

# Spectroscopic Behavior of Poly(vinyl alcohol) Films with Different Molecular Weights after UV Irradiation, Thermal Annealing, and Double Treatment with UV Irradiation and Thermal Annealing

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**ABSTRACT:** Pure poly(vinyl alcohol) (PVA) films with molecular weights 5,000, 72,000, and 125,000 g/mole were prepared by casting technique. The thickness of prepared samples was 0.21 mm. Xenon arc lamp was used to irradiate two samples from each molecular weight at 400 W for 5 min. One from each irradiated PVA samples was heated at 423 K for 2 h. An additional PVA sample unirradiated from each molecular weight was heated at 423 K for 2 h. Optical absorption measurements have been carried out in the wavelength range of 190–900 nm for untreated, UV-irradiated, heated, and double-treated samples by UV irradiation and heat. The double-treated PVA samples with molecular

weights 5,000 and 72,000 g/mole showed approximately zero transmission in comparison with untreated PVA sample in the wavelength range of 190–320 nm. PVA sample with 125,000 g/mole was irradiated with 600 W for 5 min to obtain the zero transmission in the same wavelength range. Identification of the structure and assignments of energy bands were studied also by using FTIR. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 589–594, 2003

**Key words:** annealing; irradiation; UV-vis spectroscopy; FTIR

## INTRODUCTION

Recently, poly(vinyl alcohol) (PVA) has been the subject of intensive research because it has many applications in industry and it is of relatively low cost in manufacture.<sup>1–8</sup> There are a large number of reports on PVA with different additives in order to modify and improve its properties.<sup>5–7</sup> Inorganic additives, such as transition metals salts, have considerable effect on the optical and electrical properties of PVA polymer.<sup>8</sup> Or on PVA with different molecular weights.<sup>2,4</sup> Irradiation with UV, X-rays, alpha-, beta-, and gamma-radiation also have a significant effect on polymer properties, and certain physical properties in particular may be modified dramatically.<sup>1,3,9–11</sup> Stability is of great importance to relate the chemical structure to the physical properties of polymers.

Until now, no systematic studies on spectroscopic behavior of PVA films with different molecular weights after UV irradiation and double treatment with UV irradiation and thermal annealing are available. The purpose of the current investigation was to study the spectroscopic behavior of PVA films with

different molecular weights after UV irradiation, thermal annealing, and double treatment with UV irradiation and thermal annealing.

## EXPERIMENTAL

PVA of molecular weights 5,000, 72,000, and 125,000 g/mole (BDH, U.K.) were used as a basic polymeric material in this work. PVA films were prepared by using a casting technique.<sup>1</sup> PVA solution was prepared by dissolving PVA in double-distilled water and then maintained for 24 h at room temperature to swell. The solution was then warmed up to 333 K and stirred, using magnetic stirrer, thoroughly for 4 h until the polymer became completely soluble. The solution was poured into a flat glass plate dishes. Homogeneous films were obtained after drying in air oven for 48 h at 313 K. The thickness of the produced films was 0.21 mm. Table I shows the experimental conditions for PVA samples.

The optical absorption and transmission measurements of all PVA films were measured by using a JASCO V-570 spectrophotometer in the range from 190 to 2,500 nm. The infrared spectra of all PVA films were recorded using a JASCO FTIR 420 spectrophotometer in the wave number range from 400 to 4,000  $\text{cm}^{-1}$  with scan resolution of 4  $\text{cm}^{-1}$ .

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TABLE I  
Experimental Conditions of PVA Samples

Molecular weight (g/mole)	Original sample	UV-irradiated sample at 400 W for 5 min	Thermal-annealed sample at 423 K for 2 h	Double-treated sample with UV irradiation and thermal-annealed at 423 K for 2 h	Double-treated sample with UV irradiation at 600 W for 5 min and thermal-annealed at 423 K for 2 h
5,000	a1	a2	a3	a4	
72,000	b1	b2	b3	b4	
125,000	c1	c2	c3	c4	c5

## RESULTS AND DISCUSSION

### Pure PVA films

The transmission spectra of PVA films with different molecular weights and different treatment conditions are shown in Figures 1–3. Investigation of these figures reveals that for sample a1, a nearly zero transmission intensity in the wavelength range 190–350 nm, a sharp increase in the transmission intensity reaches 70% at 450 nm and then the transmission intensity is approximately constant at 80% in the wavelength range 500–900 nm. For the samples b1 and c1, the same trend is observed but the transmission intensity at 250 nm increases with the increase in the molecular weights of PVA samples.

