Crystallization-sensitive Band of Polyvinyl Alcohol

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So-called "crystallization-sensitive bands" in the infrared absorption spectra have recently been found with various kinds of high polymers, such as polyethylene[1-5], polyethylene terephthalate[6-8], polychlorotrifluoroethylene[9], rubber hydrochloride[10], neoprene[11], polyamides[12-14], polyethylene glycol[15], polyvinylidene chloride[16], gutta percha[17], etc. Bands of this kind have at present interested many investigators as one of the powerful measures of the degree of crystallinity, or as a useful clue for the elucidation of the fine structure of the crystalline high polymers[12].

As to the $1141\,\text{cm}^{-1}$ band in the infrared spectrum of polyvinyl alcohol (PVA), Elliott, Ambrose and Temple[18] reported that this band shows strong dichroism, and Nagai and his coworkers[19] found that this band becomes more and more intense as heat-treatment proceeds, up to the temperature at which the sample becomes colored. In a previous paper[20] they have concluded that degrees of crystallinity determined by density, sorption of water vapor and infrared absorption methods are approximately in linear relationship unless the thermal decomposition is considerable, and that the $1141\,\text{cm}^{-1}$ band is recognized as a so-called crystallization-sensitive band. The nature of this band has been discussed by several authors as will be described below, but is still in a stage of speculation. Accordingly it is highly desirable that further new experimental facts should be accumulated. In the present paper the author will report the experimental results obtained on the proposed crystallization-sensitive band of PVA.

Experimental

a) **Samples.**—Film specimens were prepared by the same procedures as those described in the previous paper[21].

b) **Measurements of the Pleochroism.**—A doubly oriented specimen was prepared as follows. A uniaxially oriented PVA film* was rolled with a hot roller at about 90°C (to about four times its length compared with the original one) by holding it between two sheets of nylon 610**. In this procedure the direction of rolling was the same as that of stretching. The double orientation of the sample prepared in this way was ascertained by taking an X-ray Sauter photograph.

Fig. 1 shows schematically the relation between the cross-section perpendicular to the direction of rolling (the direction of the molecular chain axis) of the doubly oriented PVA film and the incident polarized infrared radiation***. As is shown in this figure, both the electric vector and the direction of propagation of the polarized infrared beam are perpendicular to the direction of rolling which is normal to the plane of the figure. The infrared spectra were observed at various angles of the incident beam, namely, 0, 45, 60, 70 and 75°. These infrared measurements were carried out by using a Perkin-Elmer Model 21 Infrared Spectrophotometer with AgCl polarizer.

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[4] S. Krimm, C. Y. Liang and G. B. B. M. Sutherland, *J. Chem. Phys.*, **25**, 549 (1956).

[5] M. C. Tobin, ibid., **23**, 891 (1955).

[6] W. H. Cobbs, Jr. and R. L. Burton, *J. Polymer Sci.*, **10**, 275 (1953).

[7] R. G. J. Miller and H. A. Willis, ibid., **19**, 485 (1956).

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[10] P. B. Checkland and W. H. T. Davison, *Trans. Faraday Soc.*, **52**, 151 (1956).

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[13] I. Sandeman and A. Keller, *J. Polymer Sci.*, **19**, 401 (1956).

[14] H. W. Starkweather, Jr. and R. E. Moynihan, ibid., **22**, 363 (1956).

[15] W. H. Davison, *J. Chem. Soc.*, **1955**, 3270.

[16] R. L. Burton, W. H. Cobbs, Jr. and V. C. Haskell, *J. Polymer Sci.*, **7**, 569 (1951).

[17] G. B. B. M. Sutherland and A. V. Jones, *Discussions Faraday Soc.*, **9**, 281 (1950).

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

[19] E. Nagai, S. Mima, S. Kuribayashi and N. Sagane, *Chem. High Polymers* (*Kobunshi Kagaku*), **12**, 199 (1955).

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

[21] H. Tadokoro, ibid., **32**, 1252 (1959).

* See Ref. 21.

** Kindly supplied by Dr. H. Yumoto of Tôyô Rayon Co., Ltd.

*** It may be noticed that the angle β of the crystal lattice given in the text of Bunn's paper[22] is different from that of the figure. Fig. 1 in the present paper was reproduced according to the text of Bunn's paper.

