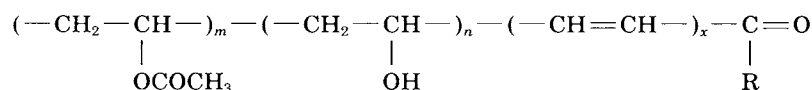# Spectral Study of Modified Polyvinylic Alcohol Submitted to Chemical and Heat Treatments

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SYNOPSIS

The IR and UV spectra of modified polyvinyl alcohol with the following structure were investigated:

$$(-CH_2-CH-)_m-(-CH_2-CH-)_n-(-CH=CH-)_x-C=O$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad OCOCH_3 \quad\quad OH \quad\quad\quad\quad\quad\quad R$$

(x = 1–3; R = alkyl radical, preferably methyl). The specific absorptions were identified and correlated with the structural changes produced by the chemical and heat treatment of the polymer precursor. © 1995 John Wiley & Sons, Inc.
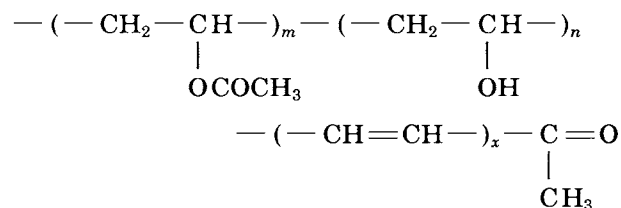
INTRODUCTION

Recent studies concerning surface agents are connected with modified polyvinyl alcohol (MPVA). The special interest results from its superior surface properties and high water solubility.

In previous articles[1-6] we examined the synthesis and thermal behavior of PVAs containing terminal carbonyl groups conjugated with double bonds. The present article deals with the IR and UV spectral study performed on a series of PVAs submitted to chemical and heat treatments. The main steps[1-3] in the synthesis of the investigated MPVA were the following:

1. the polymerization of vinyl acetate in the presence of known quantities of acetaldehyde, used as a chain transfer agent for the introduction of the terminal carbonylic groups;
2. the alcoholysis of the polyvinyl acetate obtained; and
3. the heat treatment of the PVAs in order to ensure the formation of double bonds conjugated with terminal carbonylic groups.

Thus the obtained polymers have the following structure:

$$-(-CH_2-CH-)_m-(-CH_2-CH-)_n$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad OCOCH_3 \quad\quad\quad OH$$
$$-(-CH=CH-)_x-C=O$$
$$\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad\quad CH_3$$

The aim of the present study was to attempt a characterization of the products obtained at different moments of the synthesis by IR and UV spectroscopy. Depending on their content of terminal carbonyl groups, the samples were numbered from 1 to 3; within each series the samples were heated at 150°C for 0.5 h (a), 1 h (b), 2 h (c), and 3 h (d). The main characteristics of the investigated MPVA samples are summarized in Table I.

EXPERIMENTAL

The IR spectra were registered on an IR-71 spectrophotometer in thin films obtained from water, the only solvent in which the polymers were soluble. The attempts to use the KBr pellet technique failed, as the spectra were not reproducible.

Table I   Main Characteristics of Investigated MPVA Samples

Polymer Code Series	Concentration of CH$_3$CHO (%)	$\bar{M}_n$ of Polyvinyl Acetate	Degree of Hydrolysis (%)	Time of Heating (h)			
				a	b	c	d
1	0.5	44825	80.85	0.5	1	2	3
2	1.0	37674	79.40	0.5	1	2	3
3	2.5	30726	74.52	0.5	1	2	3

The UV spectra were registered on a SPECORD UV-VIS spectrophotometer in aqueous solution and thin films.

The electronic spectra were simulated using a deconvolution program written by C. Bendic.
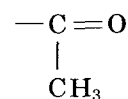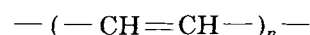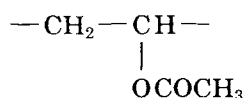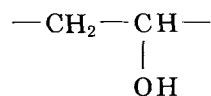
RESULTS AND DISCUSSION

IR Spectra

Taking into account the structure of the polymers discussed above, the IR spectra contain the vibration frequencies for the following groups:
acetate:

$$-CH_2-CH-$$
$$|$$
$$OCOCH_3$$

secondary alcohols:

$$-CH_2-CH-$$
$$|$$
$$OH$$

terminal carbonyl groups:

$$-C=O$$
$$|$$
$$CH_3$$

conjugated double bonds:

$$-(-CH=CH-)_n-$$

The IR spectra of the samples do not differ essentially among them and are characterized by the frequencies listed in Table II.

