Infrared Studies of Polyvinyl Alcohol by Deuteration of its OH Groups

By Hiroyuki TADOKORO

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In the previous paper[1] we have studied the density, the sorption of water vapor, and the infrared absorption spectrum of polyvinyl alcohol (PVA) films subjected to heat-treatments at different temperatures from the point of view of crystallinity, and have concluded as follows: (1) the degree of crystallinity determined by these methods is parallel unless the thermal decomposition is considerable, and (2) the 1141 cm^{-1} (8.76 μ)* band is a so-called "crystallization-sensitive" band[2-4]. Succeeding the previous work, we have carried out further studies on PVA by means of infrared spectrum, X-ray diffraction and density measurements in the hope of making some contribution to the studies of the crystallinity and fine texture[3] of high polymers.

The purpose of the present paper is to report some new information obtained by the results of deuteration of the OH groups of PVA.

We have made the infrared spectroscopic measurements of the deuterated PVA for the following purposes. The first is for the elucidation of the nature of the crystallization-sensitive band at 1141 cm^{-1}. As to the crystallization-sensitive band, a considerable number of reports have been published during these several years on polyethylene and many other polymers. Although some reasonable interpretations on the absorption mechanism of the crystallization-sensitive bands have been proposed in the cases of polyethylene, there is no conclusive one for the 1141 cm^{-1} band of PVA. The second purpose is for the assignments of the absorption bands in the region of 1500~800 cm^{-1}. There are already many publications on this problem[5-8], but it is not yet settled at all. The third is to test whether we can determine the crystallinity (or accessibilty) of PVA by means of the deuterium exchange method or not. In the case of cellulose, for instance, it is well known that the velocity of deuterium exchange reaction of the hydroxyl group in the amorphous region is much faster than it is in the crystalline region[9-11]. The fourth is to examine the fine structure of the OH stretching bands of the spectrum arising from the crystalline region, if the amorphous region is to be exclusively deuterated. Marrinan and Mann[11] have investigated the fine structure of the OH bands of various kinds of cellulose by the use of this method.

As to the infrared absorption spectrum of deuterated PVA, Ukita, Nishino and Kominami[12] and also Krimm, Liang and Sutherland[8] have reported quite independently. Ukita and his coworkers have recognized no appreciable change of the spectrum, except the new appearance of the broad band at 4.01 μ due to the OD stretching vibration, because of the low degree of deuteration in their case. Krimm and his coworkers have measured the spectrum of PVA-*d* (degree of deuteration: about 90%) in the region of 3600~400 cm^{-1}, and have obtained experimental results similar to ours. As the assignments of the absorption bands of polymers are generally very complicated problems, we have carried out other experiments such

1) H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **28**, 559 (1955).

* Although the value 1146 cm^{-1} (8.74μ) was used in the previous paper[1], 1141 cm^{-1} seems to be more precise according to the subsequent more accurate measurements.

2) J. B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954).

3) I. Nitta and H. Tadokoro, *High Polymer* (*Kobunshi*), **5**, 296, 345 (1956). (A review of the crystallinity of high polymers).

4) H. Tadokoro, *J. Chem. Soc. Japan, Ind. Chem. Soc.* (*Kogyo Kagaku Zasshi*), **59**, 731 (1956). (A review of the application of the infrared spectroscopy for the study of the structure of high polymers).

5) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

6) E. R. Blout and R. Karplus, *J. Am. Chem. Soc.*, **70**, 862 (1948).

7) A. Elliott, E. J. Ambrose and R. B. Temple, *J. Chem. Phys.*, **16**, 877 (1948).

8) S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Polymer Sci.*, **22**, 227 (1956).

9) V. J. Frilette, J. Hanle and H. Mark, *J. Am. Chem. Soc.*, **70**, 1107 (1948).

10) K. E. Almin, *Svensk Paperstidn.* **55**, 767 (1952).

11) H. J. Marrinan and J. Mann, *J. Appl. Chem.*, **4**, 204 (1954); *Trans. Faraday Soc.*, **52**, 481, 487, 492 (1956); *J. Polymer Sci.*, **21**, 301 (1956).

12) J. Ukita, Y. Nishino and T. Kominami, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 158 (1955).

TABLE I. SAMPLES

Samples	Conditions of heat-treatment	Density at 25°C (g./cc.)	Crystallinity (density method)
I	No heat-treatment	1.291_0	0.29
III	160°C, 15 min.	1.300_7	0.42

as infrared spectroscopic measurements of oriented PVA-*d* and of doubly oriented PVA[13,14], density measurements[15], etc., to get some useful data for this purpose.