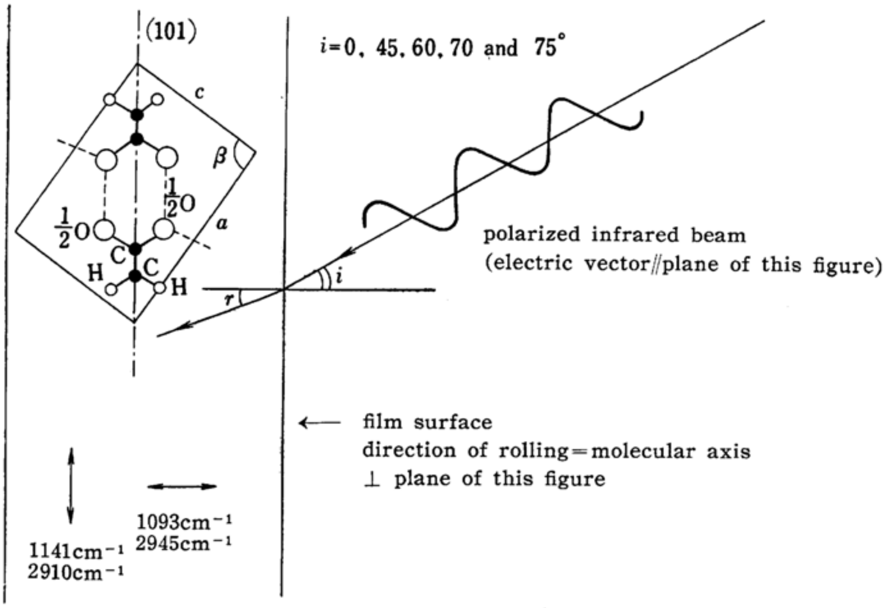

Fig. 1. The relation between the cross-section of the doubly oriented PVA film and the incident polarized infrared beam.

c) **Formalization and Swelling in Water.**—The PVA samples used for the experiments of formalization and swelling in water, were the same as samples I and III described in the previous papers[20,21]. The details of the experimental condition of the formalization was also given in the previous paper[22]. Those samples were also subjected to swelling in water at room temperature for 2 days. The degrees of swelling for samples I and III in this experimental condition are about 4.7 and 0.7, respectively. The infrared absorption spectra and X-ray diffraction photographs were taken by using a Hilger H800 Infrared Spectrophotometer and an ordinary Laue camera, respectively, before and after the treatment of formalization and swelling in water. During the X-ray measurements the swollen samples were held between aluminum foils in order to prevent the vaporization of water from the samples.

Results and Discussion

a) **Pleochroism of the 1141 cm^{-1} Band.**—When a polymer is stretched, the crystallites (or molecular chains) are so oriented that the molecular chain axes will be arranged parallel to the stretched direction, but the orientation of the molecular plane in the cross-section perpendicular to the direction of stretching remains completely random. Such a kind of orientation is called a "uniaxial orientation" and the usual fibers have more or less this kind of orientation. When the uniaxially oriented film is rolled in an adequate condition, a certain plane parallel to the molecular axis (in the case of PVA, the plane of carbon zigzag chain) is oriented further parallel to the rolled plane. Such a mode of orientation is called "double orientation". This possibility of double orientation was found for the first time by Bunn et al. on polyethylene[23] and nylon 66[24] by the use of X-ray diffraction, and afterwards this procedure was applied to the infrared studies of nylon 66, PVA and polyethylene by Ambrose and his coworkers[25] in the 3 μ region, and of polyethylene terephthalate by Miller and Willis in the 5～15 μ region[26].

The infrared studies of the doubly oriented PVA sample were carried out in the 3 μ region by Glatt et al.[27] and Elliott et al.[25] By the use of the pleochroism of the CH_2 stretching modes, they found that the plane of the carbon zigzag chain is parallel to the rolled plane of the film.

If the transition moment of an absorption band is perpendicular to the direction of rolling and exists in the rolled plane of

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[22] C. W. Bunn, *Nature*, **161**, 929 (1948).

[23] C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

[24] C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.*, **A181**, 45 (1947).

[25] A. Elliott, E. J. Ambrose and R. B. Temple, *Nature*, **163**, 567 (1949); E. J. Ambrose, A. Elliott and R. B. Temple, *Proc. Roy. Soc.*, **A199**, 183 (1949).

[26] R. G. J. Miller and H. A. Willis, *Trans. Faraday Soc.*, **49**, 433 (1953).