Figures 4–7 show the absorption spectra of the samples a1, b1, and c1 under investigation in the wavelength range 190–900 nm. In our previous communi-

cation,<sup>2</sup> we described a detailed study of the spectroscopic behavior of PVA films with different molecular weights and it was concluded that for pure PVA samples in UV region, all the samples showed two absorption bands at the same positions (284 and 327 nm), which related to high energy absorption and these bands may be assigned as  $\pi \rightarrow \pi^*$ , which come from unsaturated bonds, mainly C=O and/or C=C, which are present in the tail head of the polymer. When the molecular weight increases, the concentration of C=O, C=C decreases, and so the absorption decreases because the absorption is proportional to the number of absorbing molecules according to Beer's law.

### Effect of UV irradiation and thermal annealing treatment

In our previous communication,<sup>1</sup> we studied the effect of UV irradiation and thermal annealing on the optical

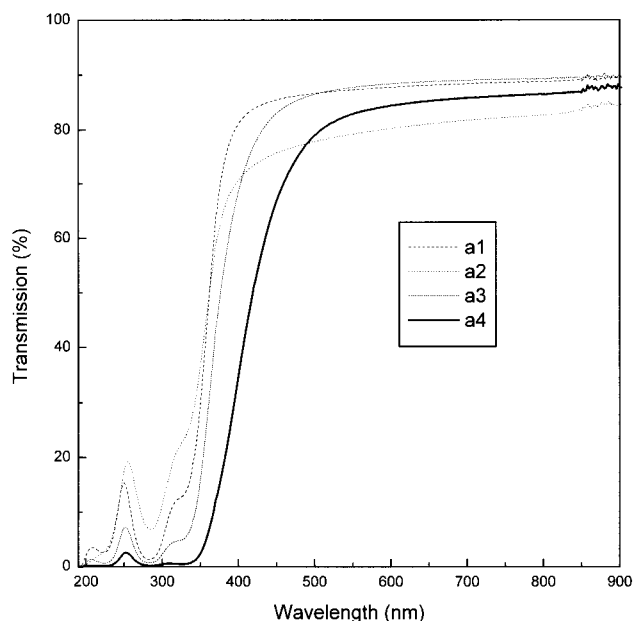


Figure 1 Transmission spectra of PVA samples: (a1) original; (a2) UV irradiated; (a3) thermal-annealed at 423 K for 2 h; and (a4) double treatment with UV and thermal-annealed at 423 K for 2 h.

