d) Electronic spectra of PVA treated with (1) 4% $CoCl_2$; (2) 8% $CoCl_2$; (3) 16% $CoCl_2$ ($KOH/CoCl_2$ 1 : 1). (e) Electronic spectra of PVA treated with (1) 4% $CoSO_4$; (2) 8% $CoSO_4$; (3) 16% $CoSO_4$ ($KOH/CoSO_4$ 1 : 1).

RESULTS AND DISCUSSION

Figure 1 represents the UV spectra of untreated and metal salts-treated films of PVA. The spectrum of the film of untreated PVA shows a strong band at 195 nm and a weak band at 280 nm. The first band is associated with the presence of some residual acetate groups in PVA. The second band corresponds to the absorption of the carbonyl groups.

Hass et al.[8] reported absorption bands in the region 220–230 nm and proposed the presence of carbonyl groups. Yamaguchi[9] and Moroso et al.[10] reported absorption bands at 230 and 280 nm and assigned them to the existence of carbonyl groups associated with the ethylenic unsaturation of the type $-CO-(C=C)-$ and $CO-(C=C)-2-$, respectively. Saturated aldehydes usually give an absorption band in the region 275–290 nm. Rao and Murthy[11] proposed the existence of carbonyl-free radicals probably with aldehyde functional groups in γ-irradiated PVA.

It is evident from Figure 1 that all spectra show no absorption bands in the region between the two bands at 280 and 195 nm. Bravar et al.[12] stated that although the intensity of the band at 230 nm is obviously affected by the absorption of residual acetate groups it is evident that the $-CO-(C=C)-$ groups prevail in comparison with the $CO-(C=C)-2-$ groups.

Comparison of the spectra in Figures 1(a), (b), and (c) reveals the following:

1. The treatment of PVA with 4, 8, or 16% from its weight of $CuCl_2$ ($KOH/CuCl_2$ = 1 : 1) causes a marked increase of the absorption of the band at 280 nm. The extent of this increase depends on the $CuCl_2$ concentration; it decreases with increasing the concentration [Fig. 1(b)].

2. Treatment with 4% of $NiCl_2$ results in an appreciable decrease of the absorption of the 280 nm band, whereas increasing the concentration into 8 or 16% results in further decreases, but it still persists in their spectra [Fig. 1(c)].

3. The treatment with 4% of either $CoCl_2$ or $CoSO_4$ causes significant decreases in the absorption of the mentioned band; increasing the concentration to 8% results in a further decrease, whereas the treatment with 16% results in the disappearance of the 280 nm band [Fig. 1(d) and (e)].

These results mean that the intensity of this band is obviously influenced by the concentration of the metal salts and the nature of metal ions. The decrease of the intensity of the 280 nm band with increasing the concentration of the metal salts can be attributed to the increase of the metal content in the film, whereas the dependence of the intensity of this band on the nature of the metal ions provides evidence for the formation of metal–polymer complex.[4]

