

EXCITATION SPECTRA OF HEAT-TREATED POLY(VINYL ALCOHOL) FILM

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Among species of general structure -(CH=CH)_n produced in the heat-treated PVA substrate, the existence of polyene systems with $n=2$ to 5 were successfully confirmed by means of the excitation spectra and the Lewis-Calvin's plot.

The spectroscopic analysis of degraded poly(vinyl alcohol) [PVA] is one of the most interested and complicated problems.¹⁾ Certainly, it is difficult to analyse the spectroscopic data closely, since the PVA substrate, degraded by heat treatment and others, has to be composite; spectroscopically, complicated phenomena will arise, especially in the emission and excitation spectra. Our purpose is to show that some of degradation products in the PVA substrate can be analysed by the excitation spectra.

The absorption spectra were measured using Shimadzu UV-360 Spectrophotometer and the fluorescence and excitation spectra were measured from the front side of a film with an incidence angle of 45 degrees using Shimadzu RF-502 Spectrofluorophotometer.

PVA used was a commercial one (Koso Chemical Co., Ltd.) of which the average polymerization degree was 1400 and the alkaline saponification 99-100%. 30 Grams of PVA powder was dissolved in distilled water of 300 cm³ at 80 °C, and the solution was poured on a horizontal plate glass. After it was dried at room temperature for ten days, a PVA film was obtained as about 300 μm thick. The film was kept for two hours at 80 °C. The absorption spectrum of this film is shown in Fig. 1(a).

Next, the film was digested in the mixed solution of 0.1 M NaBH₄ (1 M=1 mol

dm⁻³) and 0.1 M NaOH for one day to reduce carbonyl group and then it was washed with water. As the following step, the film was digested in 0.05 M HCl solution for a few hours, in distilled water for two or three days and then was dried at room temperature. The absorption spectrum of this film is shown in Fig. 1(b). The above treated sample film, which indicates the spectra (a) and (b), did not show fluorescence.

The 280 nm band and the 330 nm shoulder of Fig. 1(a) have been assigned to the π - π^* transitions of $\text{-(CH=CH)}_2\text{CO-}$ and $\text{-(CH=CH)}_3\text{CO-}$, respectively.²⁾ The treatment with the NaBH₄ solution changes these bands into the 234 nm and 273 nm bands accompanied with fine structures (Fig. 1(b)). It indicates apparently that the 234 nm and 273 nm bands are attributed to the π - π^* transitions of -(CH=CH)_2 and -(CH=CH)_3 , respectively, because NaBH₄ can reduce carbonyl group and accordingly decrease the number of double bonds by one. This consideration is supported by comparison with the reported spectra of dienes³⁾ and trienes.⁴⁾ Moreover, the intervals (cm⁻¹) of all adjacent peaks, which are listed in Table 1, well correspond to the approximate value, which is reported as about 1500 cm⁻¹ for the vibrational spacings,⁴⁾ except a large gap (3150 cm⁻¹) between the 242 nm and 262 nm peaks. For that reason, the two species for the 234 nm and 273 nm bands are identified with the structure of n=2 and 3, respectively, for R $\text{-(CH=CH)}_n\text{-R}'$ which are produced by the reduction of R $\text{-(CH=CH)}_n\text{CO-R}''$.

The PVA film obtained above did not color for the heat treatment up to 200 °C but by digestion in the HCl solution beforehand, it did. That is to say, the film colored up red when it is heated to 120 °C under a condition of 500 cm³/min flow

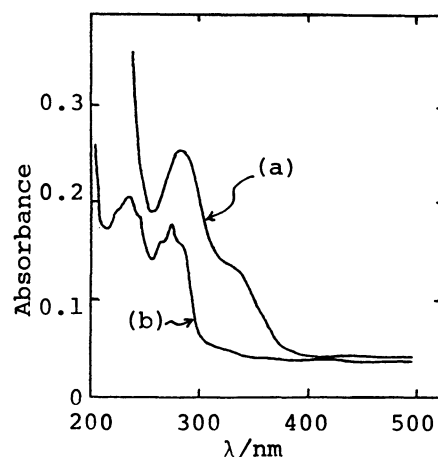


Fig. 1. Absorption spectrum of PVA film heated at 80 °C (a), and reduced by NaBH₄ (b). Film thickness: 300 μm .

Table 1. Energy gap of peaks observed in Fig. 1(b).

Band	234 nm			273 nm		
	λ/nm	226	234	242	262	273
ν/cm^{-1}	44250	42740	41320	38170	36630	35090
$\Delta\nu/\text{cm}^{-1}$	1510	1420	3150	1540	1540	

of nitrogen gas, after it was digested in the 0.05 M HCl solution for one hour and then dried in air at room temperature. The absorption spectrum of the red film is shown in Fig. 2(a) and the fluorescence spectra in Fig. 2(b), which were observed by exciting lights of 280-400 nm. The excitation spectra of the red film monitored at various wavelengths show five peaks at 295, 310, 325, 342, and 358 nm (Fig. 2(c)). Only the former three peaks among them were revealed when monitored at the 383 nm peak region. This means that the excitation spectra associated with the five peaks are composed of those of two species. The five peaks are also recognized in the absorption spectrum of Fig. 2(a). The two species are considered to have $n=4$ and 5 of the general structure $R(\text{CH}=\text{CH})_n\text{R}'$ taking into account the positions of the 234 and 273 nm band assigned already (Fig. 1(b)). In fact, the excitation spectrum monitored at 383 nm is very similar to the absorption spectrum of tetraene.⁵⁾ Furthermore, the plots of Lewis-Calvin's equation,⁶⁾ $\lambda^2=kn$, for the peak of the assigned species of $n=2, 3, 4,$ and 5 gave straight lines shown in Fig. 3, where λ and n are the wavelength and the number of double bonds of