Experimental

a) Polyvinyl Alcohol Samples.—Film specimens were prepared from the same starting material (PVA of average degree of polymerization: 1650) by the same method as that described already in the previous papers[1,16]. (See Table I). In the present work the films were cast on a polystyrene plate instead of a glass plate, because the most suitable thickness of the film for infrared measurements is about 7~10 μ, and it is difficult to strip off such a thin film from a glass plate.

The oriented film was prepared by stretching it by hand in one direction over a small flame until it could be stretched no more. Examination of the film between crossed polaroid sheets confirmed the orientation in the direction of stretching.

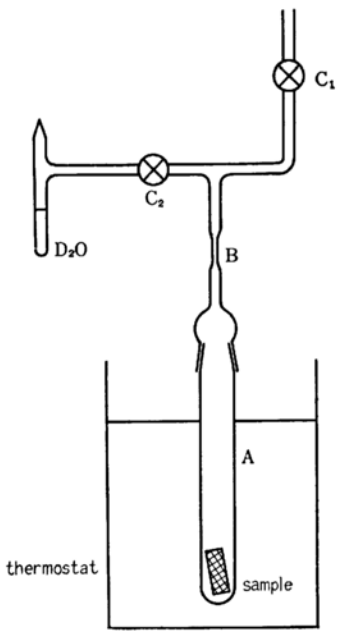

Fig. 1. Apparatus for deuteration.

b) Deuteration, Formalization and Infrared Measurements.—The deuteration of PVA was carried out by using 99.7% heavy water** in a vessel shown in Fig. 1. A PVA film (ca. 20 mm. ×30 mm.) put between the parts of folded stainless steel wire gauze (350 mesh), was inserted in a glass tube A, and was dried at 60°C for about 48 hr. under high vacuum (10^{-4} mmHg or below) by using a liquid air trap (stopcock C_1 being open, and C_2 being closed). After the drying was over, C_1 was closed, the temperature was lowered to room temperature, and then by opening C_2, the sample was equilibrated to the saturated vapor pressure of heavy water. After "being allowed to stand" for about 24 hr., the sample was dried again, and such procedures were repeated several times. At last the glass tube was sealed off at B. The measurements were carried out by putting the films between rock salt plates, with or without polychlorotrifluorocarbon oil (Difloil #3, kindly supplied by Osaka Kinzoku Kôgyô Co., Ltd.).

The oriented and deuterated PVA film for the measurement of dichroism could be prepared by successive procedures in a series of stretching, heat-treatment and deuteration.

Samples I and III were also subjected to formalization and then to deuteration. The formalization was carried out in an aqueous solution of sulfuric acid (200 g./l.), sodium sulfate (250 g./l.) and formaldehyde (40 g./l.) at about 50°C for 15 min. and 2 hr. for each sample. During the formalization treatment the film was held between the parts of a folded wire gauze of bronze (300 mesh) to be free from deformation.

Infrared absorption spectra were taken by using a Hilger H800 Recording Infrared Spectrophotometer with sodium chloride prism, and a Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer with sodium chloride prism and silver chloride polarizer.

Results and Discussion

a) Deuteration.—The obtained spectra of PVA and of deuterated PVA are shown in Fig. 2a and Table II. The possible errors of the wave number are $\pm 10\,cm^{-1}$ and $\pm 5\,cm^{-1}$ in the regions of $4000 \sim 2000\,cm^{-1}$ and $2000 \sim 700\,cm^{-1}$, respectively. Thus, our spectral data shown in Fig. 2 and Table II are in substantial agreement with those obtained by Krimm et al.[8]

It is well known that OH or NH groups are easily converted into OD or ND by exchange reaction with heavy water, but CH groups are not converted easily unless

13) H. Tadokoro, S. Seki and I. Nitta, *J. Polymer Sci.*, **22**, 563 (1956).
14) H. Tadokoro, S. Seki, I. Nitta and R. Yamadera, ibid., **28**, 244 (1958).
15) H. Tadokoro, K. Kôzai, S. Seki and I. Nitta, ibid., **26**, 379 (1957).
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16) H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **27**, 451 (1954).
17) Y. Nishino, J. Ukita and T. Kominami, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 159 (1955).
18) E. Nagai and S. Kuribayashi, *Chem. High Polymers* (*Kobunshi Kagaku*), **12**, 322, 368 (1955).
19) L. Glatt, D. S. Webber, C. Seaman and J. W. Ellis, *J. Chem., Phys.*, **18**, 413 (1950).

