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Assignment of Conjugate Double Bond Systems Produced in Heated PVA Film by Absorption and Excitation Spectra

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Absorption, emission and excitation spectra of heat-treated PVA film have been interpreted as corresponding to mixtures of -(CH=CH)$_n$- and -(CH=CH)$_n$-CO-, which are distinguishable from each other according to whether spectrum is accompanied with fine structures or not. The former shows fine structures and has had n determined to be 2—14 by analysis of peak locations on the basis of linearity for Lewis-Calvin's plot. For the latter, n has been determined to be 1—7, and Lewis-Calvin's plot between the wavelength of band maximum and n also shows a good linearity.

There are a number of reports concerning electronic spectra of heat-treated poly(vinyl alcohol) [PVA].[1] A somewhat troublesome problem for the analysis of spectra is that thermally decomposed products of PVA are mixtures of many different polymers and that it is not possible to extract each component for analysis.

Absorption spectra of a heat-treated PVA film are very much influenced by heating temperature, heating time, and impurities contained. The coloration of PVA by heat is promoted by various compounds such as sulfuric acid, hydrochloric acid, phosphoric acid,[2] and sodium acetate.[3] Actually, commercial PVA powder, which contains about 0.5 wt% sodium acetate produced by alkaline saponification, will get colored easily by heating.

PVA is a polymer composed of a main chain of C–C bond with an OH group attached. Therefore, the final pyrolytic product should be graphite. In the initial stage of heating, however, we can focus our concern on products of two types of polyenes and polyenones. In fact, electronic spectra of PVA films which underwent various treatments including heating as in this study, were explainable merely in terms of formation of conjugate doulble bonds by dehydration and dehydrogenation, nor their spectral data gave any positive suggestion for severance of the main chain of polymer. Accordingly, all kinds of π electron systems to be formed along the framework of the chain must be restricted to the two types mentioned above. Fortunately, electronic spectra of the two types are distinguishable from each other according to whether spectrum is accompanied with fine structures or not. Furthermore, a judgement on the kinds of polyenes with fine structures can be made by analysis of peak locations and their intervals. On the other hand, the kinds of polyenones which show band spectra should be distinguishable on the basis of the correlation between the wavelength of band maximum and the number n of conjugate double bonds, because the difference of adjacent band maxima is equivalent to the difference between n and n+1, *i.e.*, -CH=CH-. Practically, the authors have presupposed tacitly the above considerations and have pointed out the existence of polyenes -(CH=CH)$_n$- and polyenones -(CH=CH)$_n$-CO- with n=2—5 and 2—3, respectively.[4]

In the present study as a continuation, the authors will analyze the correlation between absorption and the number of conjugate double bonds, assuming that fine structures are due to polyenes, whereas bands are due to polyenones (to be called polyene-carbonyl in this paper).

Experimental

PVA used was a commercial one (Koso Chemical Co., Ltd.), of which the average polymerization degree was 1400 and alkaline saponification was 99—100%. PVA poweder of 10—30 g was dissolved in distilled water of 200 cm^3 at 90 °C, and the solution was poured on a horizontal glass plate (30×30 cm). After it was dried at room temperature in 10 d, a PVA film about 100—300 μm thick was obtained. This film was kept for 2 h at 80 °C and put into use as the original film to be called PVA-1.

The PVA film was digested in a mixed solution of 0.1 M (1 M=1 mol dm^{-3}) $NaBH_4$ and 0.1 M NaOH for 1 d to reduce carbonyl group, and was washed with 0.05 M HCl solution and then with distilled water. In addition, it was digested in the following solutions separately and was dried at room temperature: the film digested in CH_3COONa solution is called PVA-2; in HCl solution, PVA-3; in H_2SO_4 solution, PVA-4; in H_3PO_4 solution, PVA-5.

Heat treatment of sample film was carried out with a sample being fixed on a metal holder in order to avoid wrinkling by heating. A sample film was set in a heating compartment and heated up to the desired temperature at a rate of 10 °C min^{-1} in a 0.5 dm^3 min^{-1} flow of nitrogen.

