Syntheses and Infrared Absorption Spectra of Deuterated Polyvinyl Alcohols $-(-CD_2-CD-)_n-$[*1]
$$\overset{|}{OH(D)}$$

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We have previously reported[1] that the 1141 cm^{-1} band in the infrared absorption spectra of polyvinyl alcohol (PVA) increases the intensity sensitively with crystallization (heat-treatments), and the optical density of this band is approximately in linear relationship with the degree of crystallinity determined by the methods of density and of the sorption of water vapor. We have further concluded that the 1141 cm^{-1} band is a so-called "crystallization-sensitive" band. We have also made the deuteration of the OH group of PVA in order

to clarify the assignment of this band[2-4], and further we have undertaken the deuteration of the main-chain of this polymer for the same purpose. In addition we have measured the infrared pleochroism of the doubly oriented PVA samples, and have shown that the experimental facts obtained so far can be explained fairly well, when we tentatively assign this band to the skeletal vibration of the planar zig-zag chain in the crystalline region[3,5,6].

On the other hand, Krimm, Liang and Sutherland[7] have reported that this band

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

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

3) H. Tadokoro, S. Seki and I. Nitta, J. Polymer Sci., 22, 563 (1956).

4) H. Tadokoro, This Bulletin, 32, 1252 (1959).

5) H. Tadokoro, S. Seki, I. Nitta and R. Yamadera, J. Polymer Sci., 28, 244 (1958).

6) H. Tadokoro, This Bulletin, 32, 1334 (1959).

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

should not be assigned to the crystalline band, but to the C–O–C stretching mode of the ether linkage produced between the molecular chains by heat-treatment. On the contrary, we have reconfirmed the linear relationship between the band intensity and the density for a number of samples subjected to heat-treatments under various conditions, by using the density-gradient tube method[6,8,9]. And furthermore we have accumulated experimental evidences for assigning this band to the crystalline band, such as comparison with the X-ray diffraction data on the formalized samples, swollen samples, etc.[6,8]

Quite recently Krimm[10] has considered the band to be a crystalline band and suggested that this band may be associated with the $\nu(CO)$ mode of a portion of a chain in which an intramolecular hydrogen bond is formed between two neighboring OH groups that are on the same side of the plane of the carbon

chain. On the other hand Liang and Pearson[11] have made the factor group analysis of PVA crystal based upon the symmetry of the average crystal structure deduced from X-ray analysis[12]. Then they have assigned the 1141 cm^{-1} band to the symmetric skeletal stretching modes as follows:
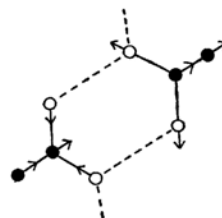
In order to make such detailed assignments, further accumulation of the experimental data as well as the calculation of the normal modes of vibrations[*4] would be necessary.

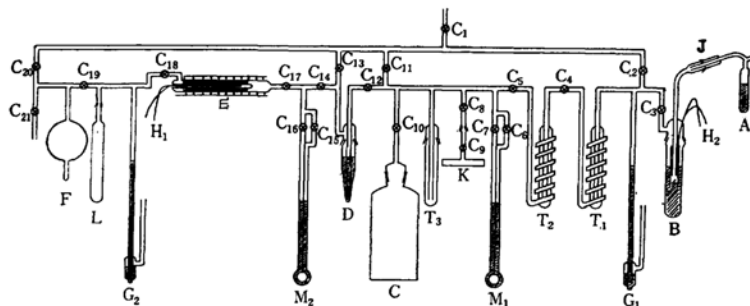In this paper we wish to report the syntheses

Fig. 1. The apparatus for the synthesis of α, β, β-trideuterovinyl acetate.