TABLE II. INFRARED SPECTRA AND VIBRATIONAL ASSIGNMENTS OF PVA AND PVA-*d*

PVA			PVA-*d*			Assignments[e]	
Frequency in cm^{-1}	Dichroism	Intensity	Frequency in cm^{-1}	Dichroism	Intensity	Previous work	This work
3340[a]		vs				ν(OH)	ν(OH)
2945	⊥	s	2945	⊥	s	ν_a(CH_2) (T, E, B, K)[d]	ν_a(CH_2)
2910	⊥	s	2910	⊥	s	ν_s(CH_2)	ν_s(CH_2)
2840	⊥	sh	2840	⊥	sh	ν(CH) (K)	
			2470[a]		vs	ν(OD)	ν(OD)
1440[b]	∥	s	1428	⊥	m	δ(CH_2) (T, B); δ(OH) or superposition of δ(OH) and δ(CH_2) (E); δ(CH+OH), 1428 cm^{-1} is δ(CH_2) (K)	superposition of δ(CH_2) and a coupling band (coupling of δ(OH) and 1383 cm^{-1} band of PVA-*d*). 1428 cm^{-1} band of PVA-*d* is δ(CH_2)
1420[b]	⊥	s					
			1383	∥	s		w(CH) or w(CH_2)
1376	⊥	w	1376	⊥?	m	δ(CH_3-C) (B); w(CH_2) (K)	δ(CH)?
			1360	⊥	sh		
1326[c] 1315	⊥	m				hydrogen deformation (E); δ(CH+OH) (K)	coupling of δ(OH) and 1383 cm^{-1} band of PVA-*d*
			1256	⊥?	sh		
1232	∥	w	1230	∥	m	acetyl group (T, E) not to be acetyl group (B) w(CH) (K)	w(CH_2) or w(CH)
1141	⊥	m	1148	⊥	s	associated with hydrogen-bond (Ni, Na) ν(C-O-C) (K) associated with oxygen-atom (E)	crystallization-sensitive band (see subsequent paper)
			1122	⊥	s		
1093	⊥	s				associated with oxygen-atom (T) ν(C-O) (B, E, K)	ν(C-O)
1083	∥	m	1083	∥	m		
			1049	⊥	s		ν(C-O)
			977	⊥	m		δ(O-D)
			930	⊥	sh		
913	⊥	w				r(CH_2) (K)	skeletal or CH_2
890	⊥	vw					
849	⊥	m				ν(C-C) (K)	
			842	⊥	m		skeletal or CH_2
835	⊥	sh	825	⊥	sh		r(CH_2)
640[f]	∥	sh				w(OH) (K)	
610	⊥	m					
480	⊥	w				δ(C-O) (K)	
410	?	w				w(C-O) (K)	
360	⊥	w					

a) The ν(OH) band at about 3340 cm^{-1} shows no appreciable dichroism at the band maximum, but perpendicular and parallel nature at the higher frequency and lower frequency side, respectively, agreeing with the descriptions of Glatt et al.[19] and Krimm et al.[8] The ν(OD) band at about 2470 cm^{-1} was also found to show the same behavior.

b) The band at about 1430 cm^{-1} splits to 1440 and 1420 cm^{-1} in the polarized spectra because of the difference of their dichroism.

c) The band at about 1325 cm^{-1} has its absorption maximum at 1326 and 1315 cm^{-1} in the case of perpendicular and parallel radiation, respectively.

d) T: Thompson and Torkington[5], E: Elliott, Ambrose and Temple[7], B: Blout and Karplus[6], K: Krimm, Liang and Sutherland[8], Ni: Nishino, Ukita and Kominami[17], Na: Nagai and Kuribayashi[18].

e) ν: stretching, ν_a: antisymmetric stretching, ν_s: symmetric stretching, δ: bending, w: wagging, r: rocking.

f) The data in the region lower than 640 cm^{-1} was reproduced from the paper by Krimm et al.[8]