Absorption spectra were measured with a Shimadzu UV-360 spectrophotometer, and emission and excitation spectra with a Shimadzu RF-502 spectrophotometer. Fluorescence spectra were measured from the front side of film with an incident angle of 35° in the region 260—650 nm.

Results

PVA-1. The film of PVA-1 itself is colorless and its spectrum shown as Fig. 1(a)-1 has two weak absorption bands at 280 and 330 nm, which are already assigned to -(CH=H)$_2$-CO- and -(CH=CH)$_3$-CO-, respectively.[5] When the PVA-1 film is heated,

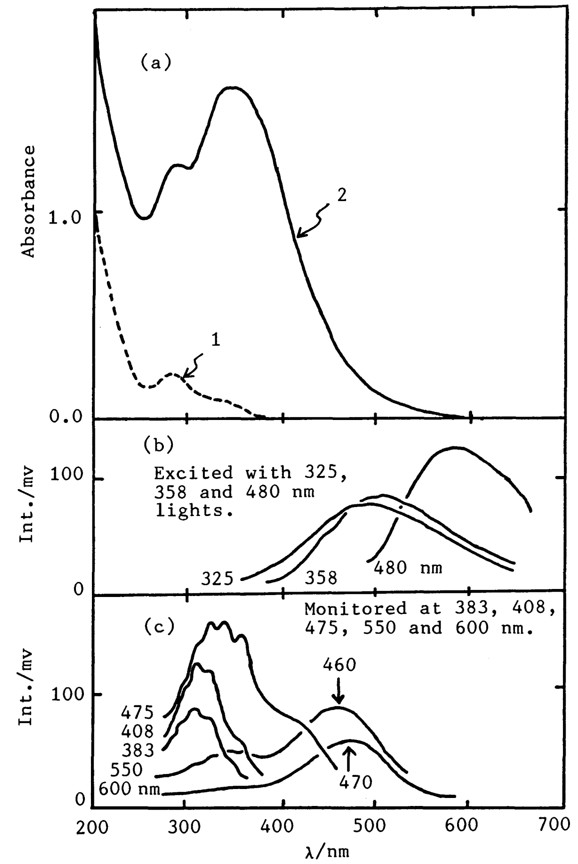

Fig. 1. Absorption (a), emission (b) and excitation spectra (c) of heat-treated PVA-1 film at 175 °C. Film thickness: 290 μm. (a)-1: Before heating, (a)-2: after heating.

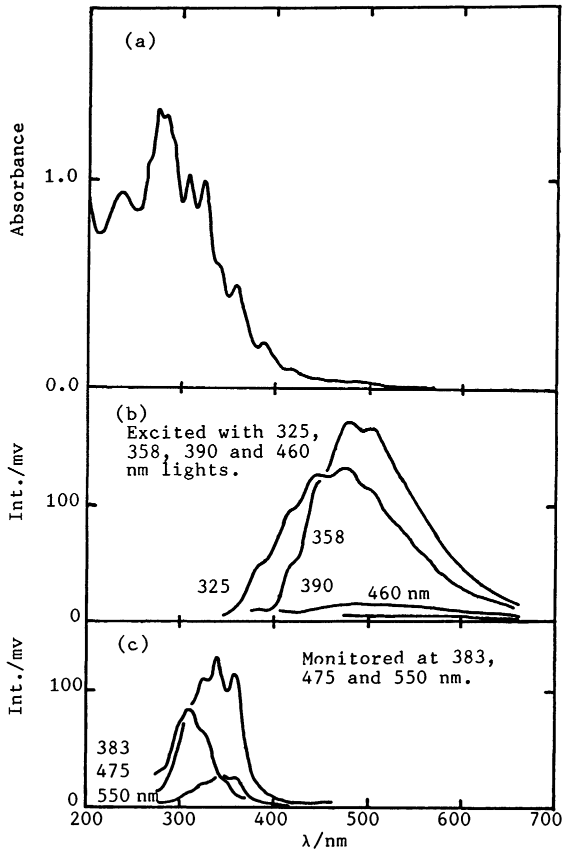

Fig. 2. Absorption (a), emission (b) and excitation spectra (c) after digestion of heated PVA-1 film (Fig. 1(a)-2) in 0.1 M NaOH–BaBH$_4$ mixed solution.

it becomes pale yellow and shows the spectrum of Fig. 1(a)-2 which has two strong bands at 280 and 340 nm. The spectral change from Fig. 1(a)-1 to (a)-2 is as follows: the 280 nm band grows without changing its maximum wavelength and the 330 nm band grows up to the 340 nm band. This indicates that the band maximum of triene-carbonyl is at 340 nm rather than at 330 nm.