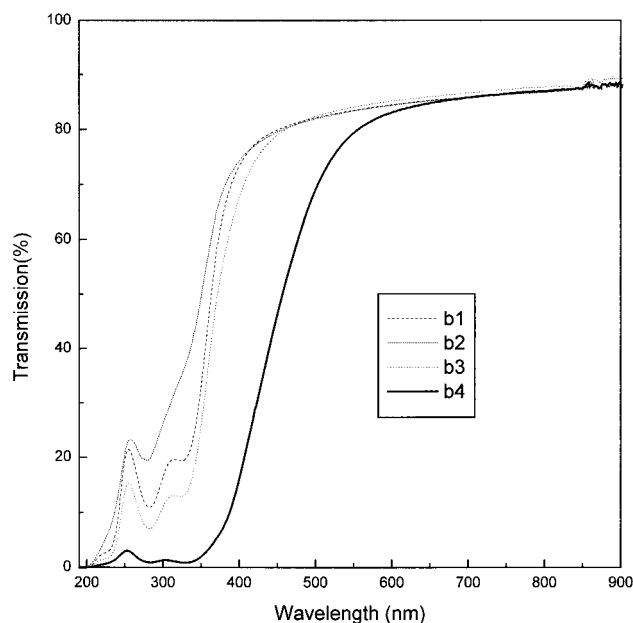
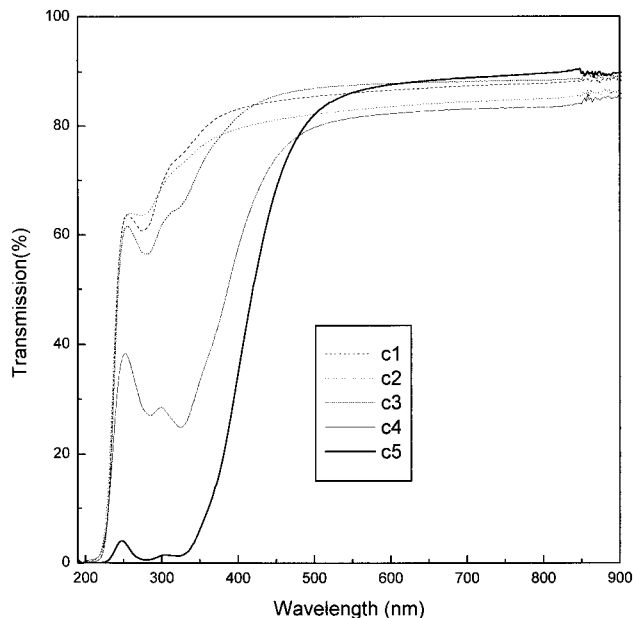
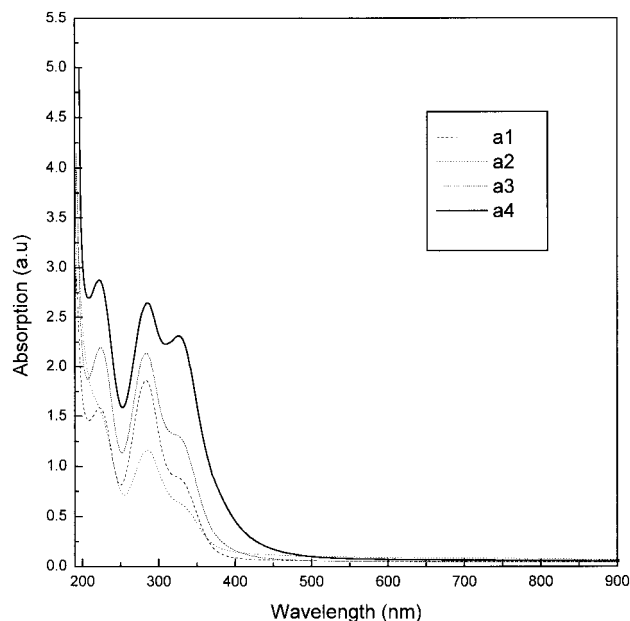


Figure 2 Transmission spectra of PVA samples: (b1) original; (b2) UV irradiated; (b3) thermal-annealed at 423 K for 2 h; and (b4) double treatment with UV and thermal-annealed at 423 K for 2 h.

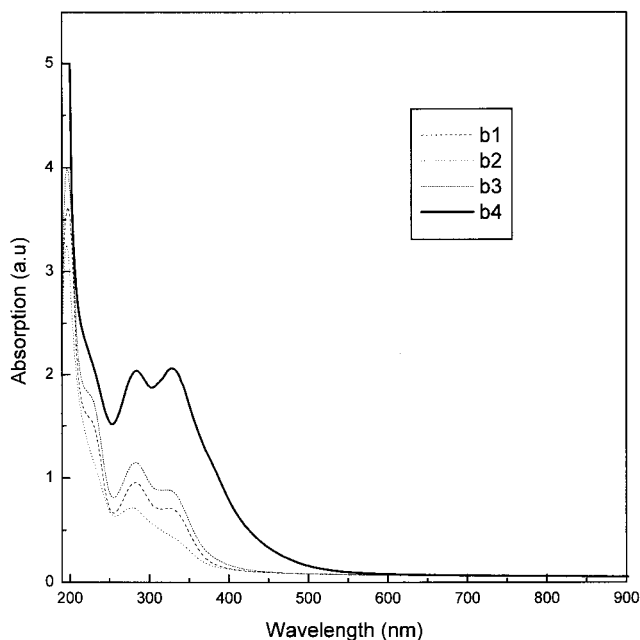


**Figure 3** Transmission spectra of PVA samples: (c1) original; (c2) UV irradiated; (c3) thermal-annealed at 423 K for 2 h; (c4) double treatment with UV at 400 W for 5 min and thermal-annealed at 423 K for 2 h; and (c5) double treatment with UV at 600 W for 5 min and thermal-annealed at 423 K for 2 h.