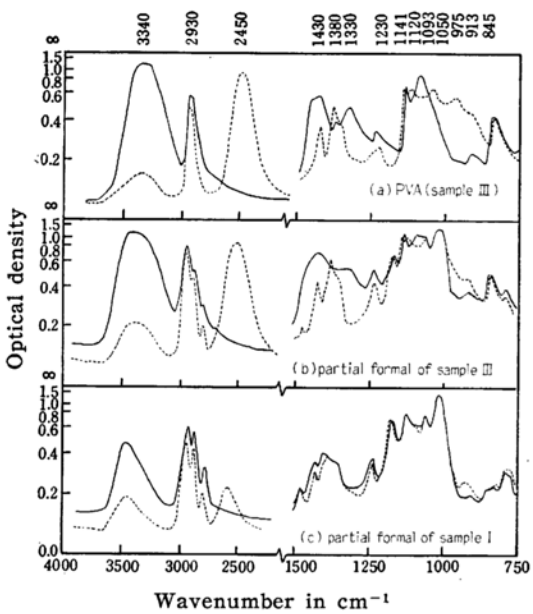

Fig. 2. Infrared spectra of (a) PVA, (b) partial formal of sample III and (c) that of sample I and their deuterated samples (broken line).

under some special conditions[20]. Thus, when PVA is brought into contact with heavy water, the following reaction will take place and the change of the structure will be detected in the infrared spectrum of the sample.

$$-(-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-)_{\bar{p}} \xrightarrow{D_2O} -(-CH_2-\underset{\displaystyle OD}{\underset{|}{CH}}-)_{\bar{p}}$$

As a result of the deuteration, the intensity of the ν(O–H) band at 3340 cm^{-1} decreases and at the same time a new intense band appears at 2450 cm^{-1}. This latter band evidently corresponds to the ν(O–D) band. While the ν(C–H) band at 2940 cm^{-1} is not affected appreciably by deuteration, this band could be used as the standard for the intensity measurements. The diminution of the optical density of the ν(O–H) band referred to this C–H band, may be used as a measure of degree of deuteration. The extent of deuteration of the sample shown in Fig. 2a is found to be about 90% by this method of estimation.

Now, the deuterations for samples I and III of Table I were studied under various conditions. When the procedures of drying and of exposure to heavy water vapor were repeated alternately several times, both the samples were deuterated up to about 90% regardless of the degree of crystallinity. On the contrary, the extent of deuteration of nylon 6 which had undergone the same procedure as the PVA sample, was much lower than that of PVA. Moreover, the lower the degree of crystallinity of the sample of nylon 6 is, the higher is the extent of deuteration as is shown in Fig. 3. The same results have been reported on the celluloses as mentioned above[9-11].

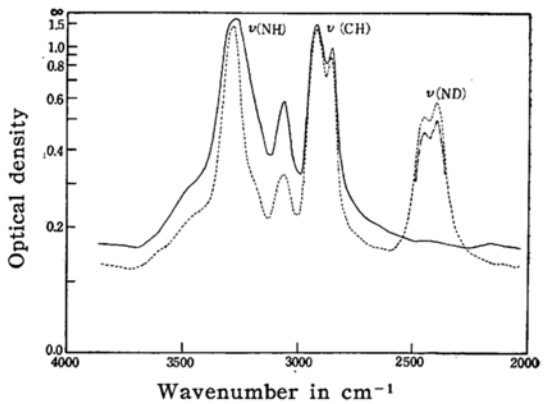

Fig. 3. Infrared spectra of nylon 6 (——) and deuterated nylon 6 (------): ——— sample subjected to heat-treatment.

In relation to these evidences, it will be quite interesting to examine whether the crystalline region of PVA, which is considered to be inaccessible to formalization[21,22], could be deuterated or not. The solid lines of Figs. 2b and 2c show the infrared spectra of samples I and III subjected to formalization. For sample I, the remarkable decrease of the intensity of the OH stretching band at 3340 cm^{-1} and its shift to the shorter wavelength side on formalization may indicate the high degree of formalization. However, for sample III the intensity of the OH stretching band decreases only to a slight extent. This result reconfirmed the fact that the crystalline region is not formalized appreciably as was reported previously by some authors[21,22]. The spectra of these partial formals after deuteration were also shown in the same figure with broken lines. This result indicates that the residual OH groups of the formal of sample III were

20) For example, M. Koizumi, Organic Deuterocompounds, "Advances in Organic Chemistry (Yûkikagaku no Shimpo)" Vol. II. Edited by M. Kotake and S. Akabori, Kyôritsu Shuppan Co. Ltd., Tokyo (1939), p. 27.