The structural modifications caused by the chemical and heat treatments are reflected in changes of the relative intensities of some bands. From this point of view several spectral regions can be observed.

Table II   General IR Data of Polymer Samples

$\bar{\nu}$ (cm^{-1})	Assignments
1740 v.i.	C—O Stretching
1720 v.i.	C—O Stretching
1650 v.w.	C—C Stretching
1600 m.	C—C Stretching
1450 m. large	Symmetric and asymmetric bending
1430 m. large	frequencies for CH$_2$, CH$_3$ in
1420 m. large	different environments O—C—C
1090	bending in secondary alcohols
1080	
1020	

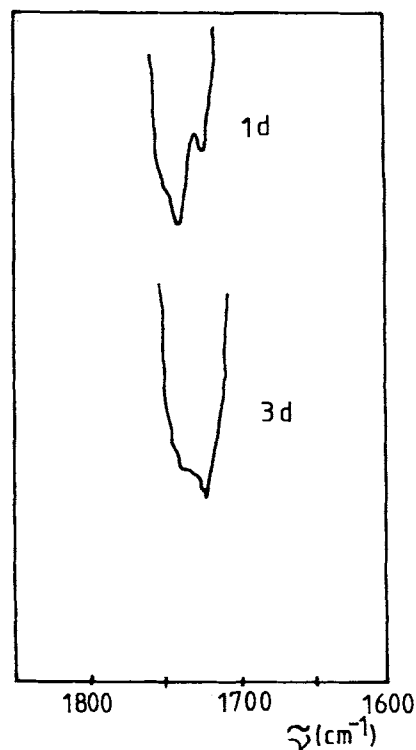v.i. = very intensive; v.w. = very weak; m. = medium.

Figure 1   IR spectral behavior in the carbonyl stretching vibration range of the polymers in series 1d and 3d.
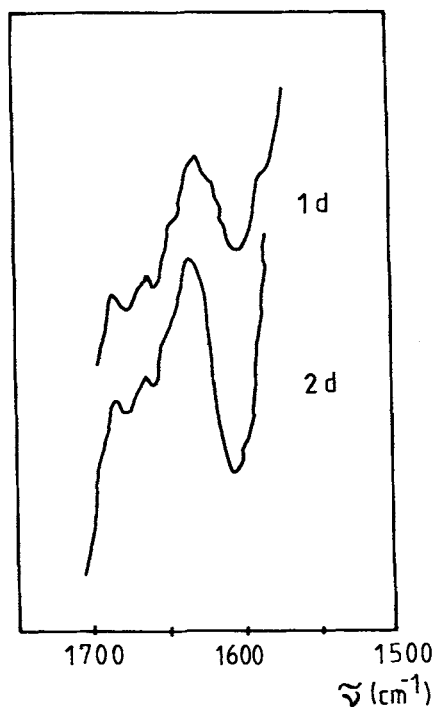
Figure 2   IR spectral behavior in the C=C stretching vibration range of the polymers in series 1d and 2d.

Figure 3   IR spectral behavior in the range 900–1000 cm⁻¹ of the polymers in series 1a and 3a.

Region of C=O Bond Stretching: 1700–1760 cm⁻¹

In this range all the compounds exhibit a large and very intense band with two or three peaks visible, located at 1760, 1740, and 1720 cm⁻¹; these peaks are assigned to the following C=O stretching vibrations[7]:

1. 1760 and 1740 cm⁻¹; the C=O stretching vibration in the acetate group;
2. 1720 cm⁻¹: the C=O stretching vibration in alkyl disubstituted ketones (e.g., in acetone this vibration occurs at 1719 cm⁻¹).