properties of PVA film with molecular weight of 17,000 g/mole. Figures 1 and 2 illustrate the same behavior for PVA samples a4 and b4. Three features are distinguished in the curves in agreement with previous

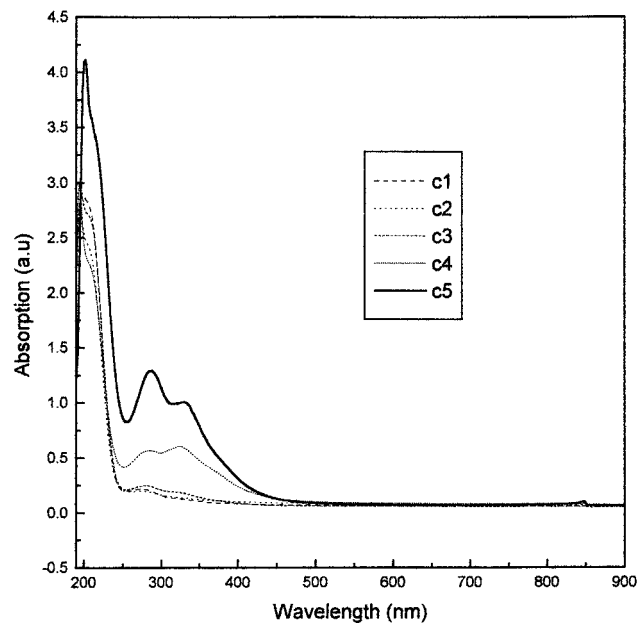


**Figure 4** Absorption spectra of PVA samples: (a1) original; (a2) UV irradiated; (a3) thermal-annealed at 423 K for 2 h; and (a4) double treatment with UV and thermal-annealed at 423 K for 2 h.



**Figure 5** Absorption spectra of PVA samples: (b1) original; (b2) UV irradiated; (b3) thermal-annealed at 423 K for 2 h; and (b4) double treatment with UV and thermal-annealed at 423 K for 2 h.

measurements<sup>1</sup>: a nearly zero transmission in the wavelength range 190–330 nm; the transmission of PVA sample increases rapidly from 5% to 85% in the wavelength



**Figure 6** Absorption spectra of PVA samples: (c1) original; (c2) UV irradiated; (c3) thermal-annealed at 423 K for 2 h; (c4) double treatment with UV at 400 W for 5 min and thermal-annealed at 423 K for 2 h; and (c5) double treatment with UV at 600 W for 5 min and thermal-annealed at 423 K for 2 h.