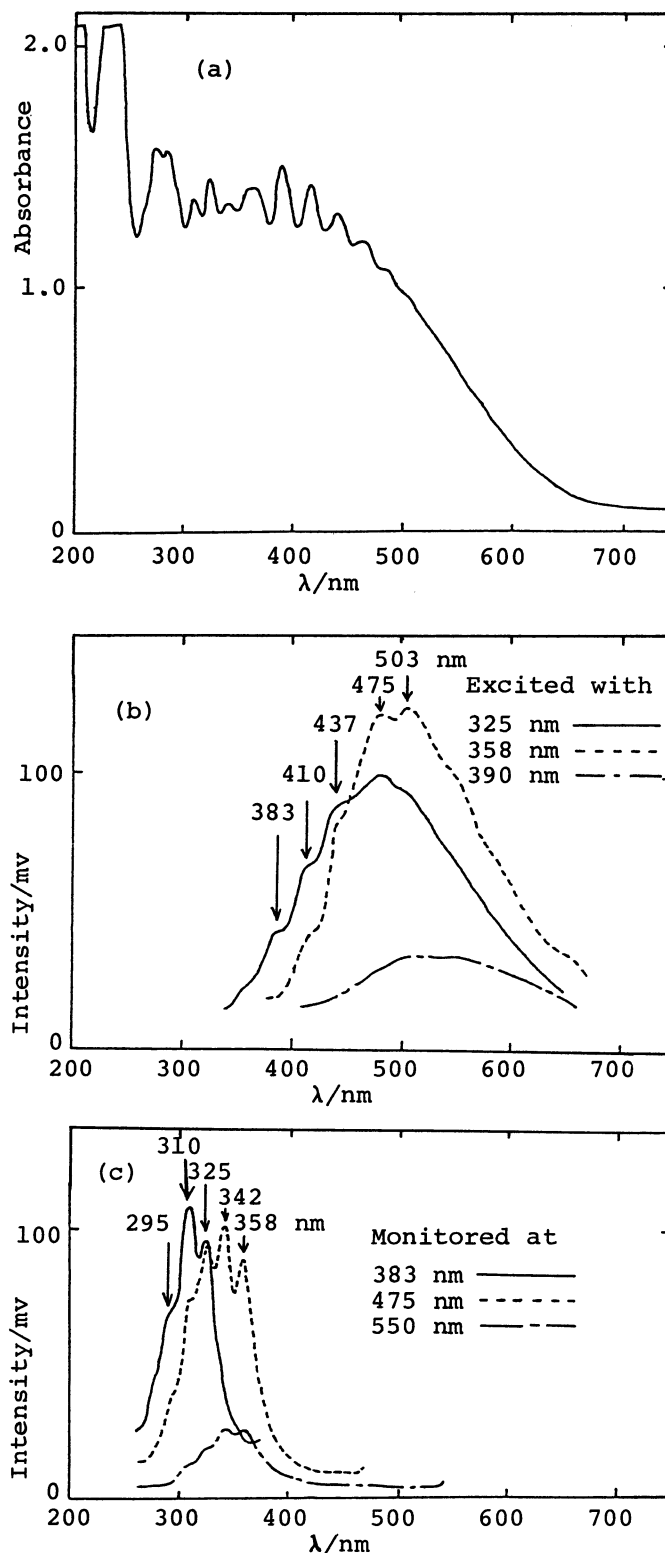


Fig. 2. Absorption(a), emission(b) and excitation(c) spectra of PVA film heated at 120 °C for 7 min, which was digested in 0.05 M HCl solution and dried before heating. Film thickness: 330 μm .

polyenes, respectively, and k is a constant. On the inspection of the Lewis-Calvin's plot, the 242 nm and the 285 nm peaks are the 0-0 transitions of diene and triene, respectively. By the prolongation of the straight lines all other peaks observed in Fig. 2(a) may be assigned. At any rate, by the procedure, it was suggested that some polyenes with n values larger than 13 are produced in the heated PVA substrate.

Incidentally, Popov et al.⁷⁾ have assigned the absorption peaks of the red-colored film; they picked up the 0-1 transitions by comparison with the absorption spectra of $\text{CH}_3(\text{CH}=\text{CH})_n\text{CH}_3$ ($n=3$ to 10 except 7). Though the present assignment concerning $n=2$ to 5 agrees with that of their result, it can be emphasized that the assignment becomes more reliable by combination with excitation spectra.

Another colored PVA film is obtained as a brown one when it is digested in the 0.05 M CH_3COONa solution instead of the HCl. The analysis could be carried out by means of the excitation spectra in the same way as above.

A report of the detailed analysis for the colored films under various conditions is in preparation.

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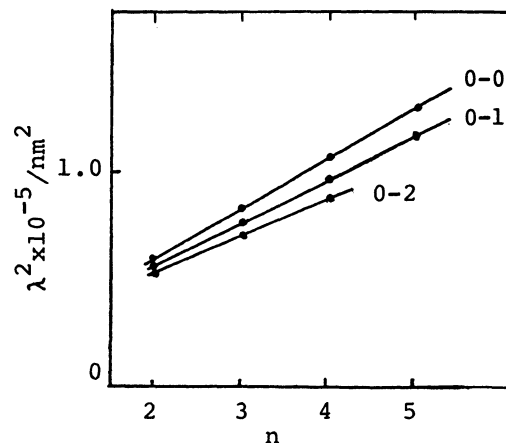


Fig. 3. Relationship of λ^2 vs. n for each classified peaks of $\text{R}(\text{CH}=\text{CH})_n\text{R}'$ observed in Fig. 1(a) and Fig. 2(c).