Comparing the spectra of all the samples in this spectral range, the following observations can be made. A change in the relative absorbances of the peaks at 1740 and 1720 cm⁻¹ from series 1 to 3 occurs (Fig. 1) in series 1 at $A_{1740} > A_{1720}$ and series 3 at $A_{1720} > A_{1740}$. These changes reflect an increase of the content of the C=O terminal groups, in agreement with the data mentioned in Table I.

Within each series there are no changes in the general aspect of the band, in agreement with the fact that the heat treatment does not produce modifications in the number of the C=O groups.

Region of C=C Band Stretching

In this range of the spectrum there are three bands of very low intensities: 1675, 1650, and 1610 cm⁻¹, the last being the most intense. The bands at 1658 and 1605 cm⁻¹ could be assigned to in phase and out of phase vibrations of a 1, 3 dienic system. It is well known that the in phase vibration is of lower intensity than the out of phase one. When a C=O group is conjugated with an unsaturated π system the positions of the stretching vibrations are modified, the s-cis conformation leads to a greater difference between the C=C and C=O frequencies than the s-trans conformation. In our case the positions of the bands after 3 h at 150°C suggest the preponderance of the s-cis conformation but the results are not very conclusive (Fig. 2).

Table III   UV Spectra of PVA Samples

Compound	λ (nm)		
1	205	227 i	263
2	200	222 i	263
3	200	223 i	263

Region of 900–1000 cm^{-1} range

Some interesting features are evidenced in this range, the spectral region of the out of phase deformation vibrations. In this range the initial compounds exhibit a single band located at 930 cm^{-1}; in the series 1a–1d there are two bands with the maxima at 945 and 910 cm^{-1} with a ratio of the intensities, determined by the baseline procedure, of 1 : 1 (Fig. 3). For the series 3a–3d, the same bands are observed but the intensities ratio is 1 : 2; within every series, the change of the ratio is not significant (e.g. for four different films of the sample 3a the values are 1 : 1.94; 1 : 1.74; 1 : 2.1; and 1 : 2.2, i.e., 1 : 2. For sample 3d obtained values are: 1 : 1.89; 1 : 1.87, etc., i.e., 1 : 2). We may assume that by the chemical process of increasing the number of terminal C=O groups, the band of 910 cm^{-1} is enhanced, but it is difficult to ascertain what is responsible for this fact.

Table IV Absorption Maxima in Range of 270–285 nm from Compounds with Related Structure

Compound	λ (nm)

—CH$_2$—CH—CH$_2$—C=O
      | |
    CH$_3$ CH$_3$
	281

—CH$_3$—CH$_2$—CH$_2$—CH$_2$—C=O
                        |
                      CH$_3$
	279

—(—CH=CH—)$_3^-$	274
—CH$_2$—(—CH=CH—)$_n$	285

UV Spectra

The UV spectra of samples 1–3 consist of three bands with the maxima listed in Table III. It can be seen that any absorption can be evidenced at wavelengths larger than 270 nm. The band at 263 nm
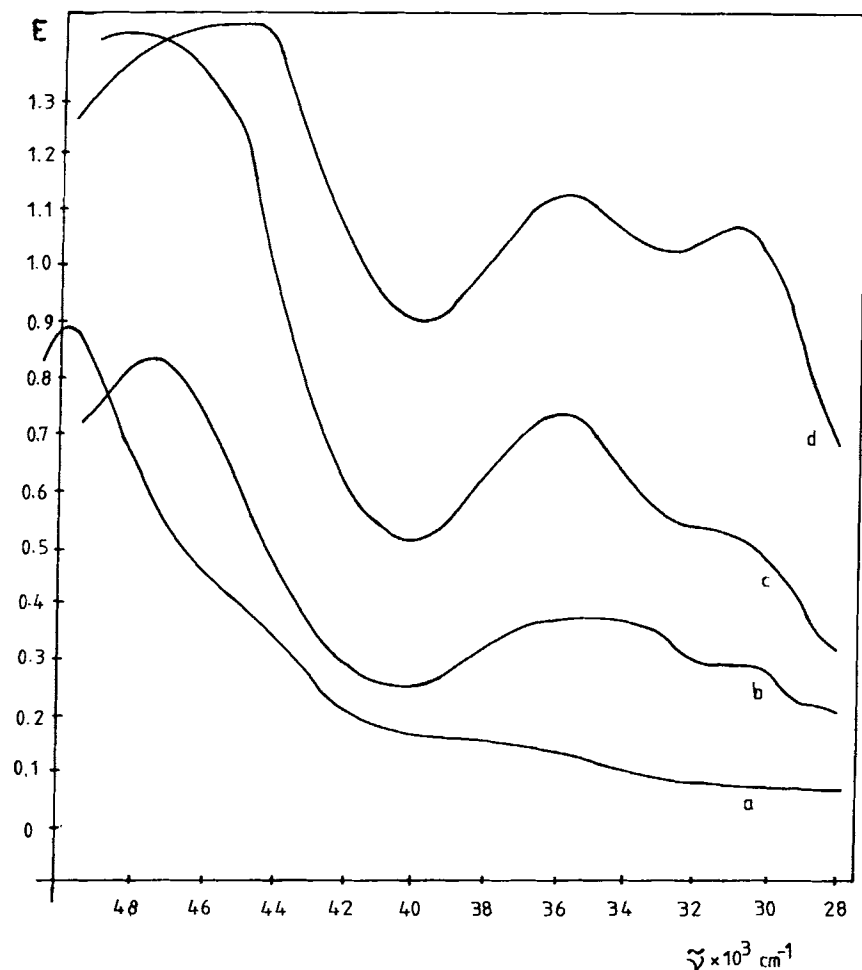