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

the doubly oriented film, the intensity of the band must be strongest when the angle of incidence, $i=0°$, and must be weaker as i increases (see Fig. 1). On the contrary, in the case when the direction of the transition moment is normal to the rolled plane, the intensity of the band should behave in the reverse manner. Utilizing this fact, it is possible to know the appoximate direction of the transition moment from the results of the absorption measurements on the doubly oriented sample.

The spectra taken with the doubly oriented specimen at different inclinations to the incident polarized beam is partly reproduced in Fig. 2. The relation between the optical density of the bands and the angle of incidence i is also given in Fig. 3.

From these measurements, it was possible to draw the following experimental conclusions: (1) the directions of the transition moments of the CH_2 symmetric stretching band at 2910 cm^{-1} and of the band at 1141 cm^{-1} are preferentially parallel to the surface of the rolled film, and (2) that of the CH_2 antisymmetric stretching band at 2945 cm^{-1} and of the band at 1093 cm^{-1} are more or less normal to the film surface, while (3) those of the other bands do not show any remarkable polarization**** (see Fig. 3).

Prior to the discussion on the nature of 1141 cm^{-1} band, it should be liked to make a short comment on the modes of vibrations of CH_2 group. As shown in Fig. 4, there are two kinds of C–H stretching vibrations of the CH_2 group of PVA[25]. The transition moment of the symmetric stretching mode at 2910 cm^{-1} should be parallel to the bisector of the angle H–C–H, and that of the antisymmetric mode at 2945 cm^{-1} perpendicular to it. The results on the CH_2 stretching modes inform us of the fact that the plane of the zigzag chain of carbon atoms is parallel to the surface of the film, in agreement with the observation of Ambrose and his coworkers[25].

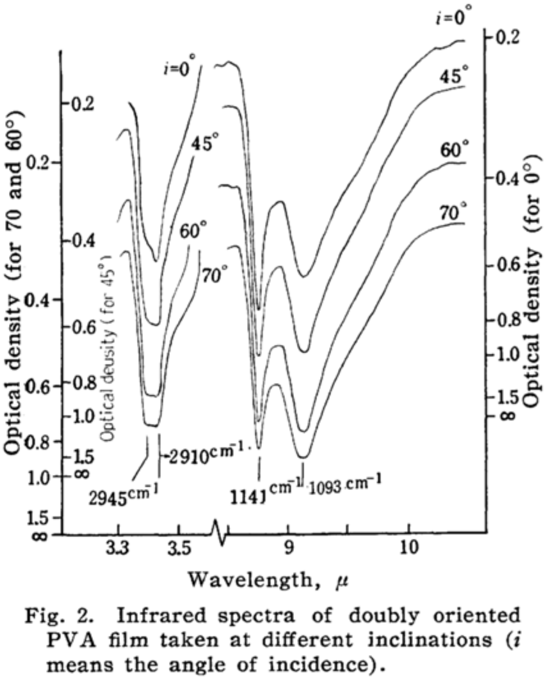


Fig. 2. Infrared spectra of doubly oriented PVA film taken at different inclinations (i means the angle of incidence).

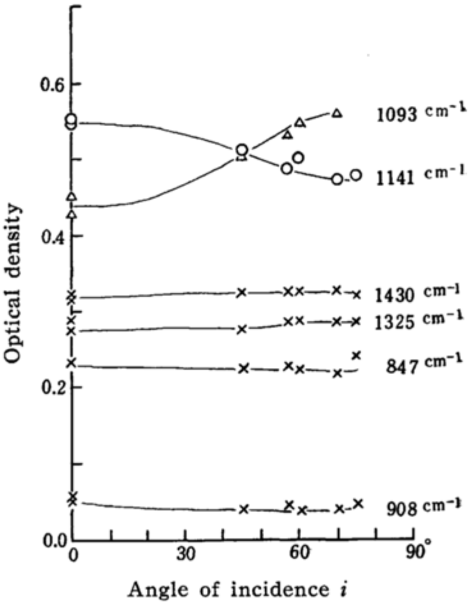
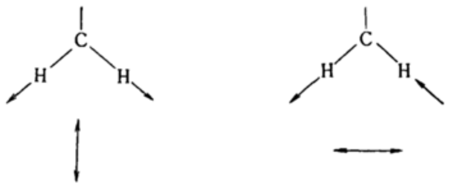


Fig. 3. Relation between the optical density of the bands and the angle of incidence i (doubly oriented PVA film).