The films treated with $NiCl_2$ were then heated at various temperatures ranging from room temperature up to 180°C for 2 h. Examination of the UV spectra of these samples revealed that heating the films treated with $NiCl_2$ at 80, 100, and 120°C causes a significant decrease of the absorption of the band at 280 nm, whereas raising the temperature above this range at 140, 160, and 180°C results in marked increases in its absorption. Figure 2 represents examples of these spectra. The increase of the intensity of this band is due to the formation of carbonyl groups as a result of heating above 120°C.
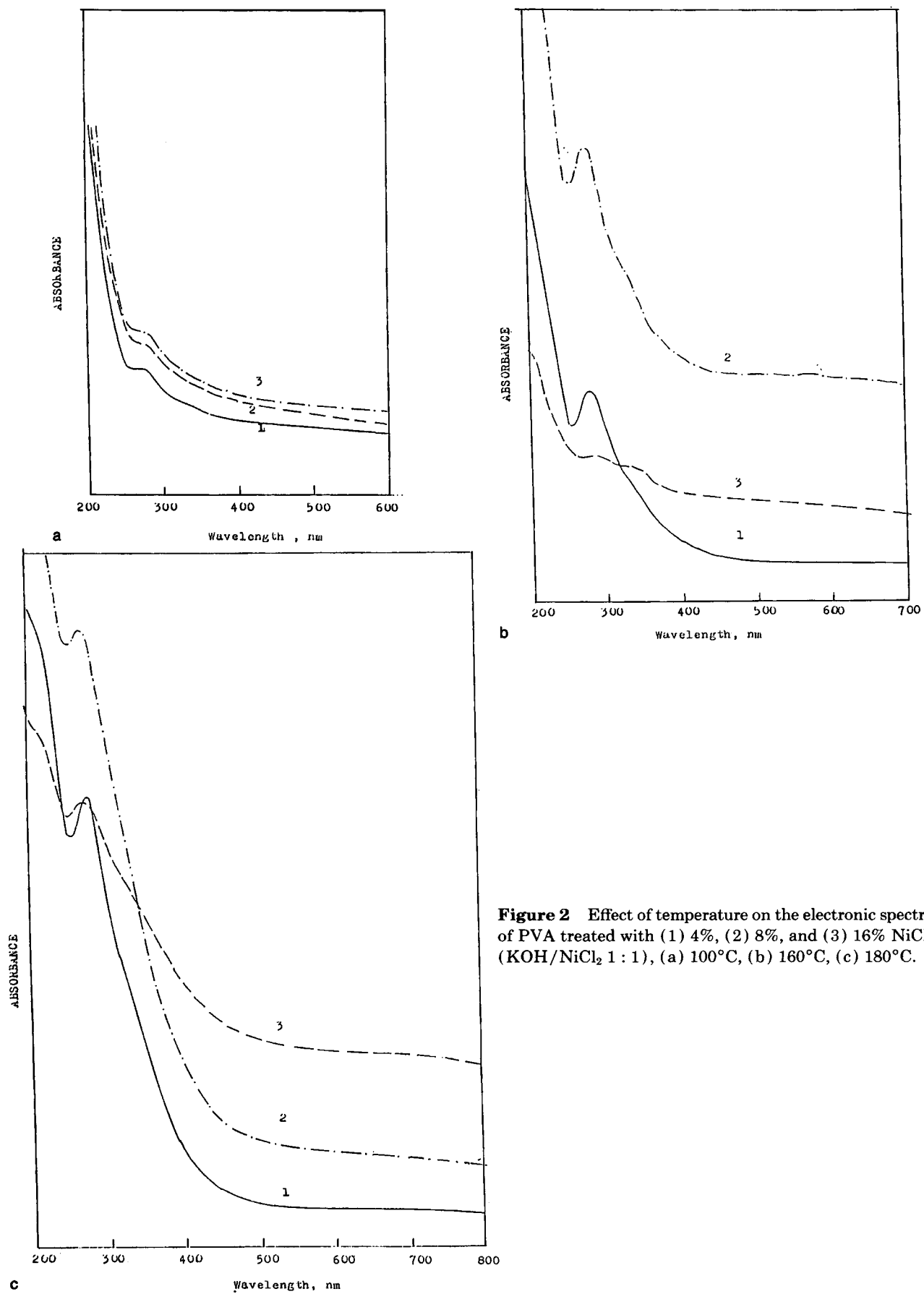
Figure 2 Effect of temperature on the electronic spectra of PVA treated with (1) 4%, (2) 8%, and (3) 16% NiCl₂ (KOH/NiCl₂ 1 : 1), (a) 100°C, (b) 160°C, (c) 180°C.
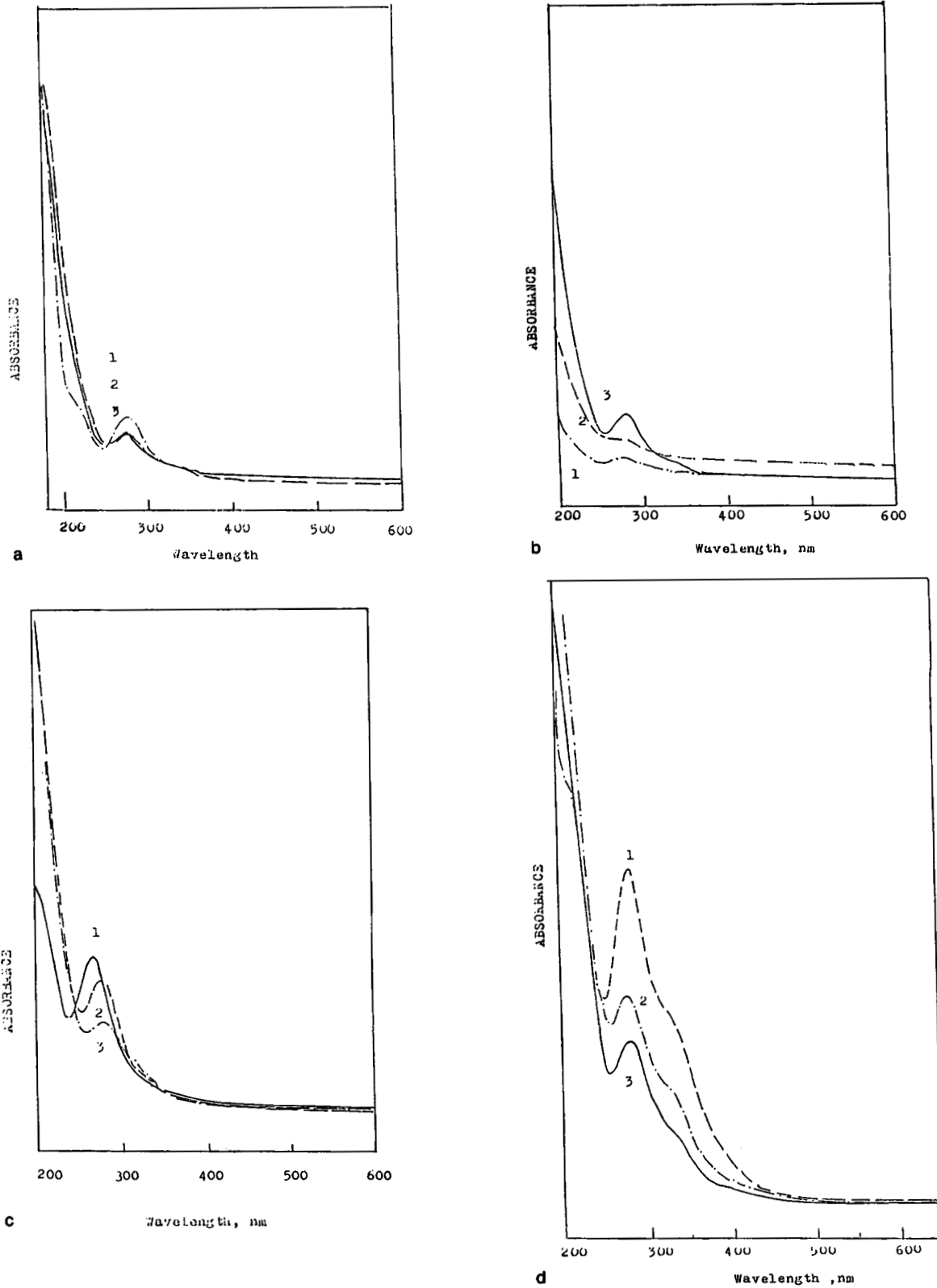
Figure 3   Effect of temperature on electronic spectra of (1) PVA, (2) PVA treated with 2% NiCl$_2$ (KOH/NiCl$_2$ 1 : 2), (3) PVA treated with 4% NiCl$_2$ (KOH/NiCl$_2$ 1 : 2), (a) 80°C, (b) 100°C, (c) 120°C, (d) 140°C.
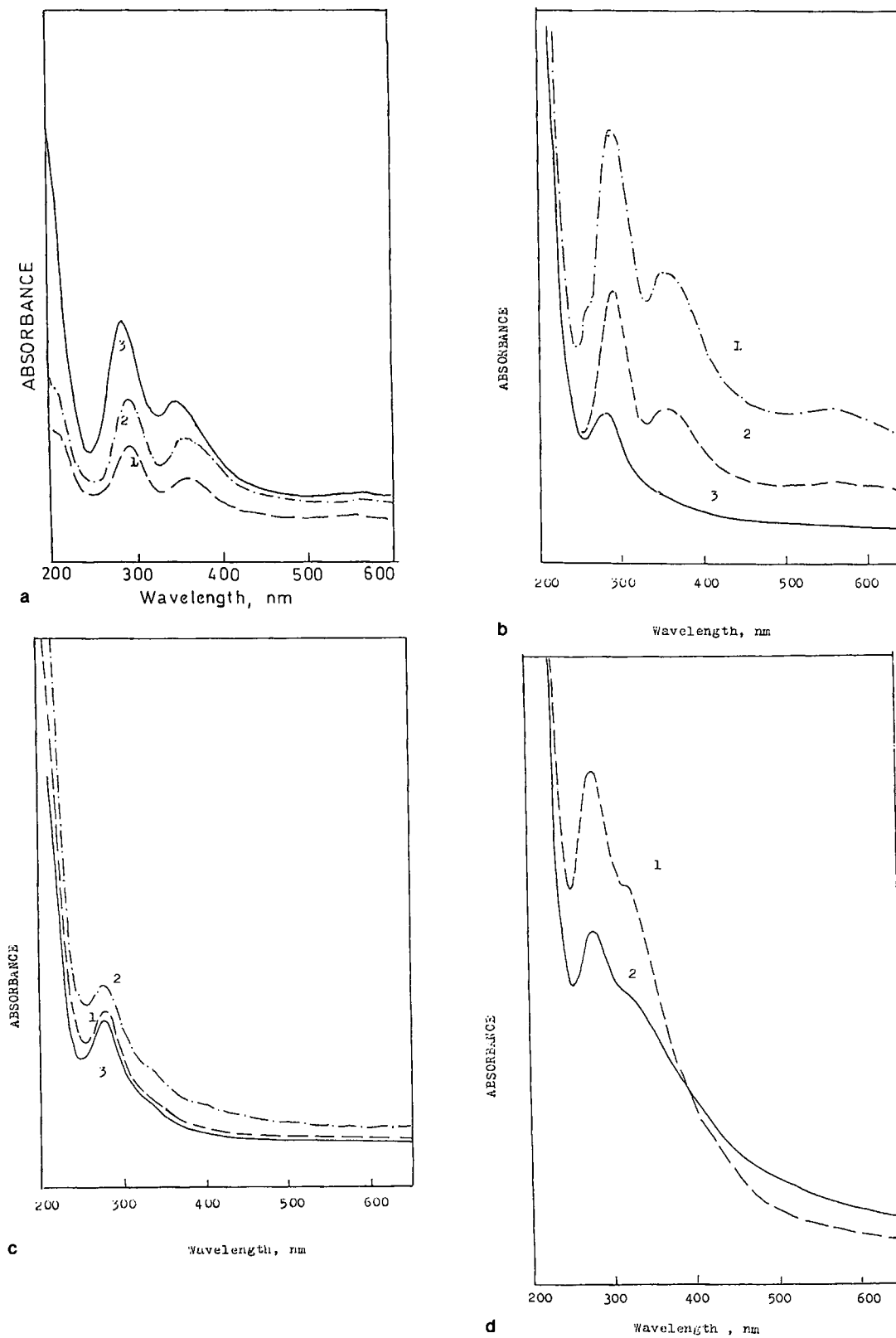
Figure 4   Effect of iodine on the electronic spectra of (1) pure PVA; (2) PVA treated with 2% NiCl$_2$ (KOH/NiCl$_2$ 1 : 2); (3) PVA treated with 4% NiCl$_2$ (KOH/NiCl$_2$ 1 : 2); (a) at room temperature; (b) after heating at 100°C for 2 h; (c) after heating at 120°C for 2 h; (d) after heating at 140°C for 2 h.