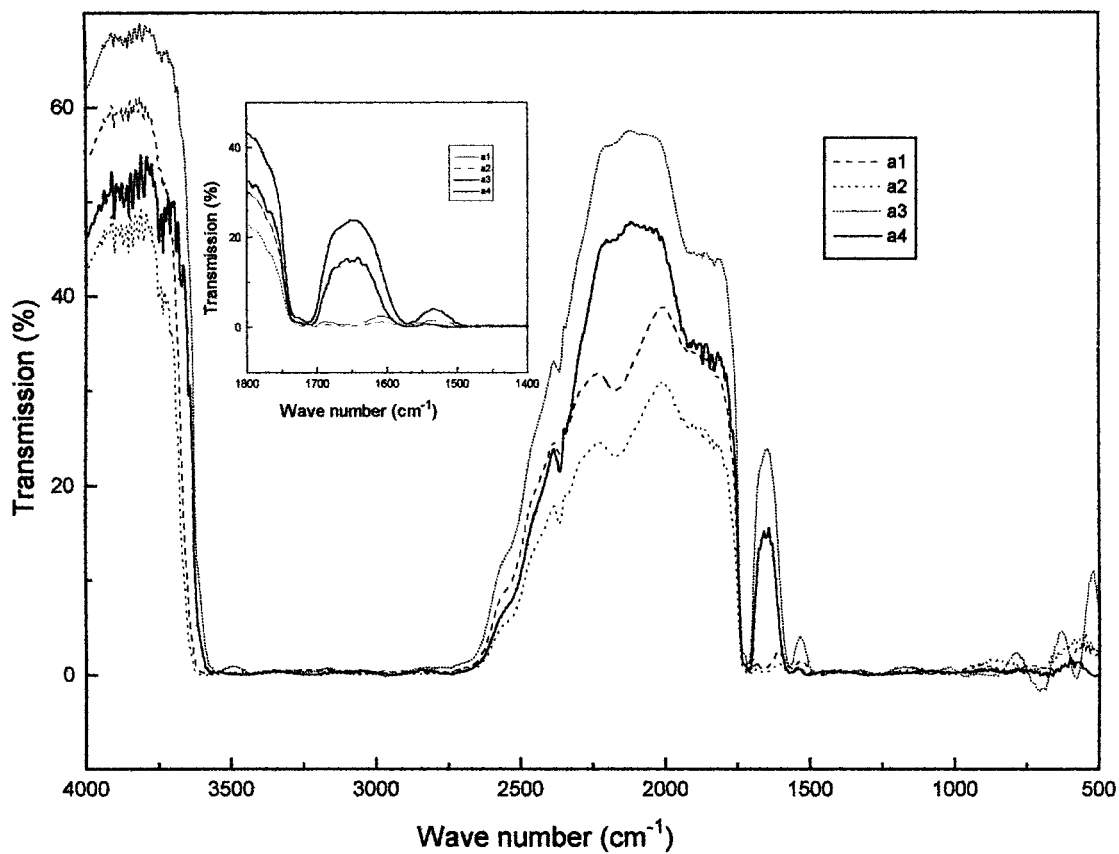


Figure 7 FTIR spectra of PVA samples: (a1) original; (a2) UV irradiated; (a3) thermal-annealed at 423 K for 2 h; and (a4) double treatment with UV and thermal-annealed at 423 K for 2 h.