CH_2 symmetric stretching 2910 cm^{-1}

CH_2 antisymmetric stretching 2945 cm^{-1}

Fig. 4. Two vibration types of CH_2 stretching of PVA.

Krimm, Liang and Sutherland[27] assigned this 1141 cm^{-1} band to the stretching of

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**** Of the other bands, 913, 849 and 835 cm^{-1} bands were found to have weak pleochroism by the infrared microspectroscopic measurements on a highly and doubly oriented PVA sample[28].

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

ether linkage produced by heat-treatment and they stated that the authors' conclusion[20] that this 1141 cm^{-1} band is the crystallization-sensitive band, is open to question. However, the experimental fact presented here together with the following sections b), c) and d) are believed to support the authors' conclusion.

b) Density Consideration. — Of the four samples (Table I) studied in the previous paper[20], sample IV subjected to heat-treatment in air at highest temperature (at 193°C for 2.5 min.) showed a deviation from the linear relationship between the optical density of the 1141 cm^{-1} band and the density of the samples, and this was interpreted as the result of a chemical change on the basis of the ultraviolet absorption spectrum. This deviation was pointed out by Krimm et al.[27] as one of the evidences for their objection to the authors' view[20]. Here, the author wishes to refer to the results of the authors' density measurements by the density gradient tube method on PVA films[29]. The samples for the measurements were treated in silicone oil for various durations at various temperatures as shown in the explanation of Fig. 5. The density of the samples was determined at 25°C by using the mixture of xylene and carbon tetrachloride as flotation medium. The ultraviolet absorption spectra of these samples were also measured with a Beckman Model DU Quartz Spectrophotometer in order to examine whether or not some chemical change occurs. Fig. 5 shows the correlation between the optical density of the 1141 cm^{-1} band and the density of the samples. As the thicknesses of the films were not the same in each case, the relative intensity of the 1141 cm^{-1} band of the samples was obtained by adjusting the intensities of the other bands to fit one another as closely as possible. This procedure was based upon the fact that the intensity of the 1141 cm^{-1} band is very sensitive to heat-treatment, whereas those of others are not. In Fig. 5 the samples denoted by △ show two strong absorption bands (280 and 330 mμ) in the ultraviolet region similarly to that for sample IV in the previous paper[20]. Twelve samples denoted by ○ clearly satisfy the linear relationship, while the samples denoted by △ deviate downwards from this. This fact indicates that this deviation is to be attributed to the thermal decomposition, and so it is less significant in the discussion of the crystallinity of PVA. Thus the observed linear relationship between the intensity of the 1141 cm^{-1} band and the density of the samples is in good agreement with the previous conclusion that the 1141 cm^{-1} band is a crystallization-sensitive band.

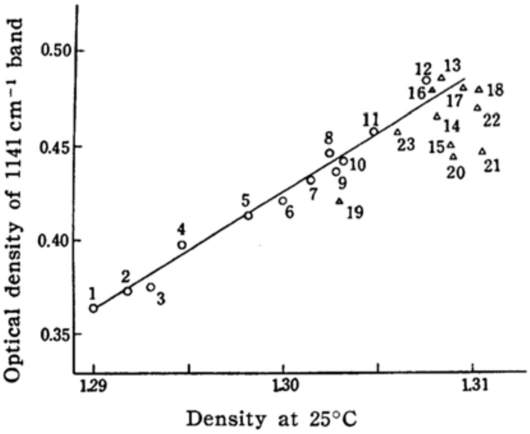

Fig. 5. Optical density of 1141 cm^{-1} band plotted against density for PVA samples subjected to heat-treatments at various conditions in silicone oil[29].

1.	no treatment		13.	180°C	60 min.
2.	100°C	5 min.	14.	190	2
3.	100	100	15.	190	5
4.	140	2	16.	190	21
5.	140	10	17.	220	1
6.	160	5	18.	220	2
7.	160	10	19.	220	15
8.	160	20	20.	240	10 sec.
9.	160	40	21.	240	40
10.	160	85	22.	240	90
11.	180	5	23.	240	120
12.	180	30			

c) Formalization and Swelling in Water.— Fig. 6 shows infrared spectra of dry and swollen PVA samples I and III, and their partial formals. The curves below the swollen samples are for those of the drying process, and were measured successively about 7 min. after the measurement on the swollen sample was done, and so on. In the case of sample I, the 1141 cm^{-1} band was observed to disappear on formalization. On the other hand, for sample III the 1141 cm^{-1} band is not affected remarkably. The 1141 cm^{-1} band of the partial formal of sample III is identified with that of sample III by its similar behavior to deuteration, namely, this band shifts slightly to a shorter wavelength side on deuteration in both cases of PVA and the partial formal of

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[29] H. Tadokoro, K. Kôzai, S. Seki and I. Nitta, ibid., **26**, 379 (1957).