Samples of PVA were treated with 2 and 4% $NiCl_2$, with the $NiCl_2$/KOH ratio equal to 2 : 1. The spectra of these samples after heating to various temperatures are represented in Figure 3. It is clear from this figure that heating those samples at 80 and 100°C causes no observable changes in the absorption of the band at 280 nm, but elevating the heating temperature to 120°C resulted in a remarkable increase in its absorption. A further increase of the temperature to 140°C resulted in the appearance of a very strong band at 280 nm and another peak at about 330 nm. The band at 330 nm was assigned to the appearance of the $-CO-(C=C)_3-$ groups. This result provides strong evidence that reducing the ratio $KOH/NiCl_2$ to half its value helps in the formation of the carbonyl groups.

It was also found that the band at 280 nm in the spectra of the sample treated with $CoSO_4$ assumes a marked increase of its absorption by heating above 120°C.

Films of the samples treated with 2 and 4% $NiCl_2$ and $KOH/NiCl_2$ equal to 1 : 2 were then dipped into a solution of iodine (iodine is produced by El-Nasr Co. for Pharmaceuticals and Chemicals, Egypt) in acetone and dried at 100°C until maintaining constant weight.

The UV spectra of the samples modified with iodine are represented in Figure 4. As can be seen from Figure 4, the UV spectra of the iodine-modified film of PVA exhibits, in addition to the strong band at 190 nm associated with the presence of acetate residue, a strong band at 290 nm and another band of medium absorption at about 360 nm. It is very important to mention that pretreatment of the samples with 2 or 4% $NiCl_2$ produces marked decreases in the intensities of their absorption bands and the extent of decrease in case of the sample treated with 4% is greater than that for the sample treated with 2%. Heating the films at 100°C for 2 h resulted in further decreases in the intensities of these bands. The band at 360 nm disappeared from the spectra of samples treated with 4% $NiCl_2$. Moreover, heating to 100°C for 2 h shifted the band at 290 nm to lower wavelengths. This band appeared at its normal position at 280 nm in the spectra of the sample treated with 4% $NiCl_2$. Raising the heating temperature to 120°C resulted in the disappearance of the band at 360 nm and a further decrease of the absorption of the band at 290 nm, which showed a shift to 280 nm. Elevating the heating temperature to 140°C resulted in a marked increase in the intensity of the 280 nm band and the appearance of a weak band at 330 nm. This means that heating the metal-treated samples above 120°C either before or after treatment

with iodine increases the intensity of this band. It can be easily seen that the absorption of the band at 280 nm in the spectra of the sample treated with 2% is stronger than that for the sample treated with 4%. Bravar et al.[12] reported that bromination of dichromated exposed films of PVA causes the disappearance of the absorption bands at 270 and 230 nm and a very marked decrease of the absorption band at 230 nm and stated that this result confirms the influence of ethylenic unsaturation on the absorption at these wavelengths.

The infrared spectra of the samples under investigation are shown in Figure 5. Careful examination of these spectra showed that the only difference in the spectral features is that the spectrum of the samples treated with $CoCl_2$ or $CoSO_4$ (because there is no remarkable difference between the spectra of these two samples, only the spectrum of $CoCl_2$ is represented in the Figure) exhibits a well-defined absorption band at 1140 cm^{-1}. No substantial changes in the position or intensity of the $O-H$ stretching band at 3300 cm^{-1} are observed as a result of metal salts treatments. However, for quantitative measurements, the absorbances of this band and the $C-H$ stretching band at 2950 cm^{-1} were determined and the absorbances ratio A 3300/A 2950 was determined. The reason for choosing the 2950 cm^{-1} band is that it does not modify during the process. The absorbances of the two bands were measured by using the baseline method. A base line was taken as a horizontal line intersecting the higher frequency wing of the band 3300 at 3600 cm^{-1}. The absor-
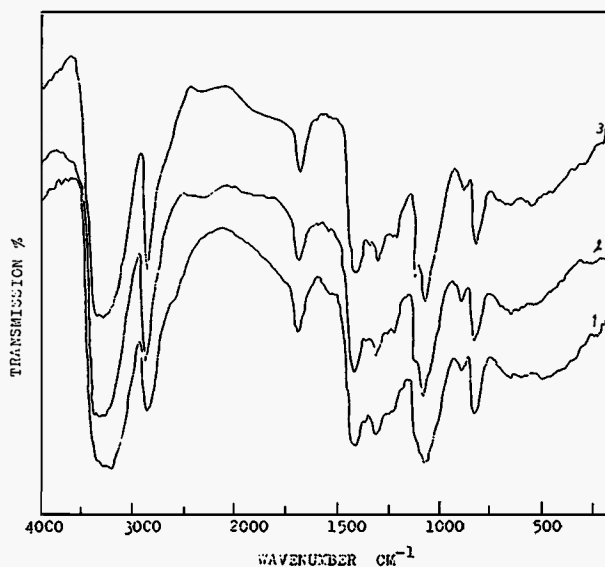