Figure 4 UV spectral behavior of the polymer in series 1, heated (a) 0.5 h, (b) 1 h, (c) 2 h, and (d) 3 h.

was assigned, by comparison with literature data, to a $n-\pi^*$ transition in an unconjugated carbonyl group, that is the terminal carbonyl groups; the other bands are due to the PVA chains.

The heat treatment produces a change in the UV spectra of all the samples, as a shift of the band at 263 to 273 nm and the appearance of a new absorption band at 328 nm. Increasing the time of heating from 0.5 to 3 h, the relative intensities of these two bands are modified until a ratio of nearly 1 : 1 is reached.

A typical example for this behavior is shown in Figure 4 for the series 3 (3a–3d).

In all compounds the band at 273 nm exhibits an asymmetric shape, suggesting a superposition of several bands. The assignment of this band is difficult because there are many compounds with related structures containing parts that could be present in our samples, which absorb in this range of the spectrum. Some of them are listed in Table IV.

It can be seen that the absorption in this range can be either due to the $n-\pi^*$ transition in the carbonyl groups with different neighbors or to a $\pi-\pi^*$ transition in the π system just formed.

Table V   Ratios of Absorbance of Bands at 273 and 328 nm

Code	1a	1d	2a	2d	3a	3d
E_{273}/E_{380}	1.51	0.99	2.26	0.83	2.37	0.97

The band at 328 nm can be assigned without any doubt to the $n-\pi^*$ transition in a carbonyl group conjugated with a π system. An increase in the heating time is reflected in an increase of the intensity of this band, which means that this belongs to a species favored by the temperature. We consider this as a confirmation of the expected elimination of the water molecules between the vicinal OH groups near the terminal carbonyl groups and the formation of the following structure:

$$-(-CH=CH-)_n-C=O$$
$$|$$
$$CH_3$$

To obtain a more precise location of the maxima and the real number of bands, we performed a de-

Figure 5   Computer deconvoluted and experimental UV spectra of the polymers in series (O) 1a and (X) 1d.

convolution of the spectrum using a program written by C. Bendic. The experimental and also the calculated spectrum are presented in Figure 5. It can be seen that although seemingly only two bands could be observed, there are in fact four bands with very different intensities and maxima.

Using the absorbances of the "pure" bands, we attempted to evidence in a quantitive manner the increase of the intensity of the band at 328 nm, that is, the accumulation of the species with conjugated double bonds. The values of the calculated ratio E_{273}/E_{328} are presented in Table V.

The data in Table V reflect the already discussed behavior and certify that 3 h of heat treatment are sufficient to obtain the maximum quantity of conjugated species. The prolongation of the heating time is not necessary and does not lead to changes in the polymer structure.

It can also be observed that the differences between the intensities of both bands after the first period of heating increase from series 1 to 3. The attempts for obtaining some reliable information from the bands at 244 and 286 nm failed, probably due to their low intensities that are more affected by errors.

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