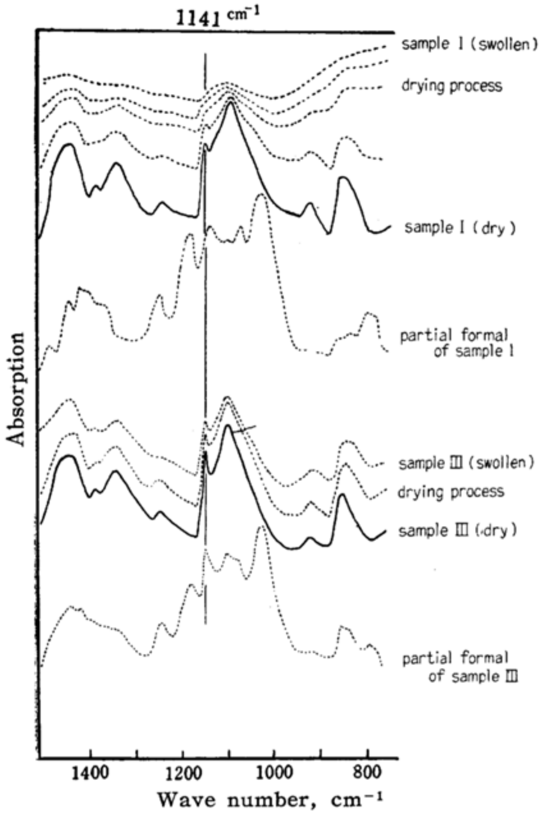

Fig. 6. Infrared spectra of dry and swollen PVA samples I and III and of their partial formals. The curves below the swollen one were measured successively ca. 7 min. after the measurement of the swollen sample was done, and so on.

sample III[30]. The 1141 cm^{-1} band is hardly found in the spectra of the swollen sample I, but appears progressively as the samples are being dried. On the other hand, in the case of sample III this band seems not to be influenced strongly by swelling.

Fig. 7 shows the X-ray photographs of the samples in Fig. 6. In Fig. 7, a) is for dried sample I, b) swollen sample I, c) partial formal of sample I, d) dried sample III, e) swollen sample III, and f) partial formal of sample III. The spots in the photographs a), b) and e) arise from the aluminum foil used for sealing the samples in order to prevent vaporization of water from the samples. The spots in c) and f) are due to the residual sodium sulfate being used for formalization. The haloes in b) and e) are due to liquid water. The diffraction rings due to PVA disappear in photograph b) of the swollen sample I, but the rings seem not to be affected remarkably in the case e) of sample III. In photograph c) of the partial formal of sample I, the intense diffraction rings of PVA give place to a new halo of smaller diffraction angle. This change corresponds to the increase of the apparent lattice distance from 4.51 to 4.72 Å.

The authors' previous observations by use of the infrared absorption and X-ray photographs indicate evidently that the 1141 cm^{-1} band behaves in parallel with the diffraction rings due to the crystalline region of PVA on formalization and swelling in water; namely, both the band and the rings disappear in the case of sample I, but are not affected remarkably in the case of sample III. This fact may also be considered to support the conclusion that this band is a crystallization-sensitive band.

d) On the Assignment of the 1141 cm^{-1} Band.—As to the assigment of the 1141 cm^{-1} band, various interpretations have already been proposed. Elliott and his coworkers[18] explained that this band is connected with the presence of the oxygen atom because of the lack of this band in the case of polyvinyl chloride. Nishino and his coworkers[31] as well as Nagai and his coworkers[32] considered this band to be associated with the formation of hydrogen bond. Krimm and his coworkers[27] suggested that this band may be the stretching of C–O–C linkage produced as the result of the heat-treatment of the sample.

It is considered to be necessary that the assignment of this band should satisfy the following experimental facts:

(1) The strongly perpendicular dichroism of this band (Fig. 4 of Ref. 21).

(2) The fact that the transition moment of the band is nearly parallel to the plane of the zigzag chain (Fig. 2).