A: D_2O. B: CaC_2 (vessel made of Telex). C: Gas vessel for C_2D_2 (20 l.). D: CH_3COOD. E: Reaction tube (made of Telex). F: Gas vessel for adjusting the pressure. G: Safety valve. H_1: Thermocouple (copper-Constantan). H_2: Thermocouple (Chromel-Almel). J: Joint K: Gas cell for infrared measurements. M: Mercury manometer. T_1 and T_2: Trap. T_3: Trap made of Telex. L: Trap for product. C_1–C_{21}: Cock.
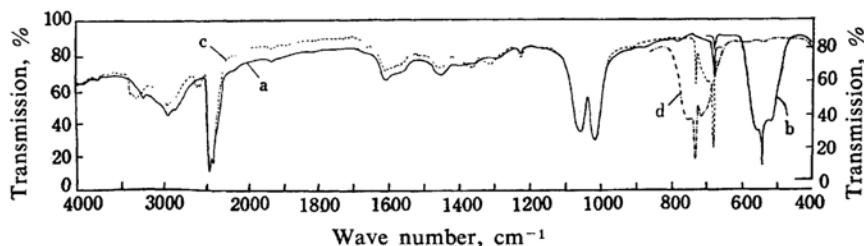

Fig. 2. Infrared spectra of acetylene-d_2 and acetylene.

a: C_2D_2 (degree of deuteration 97% at 200 mmHg)
b: C_2D_2 (degree of deuteration 97% at 70 mmHg)
c: C_2D_2 (degree of deuteration 94% at 200 mmHg)
d: C_2H_2 (at 70 mmHg)

8) H. Tadokoro, K. Kôzai, S. Seki and I. Nitta, ibid., **26**, 379 (1957).
9) H. Tadokoro, K. Kôzai, S. Seki and I. Nitta, *Chem. High Polymers (Kôbunshi Kagaku)*, **16**, 418 (1959).
10) S. Krimm, *Fortschr. Hochpolym.-Forsch.*, **2**, 51 (1960).
11) C. Y. Liang and F. G. Pearson, *J. Polymer Sci.*, **35**, 303 (1959).

12) C. W. Bunn, *Nature*, **161**, 929 (1948).
*4 The calculation of the normal modes of vibration of PVA is going on at Professor T. Shimanouchi's Laboratory of the University of Tokyo (T. Shimanouchi and M. Tasumi, Annual Meeting of the Society of Polymer Science, May, 1960).

and the infrared spectra of the deuterated PVA's $-(-CD_2-CD-)_n-$, and also the spectra of $\underset{OH(D)}{|}$ the intermediate products.

Preparation of the Samples

As has already been reported, the OH group of PVA can be easily deuterated by the isotope exchange reaction with deuterium oxide, but the CH group can not be deuterated by such a simple method. Hence we have synthesized deuterated PVA's according to the following scheme:
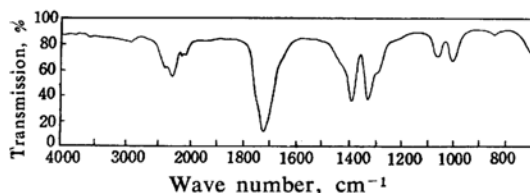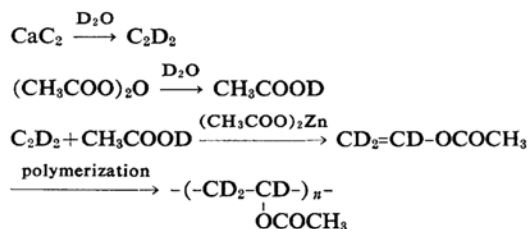
$$CaC_2 \xrightarrow{D_2O} C_2D_2$$

$$(CH_3COO)_2O \xrightarrow{D_2O} CH_3COOD$$

$$C_2D_2 + CH_3COOD \xrightarrow{(CH_3COO)_2Zn} CD_2=CD-OCOCH_3$$

$$\xrightarrow{polymerization} -(-CD_2-CD-)_n- \atop OCOCH_3$$

Fig. 3. Infrared spectrum of acetic acid-d (degree of deuteration 92%, at liquid state).