Figures 1(b) and 1(c) show emission and excitation spectra for the absorption of Fig. 1(a)-2, respectively. For the emission spectra, it is noticed that the broad band at about 590 nm due to excitation by 480 nm light is most intense, in spite of the fact that the absorption intensity at 480 nm is weaker than those at the other excitation wavelengths. In the excitation spectra of Fig. 1(c), the peaks of the fine structures are at the same wavelengths as those of tetraene and pentaene assigned previously.[4] Therefore, the absorptions by these polyenes should be contained in the absorption spectrum of Fig. 1(a)-2, though any fine structures are not observable. In the excitation spectra, the other broad bands without fine structures appear at 460 and 470 nm. These bands changed their maximum wavelengths depending on monitor wavelengths, which indicates that respective bands consist of two overlapped bands.

The heat-treated PVA-1 film turned almost colorless in the aqueous solution of NaBH$_4$ in 1 d. Its absorption, emission, and excitation srectra are shown in Figs. 2(a), (b), and (c), respectively. By the treatment with NaBH$_4$, the 280 and 340 nm bands of Fig. 1(a)-2 are caused to disappear and instead a fine structure is caused to reveal itself as shown in Fig. 2(a). This change indicates that diene–carbonyl (280 nm band) and triene–carbonyl (340 nm) become diene and triene, respectively, as a result of reduction of the carbonyl group by NaBH$_4$, and that the other polyene–carbonyls (longer wavelengths) are reduced to the corresponding polyenes such as tetraene, pentaene, *etc.*

In the emission spectra of Fig. 2(b), any bands similar to the intense band at about 590 nm in Fig. 1(b) could not be observed. This may be due to too weak an absorption intensity (Fig. 2(a)) at the excitation wavelength (460 nm). In the excitation spectra of Fig. 2(c), such intense bands as shown at 460 nm in Fig. 1(c) are lacking completely for the monitor at 550 nm in spite of the sufficient intensity of emission (see Fig. 2(b)).

PVA-2. Figure 3(a)-1 shows the absorption spectrum for the purified PVA film called PVA-2.

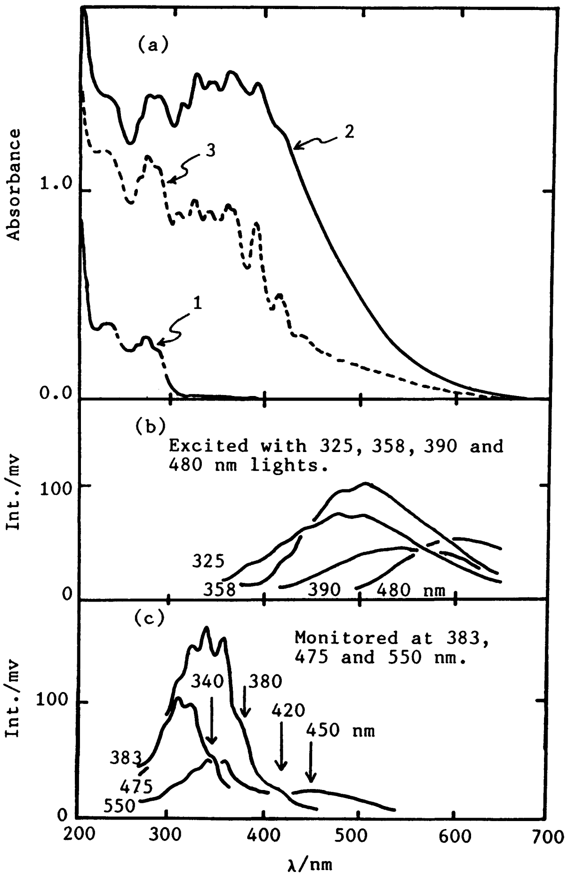

Fig. 3. Absorption (a), emission (b) and excitation spectra (c) of heated PVA-2 film at 175 °C. Film thickness: 290 μm. (a)-1: Before heating, this is doubled spectrum in absorption, (a)-2: after heating, (a)-3: after digestion of heated PVA-2 film ((a)-2) in 0.1 M NaOH–$NaBH_4$ mixed solution.