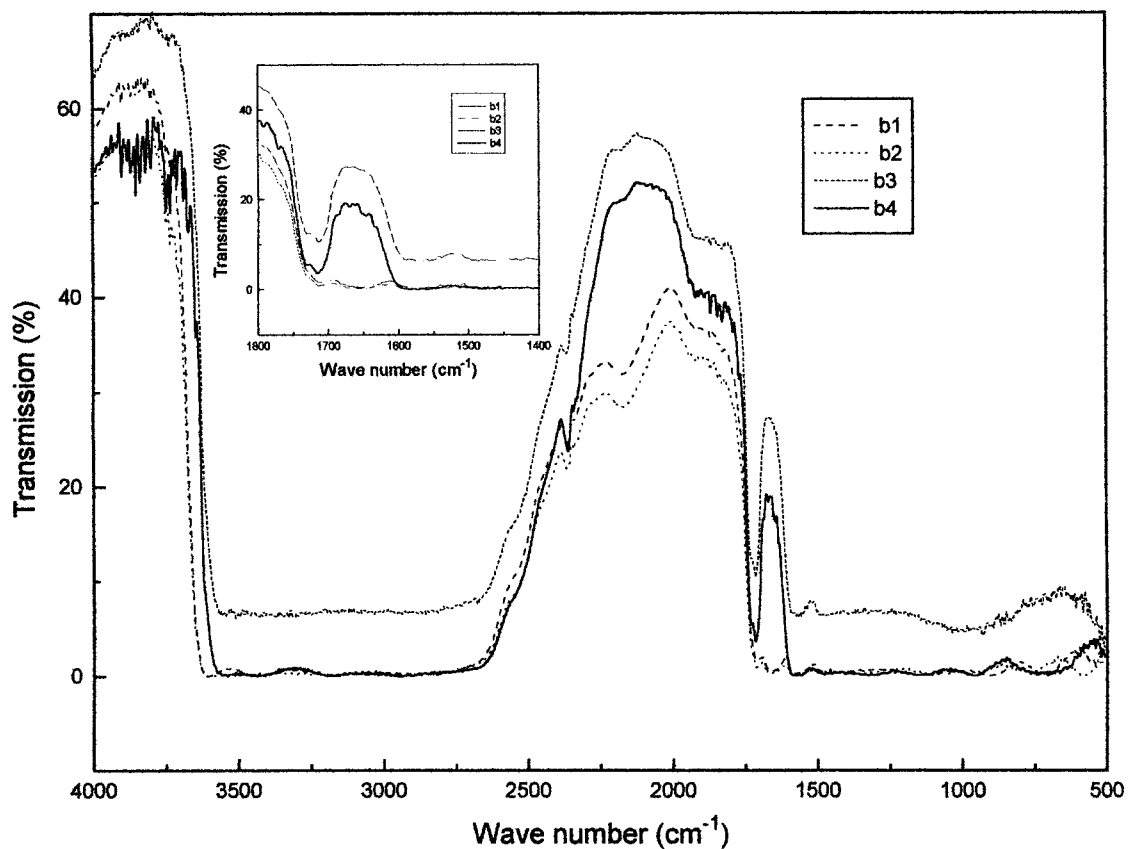


Figure 8 FTIR spectra of PVA samples: (a1) original; (a2) UV irradiated; (a3) thermal-annealed at 423 K for 2 h; and (a4) double treatment with UV and thermal-annealed at 423 K for 2 h.

TABLE II  
Analyzed Data of UV Absorption Spectra  
for PVA Samples

Significant samples	Bands (nm)	Absorption (arbitrary unit)	Assignment
a1	194 (s)	3	$n \rightarrow \pi^*$
	222 (w)	1.84	$\pi \rightarrow \pi^*$
	284 (w)	2	$\pi \rightarrow \pi^*$
	332 (w)	0.8	$\pi \rightarrow \pi^*$
a2	194 (s)	3.3	$n \rightarrow \pi^*$
	222	0	
	284 (w)	1.16	$\pi \rightarrow \pi^*$
	332 (sh)	0.6	$\pi \rightarrow \pi^*$
a3	194 (s)	4	$n \rightarrow \pi^*$
	224 (w)	2.2	$\pi \rightarrow \pi^*$
	284 (w)	2.1	$\pi \rightarrow \pi^*$
	332 (sh)	1.2	$\pi \rightarrow \pi^*$
a4	194 (s)	5	$n \rightarrow \pi^*$
	222 (w)	2.9	$\pi \rightarrow \pi^*$
	285 (w)	2.7	$\pi \rightarrow \pi^*$
	332 (w)	2.3	$\pi \rightarrow \pi^*$
b1	200 (s)	3.6	$n \rightarrow \pi^*$
	284 (w)	0.96	$\pi \rightarrow \pi^*$
	332 (sh)	0.69	$\pi \rightarrow \pi^*$
b2	198 (s)	3.2	$n \rightarrow \pi^*$
	284 (w)	0.72	$\pi \rightarrow \pi^*$
	332	0	
b3	200 (s)	4	$n \rightarrow \pi^*$
	284 (w)	1.2	$\pi \rightarrow \pi^*$
	332 (w)	0.9	$\pi \rightarrow \pi^*$
b4	194 (s)	5	$n \rightarrow \pi^*$
	284 (w)	2.1	$\pi \rightarrow \pi^*$
	332 (w)	2.1	$\pi \rightarrow \pi^*$
c1	200 (s)	3	$n \rightarrow \pi^*$
	284 (w)	0.5	$\pi \rightarrow \pi^*$
	332 (sh)	0.5	$\pi \rightarrow \pi^*$
c2	194 (S)	3	$n \rightarrow \pi^*$
	284 (w)	0.2	$\pi \rightarrow \pi^*$
	332	0	
c3	200 (s)	3	$\pi \rightarrow \pi^*$
	284 (w)	0.25	$\pi \rightarrow \pi^*$
	332 (w)	0	
c5	194 (s)	4.2	$n \rightarrow \pi^*$
	284 (w)	1.3	$\pi \rightarrow \pi^*$
	332 (sh)	1	$\pi \rightarrow \pi^*$

S, strong; sh, shoulder; w, weak.

range 350–500 nm; in the wavelength range 500–900 nm, Figures 1 and 2 show approximately constant value of transmission (approximately 90%).