$$\xrightarrow{saponification} -(-CD_2-CD-)_n- \atop OH$$

$$\xrightarrow{D_2O} -(-CD_2-CD-)_n- \atop OD$$

Fig. 1 shows the outline of the apparatus used for the synthesis of α, β, β-trideuterovinyl acetate. The system can be highly evacuated by using a mercury diffusion pump and a rotary pump. The vessel B made of Telex*5 holds calcium carbide which was dried at about 580°C for about four hours under high vacuum (10^{-4} mmHg or below). The container of deuterium oxide A may be rotated at the joint J, and acetylene-d_2 is generated by dropping deuterium oxide into B. The generated acetylene-d_2 is transferred to the trap T_1 cooled with liquid nitrogen, and then warmed up to the dry-ice temperature by exchanging the refrigerant. The same procedure was repeated at the trap T_2 and then acetylene-d_2 is transferred to the trap T_3 cooled with liquid nitrogen. In this way impurities and excess deuterium oxide were eliminated from acetylene-d_2. Then acetylene-d_2 is held in the gas vessel C (about 20 l.). The purity of the acetylene-d_2 gas was checked by measuring the infrared spectra. K is the gas cell for this purpose equipped with the windows of AgCl plates.

Acetic acid-d was prepared by heating the equal mole mixture of acetic anhydride and deuterium oxide at 110°C for about four hours in a sealed tube. The acetic anhydride used had been purified by distillation, standing for several days with sodium metal and subsequent distillation (b. p.:
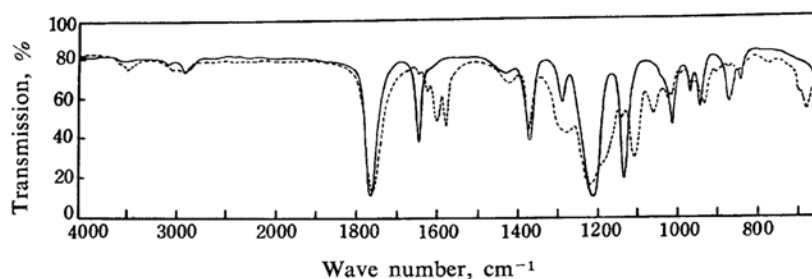
Fig. 4. Infrared spectra of α, β, β-trideuterovinyl acetate (----) and vinyl acetate (——) at liquid state.
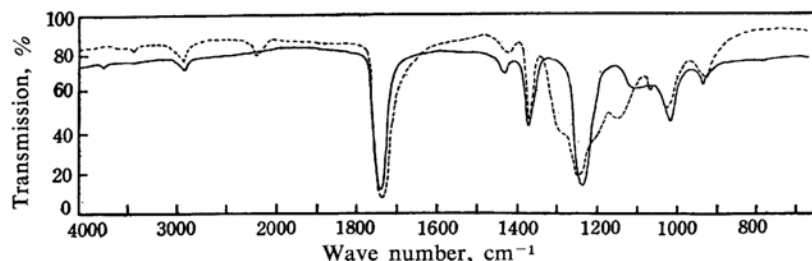
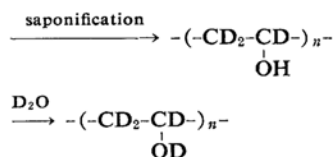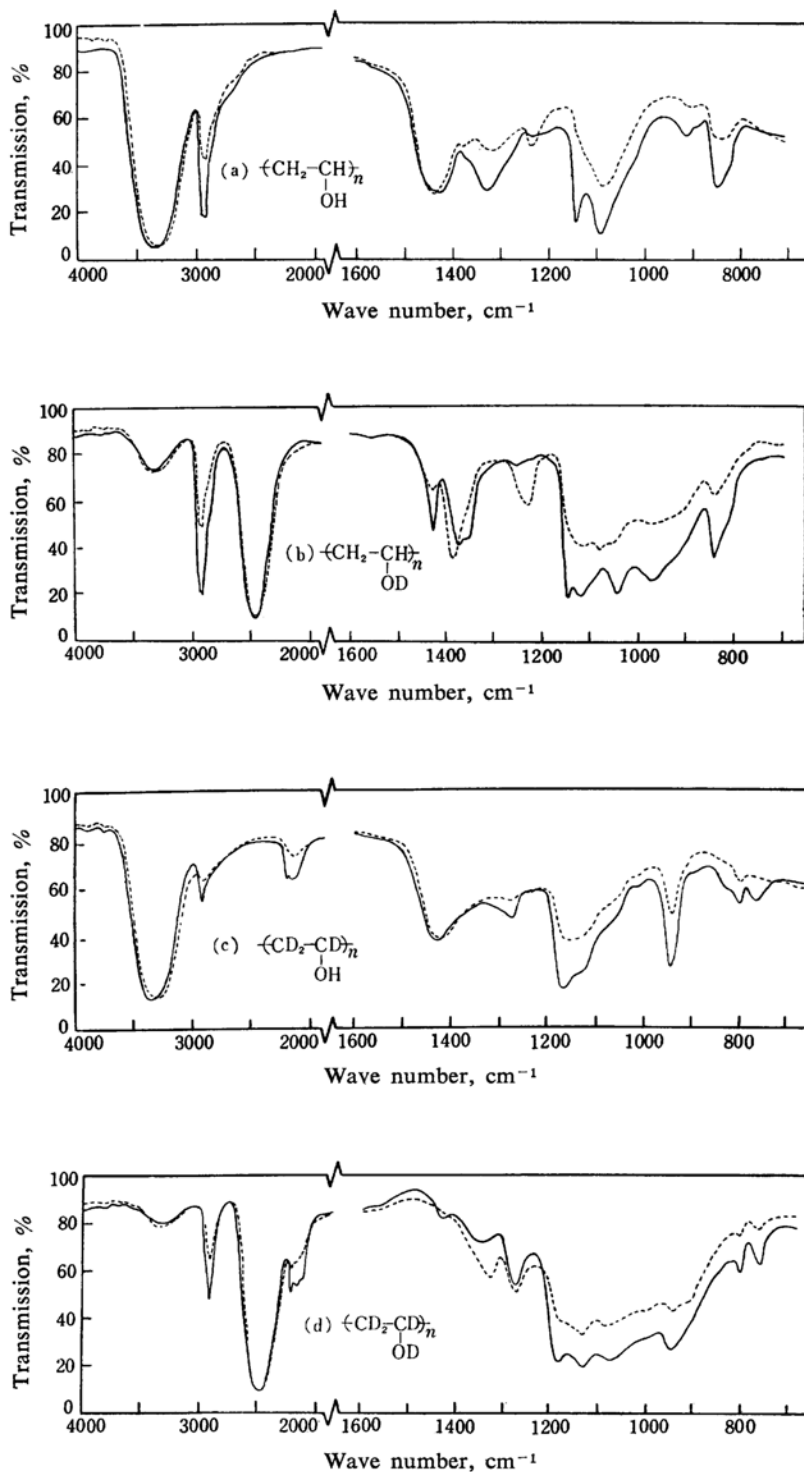Fig. 5. Infrared spectra of poly-α, β, β-trideuterovinyl acetate (----) and polyvinyl acetate (——).

*5 Boro-silicate glass manufactured by Tôshiba Electric Co., Ltd.

Fig. 6. Infrared dichroism of (a) PVA, (b) PVA-*d*, (c) PV-*d*₃A and (d) PV-*d*₃A-*d*.
——— Electric vector perpendicular to elongation.
- - - - Electric vector parallel to elongation.