There are two bands with maxima at 234 and 273 nm, and in both sides of each band faint fine structures are recognized. The spectral change from Fig. 1(a)-1 to 3(a)-1 shows that by purification diene–carbonyl (280 nm) changes to diene (234 nm) and triene–carbonyl (340 nm) to triene (273 nm).

Figures 3(a)-2, (b), and (c) show, respectively, the absorption, emission and excitation spectra of a brown film of heated PVA-2. The wavelengths of the peaks and shoulders of the fine structure in Fig. 3(a)-2 coincide well with those of the corresponding peaks appearing in Fig. 2(a). The emission spectra of Fig. 3(b) and the excitation spectra of Fig. 3(c) are similar in character to those of Figs. 1(b) and (c), respectively: the broad emission band at about 590 nm due to the excitation at 480 nm, and the excitation bands at 420 (shoulder) and 450 nm by the monitor at 475 and 550 nm, respectively. All the wavelengths of the peaks of the fine structures of Fig. 3(c) coincide with those of some peaks in Figs. 1(c) and 2(c).

Figure 3(a)-3 shows the absorption spectrum for the case when the heated PVA-2 film was reduced by $NaBH_4$. The emission and excitation spectra, which are not inserted here, did not show any emission (590 nm) or excitation bands (420—470 nm) in the longer wavelength region, in common with the cases of Figs. 2(b) and (c).

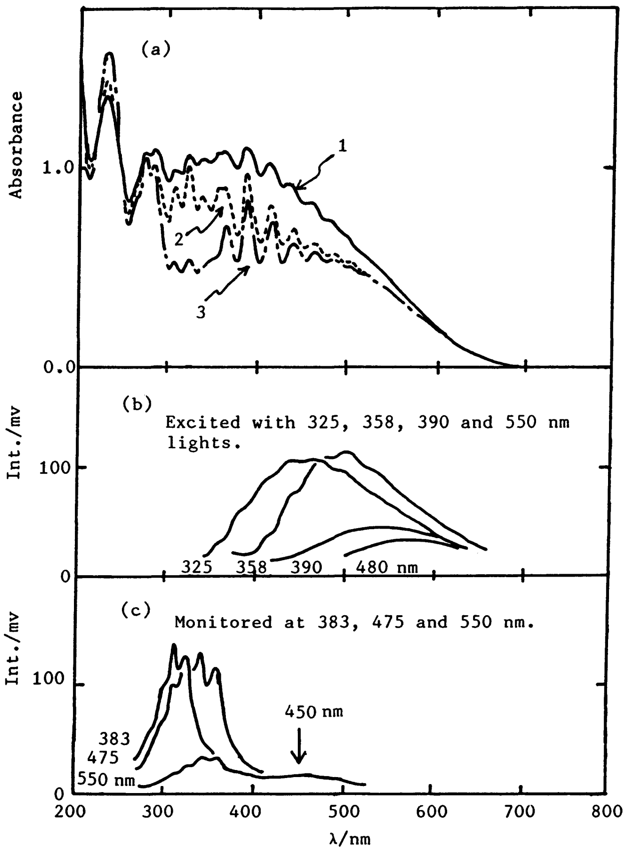

Fig. 4. Absorption (a), emission (b) and excitation spectra (c) of heated PVA-3 film at 120 °C. Film thickness: 120 μm. (a)-1: After heating, (a)-2 and (a)-3: after digestion of heated PVA-3 film ((a)-1) for 1 day and further 3 days, respectively, in 0.1 M NaOH–$NaBH_4$ mixed solution.

PVA-3 and PVA-4. When the films of PVA-3 and PVA-4 were heated, they got colored red. Both the red films showed similar absorption, emission, and excitation spectra. Therefore, only the case of PVA-3 is presented here in Fig. 4.