Figure 3 shows the transmission spectrum of PVA sample c4 in the region 190–900 nm. One can observe slow increases in the transmission up to 39% in wavelength range 190–250 nm, decreases in the transmission from 39% to 25% corresponding to wavelength range 250–310 nm, and the transmission intensity rising and then remaining constant at 77% in the region 310–900 nm. Figures 4–6 show the absorption spectra for the three samples (a–c) and Table II contains the analyzes for these spectra.

The band at 200 nm as a strong one for all the samples may be assigned as an  $n \rightarrow \pi^*$  transition due

to the presence of the C=O group; meanwhile, there are two bands at 285 and 332 nm assigned as  $\pi \rightarrow \pi^*$  and the bands are described as weak, strong and shoulder for all the samples, may be due to the presence of different conjugated system (see Table II).<sup>12</sup> Figures 4 and 5 show that the absorption intensity of the samples a4 and b4 was found to be higher than the absorption intensity of the other samples (a1–a3 and b1–b3).

These results could be explained as follows. The principal radiolysis effect of PVA is to evolve hydrogen.<sup>13</sup> The loss of one hydrogen atom from the  $\alpha$ -carbon of hydroxyl group produces a main intermediate,  $\alpha$ -hydroxyalkyl radical, and ultimately gives carbonyl groups by loss of another hydrogen atom. The dehydration in the following thermal treatment is probably starting from the carbonyl groups, resulting in the conjugating structures of polyenones.

In Table II, the absorption intensity of sample a4 is higher than the absorption intensity of samples b4 and c5 because, as mentioned before, when the molecular weight increases the concentration of C=O and C=C decreases and so the absorption decreases. The absorption intensity in PVA sample c5 could be increased via increase in the incident energy or the time of exposure. Figure 3 shows the obtained results for PVA sample c5.