TABLE I. INFRARED SPECTRA AND TENTATIVE

PVA			PVA-d			PV-d_3A		
Frequency cm^{-1}	Plechroism	Intensity	Frequency cm^{-1}	Dichroism	Intensity	Frequency cm^{-1}	Dichroism	Intensity
3340[a]	—	vs				3340[a]	—	vs
2937	⊥ (⊥)[g]	s	2937	⊥	s			
						(2905)[b]	⊥	m
2908	⊥ (‖)	s	2908	⊥	s			
2840	⊥	sh	2840	⊥	sh			
			2470[a]	—	vs			
						2200	⊥	m
						2145	⊥	m
						2105	⊥	sh
1440[c]	‖	s						
			1428	⊥	m	1425[c]	⊥	m
1420[c]	⊥	m				1420[c]	‖	m
			1383	‖	s			
1376	⊥	w	1376	⊥ ?	m			
			1360	⊥	sh			
1326[d] 1315	⊥	m						
			1256	⊥ ?	sh	1265	⊥	m
1232	‖	w	1230	‖	m			
1141	⊥ (‖)	s	1148	⊥	s	1165	⊥	s
						1125	⊥	sh
			1122	⊥	s			
1093	⊥ (⊥)	s						
1083	‖	m	1083	‖	m			
						1055	⊥	sh
			1094	⊥	s			
			977	⊥	m			
						940	⊥	s
			930	⊥	sh			
913	⊥ (‖)	m						
890	⊥ (‖)	vw						
849	⊥ (‖)	m	842	⊥	m			
835	⊥ (⊥)	sh	825	⊥	sh			
						823	⊥	sh
						797	⊥	w
						760	⊥	w
640[e]	‖	sh						
610	⊥	m						
480	⊥	m						
410	?	w						
360	⊥	w						

a) The ν(OH) band at about 3340 cm^{-1} shows no appreciable dichroism at the absorption peak, but shows a perpendicular and parallel nature at the higher frequency and lower frequency sides, respectively. The ν(OD) band at about 2470 cm^{-1} also shows the same behavior.

b) The wave numbers in parentheses are for the bands associated with the residual hydrogen atoms because of the incompleteness of deuteration.

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

ASSIGNMENTS OF PVA, PVA-d, PV-d_3A AND PV-d_3A-d

PV-d_3A-d			Tentative assignments[f]
Frequency cm^{-1}	Dichroism	Intensity	
			ν(OH)
			ν_a(CH$_2$)
(2905)[b]	$\perp$	m	ν(residual CH)
			ν_s(CH$_2$)
2470[a]	—	vs	ν(OD)
2200	$\perp$	m	ν_a(CD$_2$)
2145	$\perp$	m	ν_s(CD$_2$)
2105	$\perp$	sh	
(1428)[b]	$\perp$	vw	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$_2$)
			w(CH) or w(CH$_2$)
			δ(CH) ?
1330	‖	m	
			Coupling of δ(OH) and 1383 cm^{-1} band of PVA-d
1272	$\perp$?	m	
			w(CH$_2$) or w(CH)
1185	$\perp$	s	Crystalline band (see text)
1135	‖	m	
1130	$\perp$	s	
			Mainly due to ν(CO)
1085	‖	m	
1080	$\perp$	s	
			Mainly due to ν(CO)
			δ(OD)
940	$\perp$	s	
			Skeletal or CH$_?$
905	—	sh	
			Skeletal or CH$_2$
			r(CH$_2$)
797	$\perp$	w	
757	$\perp$	w	

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

e) The data in the region lower than 640 cm^{-1} is reproduced from the paper by Krimm et al.[7]

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

g) The notation $\perp$ and ‖ in parentheses refer to the polarization with respect to the plane of the zig-zag carbon chain[5,14].