The emission and excitation spectra obtained for the absorption of Fig. 4(a)-1 are in Figs. 4(b) and (c), respectively, which resemble those of Figs. 3(b) and (c), respectively.

In the absorption spectra of Fig. 4(a), the fine structures continue over a longer wavelength region than those of the other samples. Figure 4(a)-1 shows the absorption spectrum of the heated PVA-3 film, and Figs. 4(a)-2 and -3 show the spectra after the treatment by $NaBH_4$, *i.e.*, 1 d digestion for the former and 3 d for the latter in 0.1 M NaOH–$NaBH_4$ mixed solution. By the 1 d digestion, the absorption intensity of Fig. 4(a)-1 is decreased in the range about 300—600 nm and the fine structure is sharpened (Fig. 4(a)-2). Further digestion causes the intensity to decrease further, especially for the peaks at 310 and 325 nm (to be assigned to tetraene) and at 342 and 358 nm (to pentaene) (Fig. 4(a)-3). On the other hand, the 234 nm band of diene increases during the digestion. The change from Fig. 4(a)-1 to (a)-3 by the $NaBH_4$ treatment indicates that the conversion of long polyenes to diene and momoene is effected by the reduction, and that tetraene and pentaene are especially easier to be reduced.

PVA-5. When the PVA-5 film was heated, it turned yellowish brown. The absorption spectrum of this colored film is similar to that of Fig. 3(a)-3. The excitation spectra, however, show only the peaks of tetraene and pentaene lacking the broad band, in spite of the condition of heating temperature being similar with the heated PVA-2 film (Fig. 3(c)).

Discussion

Assignment of Peaks of Fine Structures. *(a) Absorption Spectra*: In our experiment, the peak wavelengths of fine structures revealed in the spectra of the treated PVA films almost coincide with one another regardless of any sorts of treatments upon PVA films. The peak wavelengths range from 226 to 540 nm. Of the peaks, those in the region 226—358 nm have been assigned to the 0←0, 1←0, and 2←0 transitions of polyenes $-(CH=CH)_n-$ with n=2—5.[4] Moreover, the peaks for each transition have resulted in a linear relation with respect to Lewis-Calvin's plot,[6] *i.e.*, the relationship between λ^2 (λ is peak wavelength) and n.[4]

In Fig. 5, λ^2 of the rest peaks over n=5 are plotted in white circles on the extended 0←0 line for n=2—5, except the solid circle at n=6 which is assigned to 1←0 (366 nm). The white circles fall on a line broken at the position n=9. However, if we shift horizontally the white circles by a unit of n to the right, the respective circles will fall into the extended straight line of the 1←0 transition as shown by the solid circles.

Sondheimer *et al.*[7] have plotted the relationship between λ^2 and n for the free polyenes $H-(CH=CH)_n-H$ (n=3—8 and 10). According to their plot, a linear relation is obtained while n is small, but the points for n=8 and 10 turn downwards off the line. As is likewise presupposed from the absorption spectra of polyacetylenes,[8] the value of λ^2 shows a tendency to approach a certain value as n increases. It is a matter of common knowledge that λ^2 of conjugate systems in the same series approaches a certain value for larger numbers of n, but the limits of n for which λ^2 changes linearly are not always definite.

As shown in Fig. 5, if all the peaks (white circles) are assigned to the 0←0 transitions, the limits of straight line would become equal to n=9, and if assigned to the 1←0 transitions, even the point for n=14 would be put on a straight line. Though it cannot definitely be answered which is true, the latter assignment may be considered to be right for the following reason.