21) K. Hirabayashi and N. Fujimoto, *Chem. High Polymers* (*Kobunshi Kagaku*), 7, 159 (1950).

22) Y. Yoshioka and M. Nagano, ibid., 9, 36 (1952).

deuterated up to about 84%. Thus, the crystalline region of sample III, which was not accessible to formalization, was found to be highly deuterated. These facts seem to show that the difference between the velocity of deuterium exchange in the crystalline region and that in the amorphous region, is considerable in the cases of nylon 6 and cellulose, while this difference is negligibly small in PVA. In this respect, the mechanism of the deuteration reaction of the crystalline region of PVA seems to be a very interesting problem.

b) Interpretation of the Spectra. — The infrared dichroism of the deuterated PVA is shown in Fig. 4, together with that of ordinary PVA for the purpose of comparison. This sample could be prepared by the successive procedures of stretching, heat-treatment and finally deuteration. This method of preparation is based upon the aforementioned remarkable fact that the crystalline region of PVA film even after subjected to heat-treatment can be easily deuterated by exposing it to D_2O vapor.

Although we can not make conclusive assignments of the absorption bands in the region of 1500~700 cm^{-1} at present, we may give here our tentative assignments on the main bands in this region. The band at about 1430 cm^{-1} was assigned by Thompson and Torkington[5] and also by Blout and Karplus[6] to a deformation mode of CH_2 group. On the other hand, Elliott, Ambrose and Temple[7] considered this band to be the δ(O–H), or to be the superposition of the δ(O–H) and the $\delta(CH_2)$ modes. However, this band should be a superposition of the CH_2 bending and some other band connected with hydroxyl group, or probably the O–H deformation, since the intensity of this band decreases sensitively on deuteration and there remains a sharp band which is certainly attributed to the CH_2 bending mode, because of its perpendicular nature. The perpendicular band at 1325 cm^{-1} should also be related to the hydroxyl group because of the intensity decrease on deuteration, whereas Elliott and his coworkers[7] merely referred this band to a hydrogen deformation mode. Just at the middle of the above-mentioned two bands, i. e., at 1380 cm^{-1}, a new intense and sharp band appears on deuteration. We have already suggested[23] that this fact is well interpreted by assuming that these two bands (1430 and 1325 cm^{-1}) are associated with the coupling of the δ(OH) and some other mode such as the CH deformation, and the coupling is removed on deuteration. Krimm and his coworkers[8] independently made a more or less similar interpretation on the results of deuterated PVA (no orientation), and concluded that these two bands come from the interaction between the δ(OH) and δ(CH) modes. However, we have found from the dichroic data with the oriented PVA-*d* that the new band at 1383 cm^{-1} has the nature of distinguished parallel dichroism, and there appear also two perpendicular bands at 1376 and 1361 cm^{-1}, superposed with the 1383 cm^{-1} band. Thus Krimm and his coworkers' assignment of the 1383 cm^{-1} band to δ(CH) can not explain the parallel dichroism of this band. The problem of the assignments of the bands in this region is very complex, but our suggestion in the previous paper[21] does not contradict the present experimental results***.

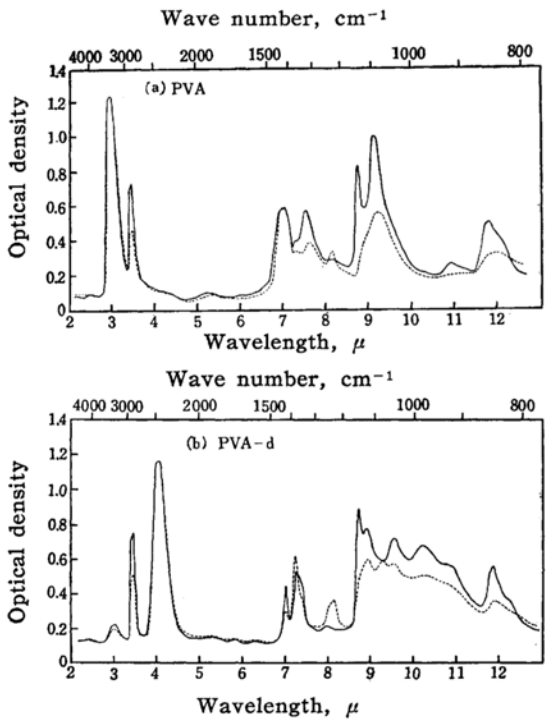

Fig. 4. Infrared dichroism of (a) PVA and (b) PVA-*d* (degree of deuteration ca. 92%): —— electric vector perpendicular to elongation: ------ electric vector parallel to elongation.