139~140°C). Acetic acid-*d* was put in the vessel D. Acetylene-*d₂* gas, after bubbling through vessel D, was introduced into the reaction-vessel E. Then the gas mixture was caught in the vessel L cooled with liquid nitrogen. The catalyst used was zinc acetate carried on active charcoal kindly supplied by Dr. T. Omae of the Nippon Gôsei Kagaku Co., Ltd. The reaction temperature was about 200°C. The obtained vinyl-*d₃*-acetate was purified by using a concentric distillation column (Taika Kôgyô Co., Ltd., Osaka). The polymerization of vinyl-*d₃*-acetate was carried out in a sealed glass tube with α, α'-azobisisobutyronitrile catalyst at 60°C for about 24 hr.

Infrared Spectra of the Intermediate Products. —Fig. 2 is the infrared spectra of acetylene-*d₂*. The degree of deuteration was estimated by using the ν_5 band (CH symmetric deformation, C_2H_2: 729.2 cm^{-1}, C_2HD: 676 cm^{-1}, C_2D_2: 538.7 cm^{-1}) assuming that the absorption coefficients of the above bands are equal in the spectra of C_2H_2, C_2HD and C_2D_2. A spectrum of the sample of lower degree of deuteration (about 94%) was reproduced for reference. The intensity of the 676 cm^{-1} band, which is absent in the spectrum of C_2H_2 (curve d), is very strong in the spectrum of the 94% C_2D_2 (curve c), but weak in the case of the 97% C_2D_2 (curve b). Accordingly the ν_5 mode of C_2HD is considered to be assigned to the 676 cm^{-1} band, although this mode has been so far assigned to the 687 cm^{-1} band by Stitt[13].

Fig. 3 is a spectrum of acetic acid-*d*, the degree of deuteration of which was estimated to be about 92% by using the intensity ratio of the bands of OH and OD stretching.

Fig. 4 shows the spectra of vinyl-*d₃*-acetate (broken line) and of vinyl acetate (solid line). Fig. 5 shows the spectra of polyvinyl-*d₃*-acetate (broken line) and of polyvinyl acetate (solid line). It should be noticed that the spectra of the monomer and polymer in the 1300~ 1100 cm^{-1} region show a change similar to that of deuteration. The 1235 cm^{-1} band of polyvinyl acetate and the 1212 cm^{-1} band of vinyl acetate, which are considered to be assigned to the stretching mode of ester linkage, shift to the higher frequency 1245 and 1220 cm^{-1}, respectively. This behavior is interesting in relation to the shift of the 1141 cm^{-1} band of PVA to higher frequency with deuteration as will be discussed later.

Spectra of PVA and Deuterated PVA's. — In Fig. 6 the polarized infrared spectra of PVA, PVA-*d*, poly-α, β, β-trideuterovinyl alcohol (PV-*d₃*A) and poly-α, β, β-trideuterovinyl alcohol-*d* (PV-*d₃*A-*d*) are shown. The solid and broken curves represent the spectra obtained with radiation polarized, respectively,

perpendicular and parallel to the direction of elongation. The spectral data and the tentative assignments for PVA and deuterated PVA's are given in Table I. In the column of pleochroism of PVA the notations $\perp$ and $\parallel$ in parenthesis refer to the polarization with respect to the plane of the zig-zag carbon chain[5,14].

The OH stretching band at 3340 cm^{-1} shifts to 2470 cm^{-1} with the deuteration of the OH group, but the CH_2 stretching bands at about 2930 cm^{-1} are not affected by this type of deuteration. By the deuteration of the CH group these bands shift to about 2200 cm^{-1}. Both these bands due to the OH and CH groups shift to lower frequencies, when all the hydrogen atoms are deuterated. The residual 2930 cm^{-1} band is due to the incomplete deuteration of the CH group.

The 1141 cm^{-1} band of PVA and the 1165 cm^{-1} band of PV-*d₃*A are inferred to be due to the similar origins of absorption mechanism from the following similarities:

1) The distinguished dichroism,
2) The similar intensity,
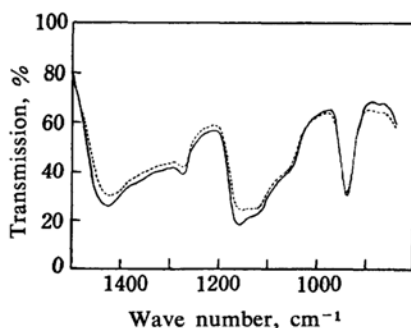3) The increase of the intensity with heat-treatment (Fig. 7), and

Fig. 7. Spectral change of PV-*d₃*A by heat-treatment.
---- No-treatment
—— Treated at 160°C for 20 min.