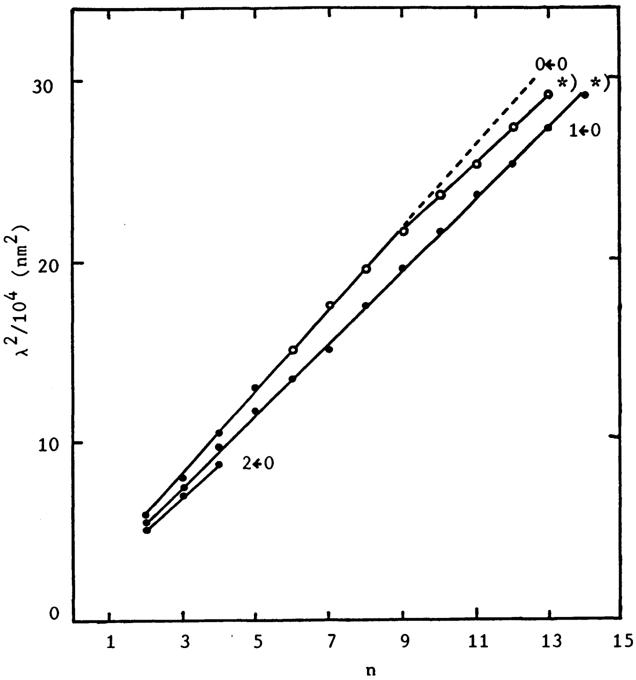

Fig. 5 Relationship of λ^2 *vs.* n for polyenes in heated PVA films. *) (539 nm) to be observed only when PVA film is uni-axially stretched before heating.

Table 1. Assignment of absorption peaks of $-(CH=CH)_n-$ produced in heated PVA film

n	Wavelength/nm		
	0←0	1←0	2←0
2	242	234	226
3	285	273	262
4	325	310	295
5	358	342	
6		366	
7		390	
8		418	
9		442	
10		465	
11		486	
12		503	
13		523	
14		540[a]	

a) Observed when PVA film is uni-axially stretched before heating.

In the present experiment, a mixture of π electron systems of the polyene type is observed. In such mixtures, peaks of a system of conjugation number n may be influenced by the overlapping effect in the $n+1$ system, in such a way that the 0←0 peak is influenced more than the 1←0 and 2←0 peaks. At the same time, the 2←0 peak may be overlapped by the 0←0 peak of the $n-1$ system. And moreover, the intensity of the 2←0 peak is generally weaker than those of the 0←0 and 1←0 peaks. For this reason, the 1←0 peak is very liable

Table 2. Assignment of absorption and excitation bands of polyene-carbonyls $-(CH=CH)_n-CO-$ produced in heated PVA films

Assigned *n* and wavelength		Observed wavelength/nm				
n	nm	Fig.1(a)	Fig.1(c)	Fig.2(c)	Fig.3(c)	Fig.4(c)
2	280	280				
3	340	340	340[a)]	350[a)]	340[a)]	
4	380			380[a)]	380[a)]	
5	420		420[a)]		420[a)]	
6	450		460		450	450
7	480		470			

a) Shoulder.

to be observed because of its least influence from other systems.

In Fig. 5, the linearity of the plot of 1←0 peaks is of remarkably long-range. At the present stage, we cannot explain the reason for the long-range linearity. However, a fact that the observed π electron system is formed locally within a very long C–C bond chain, may make a cause of the fact that the linear region extends to larger *n*'s than in the case of free molecule.

Based on the above considerations, let us assume that all the observed peaks over $n=5$ are assigned to the 1←0 transitions, and we may obtain the assignment given in Table 1.

(b) Excitation Srectra: The absorption spectra of the heated PVA films shown in Figs. 1—4 are considerably different from one another, but in their excitation spectra only the fine structures of tetraene and pentaene are commonly observed and none of the other polyenes. The reason why any fine structures for *n* larger than 5 (pentaene) could not be observed, may be that the produced amount of polyenes is too small to be detected. We thus heated enough PVA-3 film till it turned deep reddish black. Nevertheless, its excitation spectra did show only the peaks of tetraene and pentaene, and again no peaks of the other polyenes. This result indicates that the fluorescence efficiency of the other polyenes is very small. In fact, D'Amico *et al.*[9] have shown that the efficiency is markedly decreased in going from tetraene to hexaene molecule. They have estimated that the fluorescence quantum yield of hexaene molecule is at most 1/50 that of tetraene, and predicted that longer conjugate polyene molecules show no fluorescence. Hence, our result supports their prediction positively.