Figure 5   Infrared spectra of PVA treated with (1) $CoCl_2$, (2) $NiCl_2$, (3) $CuCl_2$.
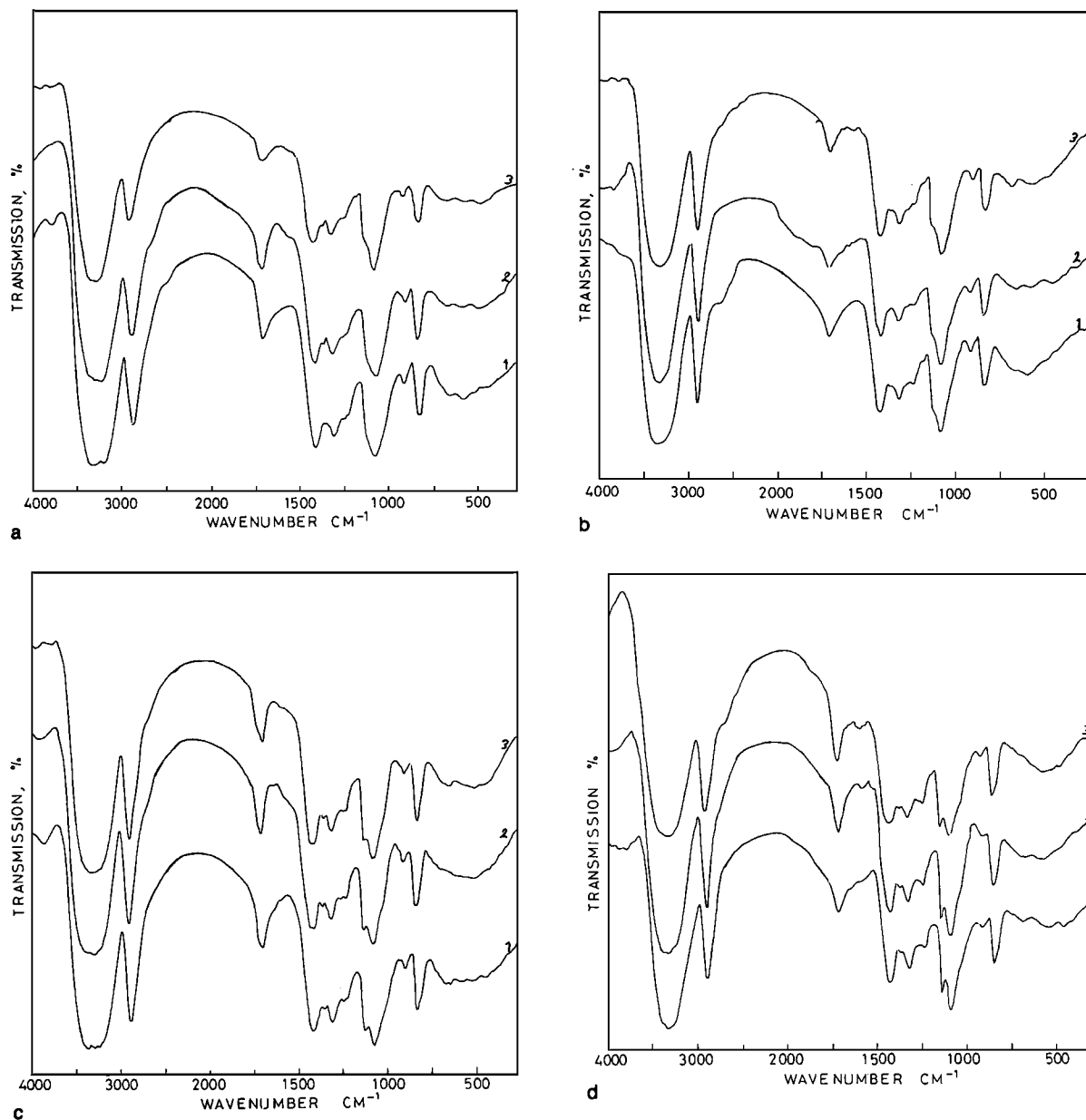
Figure 6 Effect of temperature on the infrared spectra of PVA treated with (1) 4%, (2) 8%, (3) 16% $NiCl_2$ ($KOH/NiCl_2$ 1 : 1), (a) 80°C, (b) 100°C, (c) 140°C, (d) 180°C.