4) The small shift to higher frequencies with deuteration of the OH group. The 1141 cm^{-1} band of PVA shifts to 1148 cm^{-1} and the 1165 cm^{-1} band of PV-*d₃*A to 1185 cm^{-1} with deuteration of the OH group.
Thus the 1165 cm^{-1} band of $-(-CD_2-CD-)_n-$ is
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad OH$$
considered to be the crystalline band corresponding to the 1141 cm^{-1} band of PVA.

The experimental facts we have found so far about the 1141 cm^{-1} band are summarized as follows:

13) F. Stitt, *J. Chem. Phys.*, **8**, 56 (1940).

14) E. J. Ambrose, A. Elliott and R. B. Temple, *Proc. Roy. Soc.*, A**199**, 183 (1949).

1) The intensity increases with crystallization by heat-treatment, and shows a parallel relationship with the crystallinity determined by the density and the sorption of water vapor[1,8,9].

2) The band behaves in a parallel way with the X-ray diffraction rings due to the crystalline region, when the sample is formalized or swollen in water[6,8].

3) The band exhibits strong perpendicular dichroism in the case of an elongated sample, and distinguished pleochorism in the doubly oriented sample of PVA. The transition moment of this band is parallel to the zig-zag plane, while that of the 1093 cm^{-1} band is perpendicular to the zig-zag plane[3-6]. Furthermore, we have obtained another new experimental fact as follows.

4) The shift of this band with deuteration of the CH or OH group is small. This new experimental fact also supports our tentative assignment of 1141 cm^{-1} band mainly due to the stretching vibration of the extended zig-zag chain in the crystalline region. Here, of course, a considerable coupling of the vibration of the oxygen atom with the skeletal vibrations should be expected.

Next, we proceed to the interpretation of the other bands. Although we can not make any conclusive assignments of these bands merely from the present data, we may discuss here the tentative assignments of the several main bands. We have reported already that the 1430 cm^{-1} band of PVA should be a superposition of $\delta(CH_2)$ and some other band related to the OH group (probably $\delta(OH)$), since the intensity of this band decreases sensitively on deuteration and there remains a sharp band which is certainly attributed to the $\delta(CH_2)$ mode. The 1383 cm^{-1} band was tentatively considered to be $w(CH_2)$ or $w(CH)$, and the 1376 cm^{-1} to be $\delta(CH)$. This inference was confirmed, since these bands disappear in the spectra of PV-d_3A-d.

The bands near 850 cm^{-1} of PVA were considered to be skeletal or of CH_2 vibrations, because there was quite a little effect of deuteration. Especially the 835 cm^{-1} band having the pleochroism perpendicular to the plane of zig-zag chain was assigned to $r(CH_2)$. All these bands disappear by the deuteration of the main chain. The bands near 760 cm^{-1} of PV-d_3A and PV-d_3A-d are supposed to be due to $r(CD_2)$ mode. But further inference about the origin of the bands may be difficult, because of the complexity which is possibly due to the strong coupling among the group vibrations.

At present we are aiming to accumulate results of further experiments such as the infrared measurements of the highly doubly oriented samples of $-(-CD_2-CD-)_n-$, the prepa-
$$\begin{matrix} & | \\ & OH(D) \end{matrix}$$
ration of the more highly deuterated samples, and of the selectively deuterated samples, $-(-CD_2-CH-)_n-$, $-(-CH_2-CD-)_n-$, etc.
$$\begin{matrix} | & & | \\ OH(D) & & OH(D) \end{matrix}$$

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