Assignment of Absorption Bands of Polyene-Carbonyls. Let us regard the absorption bands without fine structures as those of the polyene-carbonyls of the type $-(CH=CH)_n-CO-$, types of $-(CH=CH)_n-CO-(CH=CH)_m-$ and others being neglected because the chance of their formation is considered to be small. All such bands and shoulders observed here are collected in the column headed "Observed wavelength" of Table 2.

The 280 and 340 nm bands in Table 2 (the column headed "Fig. 1(a)") have already been assigned to diene-carbonyl ($n=2$) and triene-carbonyl ($n=3$), respectively.[5] Since the minimum difference with $-(CH=CH)_n-CO-$ is one double bond $-CH=CH-$, the change in wavelength of the band maxima for successive *n*'s ought to be step-like. In the case of polyenes $-(CH=CH)_n-$ (Table 1), for instance, the peak-intervals in the same kind of transitions are about 30—40 nm for the smaller *n*'s. With this taken into consideration, with Table 2, it is reasonabe to assign the 380 and 420 nm shoulders to $n=4$ and 5 of $-(CH=CH)_n-CO-$, respectively.

As pointed out in the "Results" section, either of the 460 and 470 nm bands in Table 2 (the column headed "Fig. 1(c)") consist of two subbands. By supposing the main component of the 460 nm band is identical with the 450 nm band of the columns headed "Fig. 3(c)" and "Fig. 4(c)" in Table 2, the shift by overlapped band is estimated to be 10 nm. Therefore, if the 10 nm shift by overlapped band (train of 450 nm band) is expected for the 470 nm band, the wavelength of the main band can be estimated to be 480 nm.

According to the above consideration, the bands and shoulders regarded as the absorptions of polyene-carbonyls are all assigned as shown in the first and second columns of Table 2.

In the above we have found that the 1←0 peaks of polyenes furnish a linearity of Lewis-Calvin's plot in a wide range of *n*. Since the polyene-carbonyls assigned in Table 2 have the structure in which a C=O bond is joined to polyene at the terminal, the shift of the band maximum for successive *n*'s of $-(CH=CH)_n-CO-$ is dependent upon the increase in number of $-CH=CH-$ bonds. Therefore, a linearity of Lewis-Calvin's plot is also expected for the band maxima of polyene-carbonyls. The plot is shown by solid circles in Fig. 6, which meets our expectation. The white circles in Fig. 6 are of the same plot for $CH_3-(CH=CH)_n-CHO$, for which are used the band maxima reported by Blout and Fields.[10] Evidently, the Lewis-Calvin's plot is curved for the case of free molecule. The difference (Fig. 6) between $-(CH=CH)_n-CO-$ and $CH_3-(CH=CH)_n-CHO$ may be due to the same sequence as the case between $-(CH=CH)_n-$ (Fig. 5) and the corresponding free molecule.

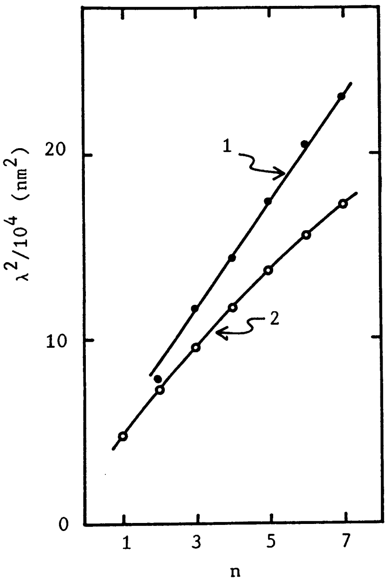

Fig. 6. Relationship of λ^2 *vs*. *n* for polyene-carbonyls in the heated PVA films. 1: This study, 2: cited from Ref. 10.

Das and Becker[11] have reported that the polyene-aldehydes CH_3-$(CH=CH)_n$-CHO of n=2—5 do not show fluorescence at room temperature but emit weak or moderately strong fluorescence at 77 K. In connection with their study, we point out that the solid PVA substrate film has a nature characterestic of a glassy solvent, though well known empirically. This is because, in our experiment, the fluoresence from polyene-carbonyls of n=3—7 could be detected, even at room temperature.

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