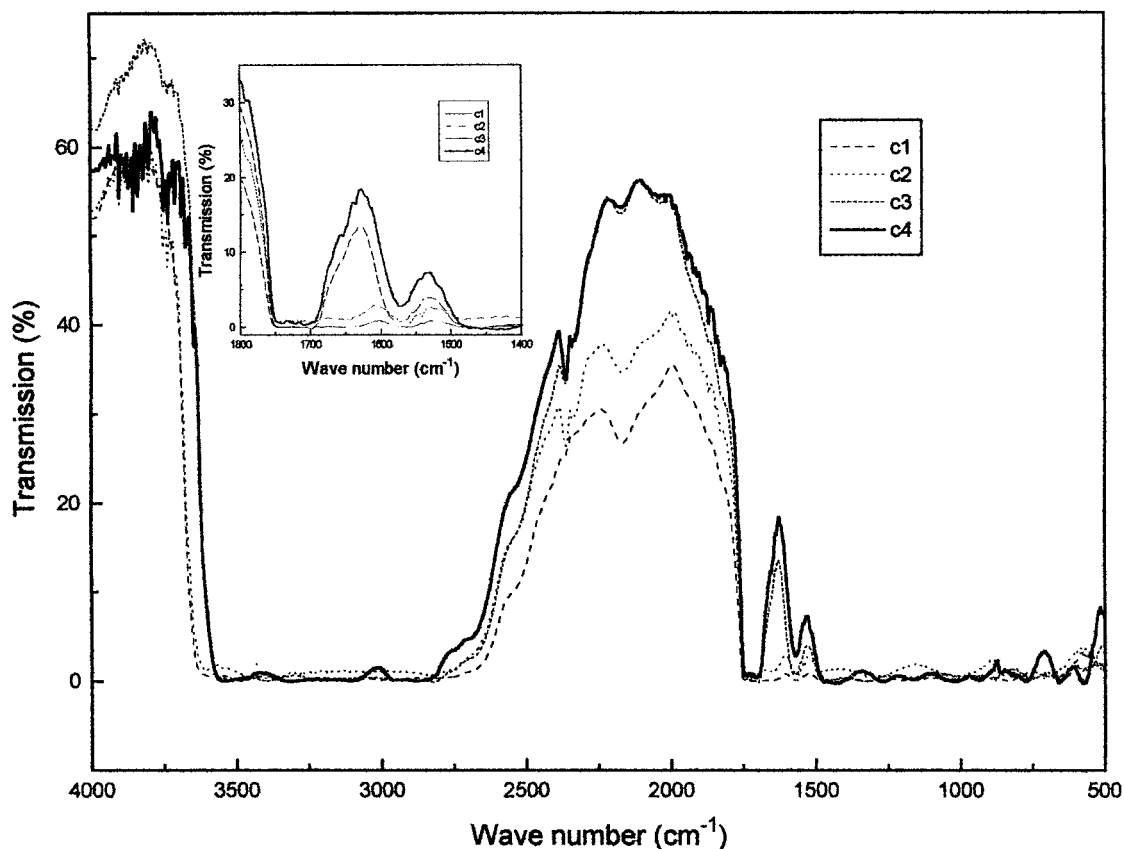
#### FTIR characterization

Figures 7–9 show the plots of infrared transmission spectra of the polymer samples under investigation. The observed features can be summarized as follows. All untreated PVA samples gave a broad and strong band centered at  $3,400 \text{ cm}^{-1}$ , which could be assigned as the stretching vibration of hydroxyl group ( $\nu_{\text{O-H}}$ ) with strong hydrogen bonding as intra- and/or inter-type.<sup>12,14,15</sup>

The carbon–hydrogen stretching vibration, which occurs at the high frequency end of the spectrum, is characteristic of the hybridization of the carbon holding the hydrogen: at  $2,800\text{--}3,000 \text{ cm}^{-1}$  for tetrahedral carbon; at  $3,000\text{--}3,100 \text{ cm}^{-1}$  for trigonal carbon (alkenes), are not observed here may be due to the strong hydrogen bond, which gave very broad band and may contain the carbon–hydrogen stretching.<sup>12</sup>

The stretching vibration bands of C=O and C=C appeared at  $1,610$  and  $1,570 \text{ cm}^{-1}$  for all the samples under investigation. The values of  $\nu_{\text{C=O}}$  and/or  $\nu_{\text{C=C}}$  indicate that these samples have the same resonating structure from alkene  $\leftrightarrow$  alkane and  $\text{C=O} \leftrightarrow \text{C-O}^-$  and/or presence of hydrogen bond with oxygen of C=O group.

For PVA samples a2–a4, b2–b4, and c2–c5, the stretching vibration bands that appear at  $1,605$ ,  $1,605$ ,  $1,625$ , and  $1,675 \text{ cm}^{-1}$  were assigned as  $\nu_{\text{C=O}}$ . The frequency values



**Figure 9** FTIR spectra of PVA samples: (c1) original; (c2) UV irradiated; (c3) thermal-annealed at 423 K for 2 h; and (c4) double treatment with UV at 400 W for 5 min and thermal-annealed at 423 K for 2 h.

of this band indicates that the C=O group entrance as coordinate site to hydrogen bond system (for C=O whose  $\nu_{\text{C=O}} = 1,700 \text{ cm}^{-1}$ ). The tendency of this behavior decreases for samples a4, b4, and c5, which may be due to breaking hydrogen bond and/or the radiation- and heating-induced structure changes on the polymer chains as well as the generated small molecular product.<sup>12</sup>  $\nu_{\text{C=O}}$ , which appeared at  $1,529 \text{ cm}^{-1}$  for all the samples, indicated that irradiation and thermal annealing has no effect on the C=C moiety.<sup>16</sup>

## CONCLUSIONS

The action of UV irradiation and thermal annealing on optical properties of PVA with different molecular weights is widely acknowledged. Thus, by controlling the energy of UV irradiation, it is possible to obtain the desirable properties.

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