23) H. Tadokoro, S. Seki and I. Nitta, *J. Chem. Phys.*, **23**, 1351 (1955).

*** Possibile assignments will be that the 1383 cm^{-1} band is the w(CH) or the $w(CH_2)$[24], and 1376 cm^{-1} band the δ(CH).

24) I. Nakagawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 540 (1955).

The parallel band at 1230 cm^{-1} was reported to be associated with the residual acetyl group by Thompson et al.[5] and Elliott et al.[7] But later this assignment was shown to be inadequate by Blout and Karplus[6] from the experimental fact that this band is not removed by acid hydrolysis, although the 1256 cm^{-1} band in unpurified samples is removed simultaneously with the 1710 cm^{-1} band. From the facts that this band is not affected by deuteration and that it becomes intense on formalization with preserving the parallel dichroic nature, this band may be supposed to be $w(CH_2)$, although Krimm and his coworkers' assignment[8] to $w(CH)$ is also undeniable.

The 1148 cm^{-1} band of PVA-*d* is supposed to correspond to the 1141 cm^{-1} band of PVA, because of the distinct perpendicular dichroism. As to the assignment of this band, various interpretations have been proposed, and this seems to be one of the most interesting problems in the infrared studies of this substance. Detailed discussions of this band will be reported in subsequent paper.

The 1093 cm^{-1} band may be mainly associated to the ν(C–O) mode from its location, perpendicular dichroism and the reasonable wave number shift by deuteration, in accordance with the interpretations of Blout et al.[6], Elliott et al.[7], and Krimm et al.[8] The parallel band at 1083 cm^{-1}, superposing the 1093 cm^{-1} band, seems not to be affected by deuteration. On deuteration the 1093 cm^{-1} band disappears and three perpendicular bands appear at 1122, 1049 and 977 cm^{-1}. Of these three bands, the 1049 cm^{-1} band may be assigned to the ν(C–O), and 977 cm^{-1} band to the δ(O–D) tentatively from the consideration of the wave number ratios of the shifts on deuteration.

The perpendicular bands at 913 and 845 cm^{-1} are considered not to be directly associated with the OH group, because of the negligibly small effect of deuteration.

Finally, we wish to refer to the results of our infrared microspectroscopic measurement on the highly doubly oriented PVA sample[14]. In this experiment the measurements were made so that the direction of the polarized infrared beam was parallel to the direction of rolling (the same as that of the carbon zigzag chain). The spectra obtained in this experiment were partly reproduced in Fig. 5. The solid line represents the spectrum with the electric vector parallel to the rolled plane (i.e., the plane of the carbon zigzag chain), and the broken line that with the electric vector perpendicular to the rolled plane. It was found that the 913 and 845 cm^{-1} bands have weak pleochroism, and the latter is a superposition of two bands. The direction of the transition moment of the $r(CH_2)$ mode is perpendicular to the plane of the carbon zigzag chain. The 835 cm^{-1} band, the transition moment of which is in this direction as is evident from the curves in Fig. 5, may be considered as assigned to this mode. The assignment of the 913 cm^{-1} band to $r(CH_2)$ by Krimm et al.[8] is not consistent with our experimental result that the transition moment of this band is parallel to the plane of the carbon zigzag chain.

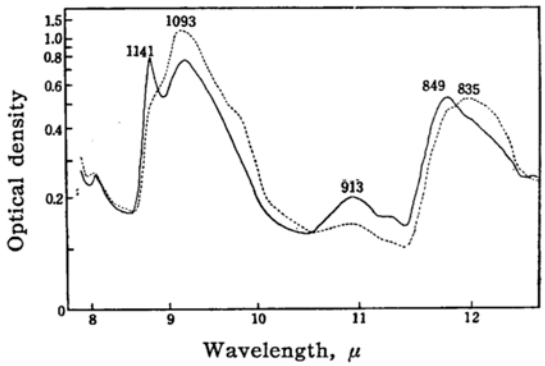

Fig. 5. Infrared spectra of highly doubly oriented PVA specimen[14]. The direction of the infrared beam is parallel to that of rolling.
—— electric vector ∥ rolled plane.
------ electric vector ⊥ rolled plane.

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Department of Polymer Science
Faculty of Science
Osaka University
Nakanoshima, Osaka