bances ratios A 3300 cm^{-1}/A 2950 cm^{-1} for untreated and treated samples showed more or less the same values of about 1.56 + 0.03. This result indicates that no formation of oxygen-to-metal bonds (M—O) occurs as a result of these chemical treatments.

The infrared spectra of the samples treated with 4, 8, 16% $NiCl_2$ with $KOH/NiCl_2$ 1 : 1 were recorded after heating to various temperatures. The spectra are shown in Figure 6. By comparing the spectra of these samples, two characteristic features are visible.

1. The appearance of a well-defined band at 1140 cm^{-1} in the spectra of the sample heated at and above 120°C. The intensity of this band decreases with increasing the $NiCl_2$ concentration.

2. The appearance of a weak band at 1590 cm^{-1} in the spectra of the samples heated at 180°C. Also, the intensity of this band decreases with increasing the concentration of $NiCl_2$.

The band at 1140 cm^{-1} is used to measure the

Table I   Variation of the Percentage Cystallinity of NiCl₂ Heated PVA with Temperature

Temperature	Percentage Crystallinity		
	4% NiCl₂	8% NiCl₂	16% NiCl₂
120	20.73	18.34	—
140	34.25	24.12	9
160	51	45.02	37.68
180	38.52	35.57	31.65

crystalline content of PVA. The 1590 cm^{-1} band may be assigned to β-dikitone groups.

The percentage crystallinity of the samples heated at and above 120°C were measured by using the relation[13]

$$\text{Percent crystallinity} = 92 \ (d/c) - 18$$

where d is the vertical distance between the 1140 cm^{-1} peak and the intercept point of a straight line drawn across the portion of the spectrum between 1125 and 1150 cm^{-1} and C is the vertical distance between the 1425 cm^{-1} line drawn across the band.

The determined values are given in Table I, which indicate that the percentage crystallinity increases with increasing the temperature up to 160°C and then decreases in the sample heated at 180°C. Moreover, at any given temperature, the crystallinity decreases with increasing the NiCl₂ concentration. The most likely explanation for the decrease of percentage crystallinity at 180°C is that metal–polymer complexes act as catalysts for the dehydrogenation of the hydrocarbon chain during pyrolysis and graphitic structures may be formed.

The absorbances ratio A 3300/A 2900 for the heat-treated samples was also determined. It was found that the heat treatment of the samples over the range 25–180°C produces no significant changes in this ratio.

The infrared spectra of the samples treated with iodine were also recorded. The analysis of the recorded spectra indicated that iodine treatment of PVA produces a remarkable increase in the intensity of the crystalline absorption band at 1140 cm^{-1}.

According to the above-mentioned considerations, one can conclude that treatment of (PVA) with Cu chloride, Ni chloride, Co chloride, and Co sulfate causes considerable changes in the intensities of the 280 nm, and the extent of these changes depends on the concentration and nature of the metal ions used. Also, it was found that the intensity of this band is influenced by heat and dopind treatments. The infrared measurements provided strong evidence that the crystallinity of the metal-treated PVA depends on the temperature of heating and the concentration of metal ions.

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