(3) The parallel relationship between the intensity of the band and the density of the sample (Fig. 5).

(4) The location of the band in the observed spectrum.

(5) The only slight shift of this band on deuteration (about 7 cm^{-1} or 0.994 in wave number ratio, to higher frequency).

(6) The crystal structure of this substance[22], etc.

As the shift of this band on deuteration is so small, this band seems to be not

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[30] See Fig. 2 of Ref. 21.

[31] Y. Nishino, J. Ukita and T. Kominami, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 159 (1955).

[32] E. Nagai and S. Kuribayashi, *Chem. High Polymers* (*Kobunshi Kagaku*), **12**, 322, 368 (1955).

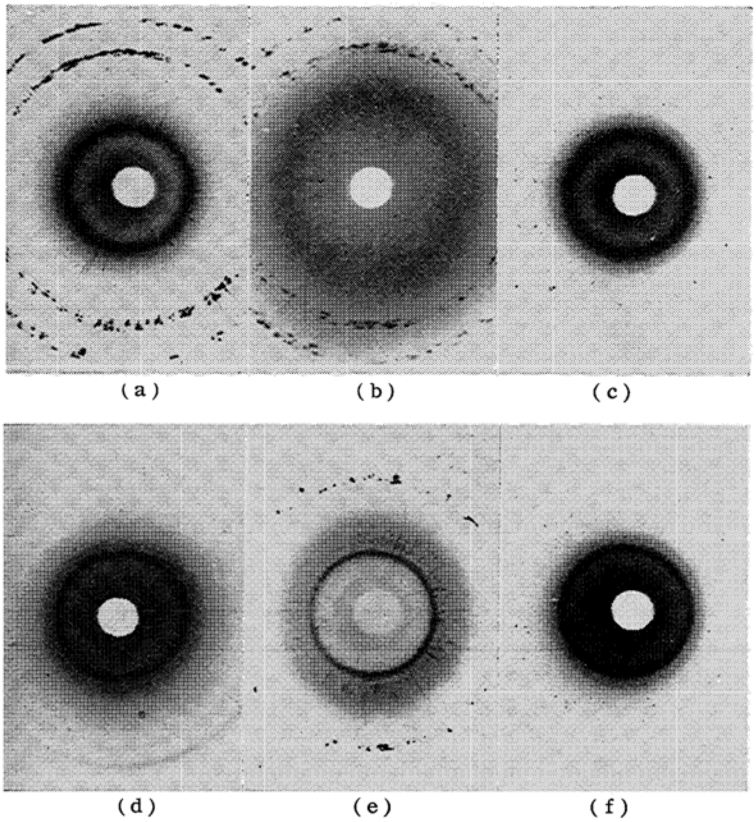
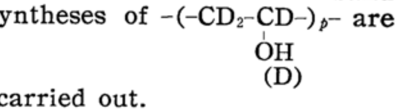


Fig. 7. X-ray photographs corresponding to the samples in Fig. 6: (a) sample I (dry); (b) sample I (swollen); (c) partial formal of sample I; (d) sample III (dry); (e) sample III (swollen); (f) partial formal of sample III.

directly associated with the motion of the hydrogen atom of hydroxyl group such as O-H deformation. The assignment of this band to the stretching of C-O-C linkage does not seem to be able to explain the experimental facts mentioned above [sections a), b) and c)] and the fact that this band exists distinctly even in the spectrum of the sample with no heat-treatment (such a sample is hardly considered to contain ether linkage). In this respect, Haas[33] has recently concluded that (1) the suggestion by Krimm et al.[27] relating this band to C-O-C vibration must be rejected, and (2) a hypothesis which relates the band with some vibrational modes associated only with crystallization is favored.

At the present stage it is still difficult to make the final assignment of this band from the present experimental data, but this band is undoubtedly due to the crystalline arrangements of the molecules and is thought to be intimately related to the regular repetition of the *trans*-configuration of the zigzag chains. For further elucidation of the nature of this band the total syntheses of  $-(-CD_2-\underset{\text{OH}}{\underset{|}{CD}}-)_p-$ (D) are now being carried out.

The author wishes to express his gratitude to Professor I. Nitta and Assistant Professor S. Seki, under whose guidance this research was carried out. He also expresses his sincere thanks to Professor T. Shimanouchi of the University of Tokyo for helpful advice and criticism, to Dr. T. Kanzawa and Mr. H. Kamio of Takeda Pharmaceutical Industries, Ltd. for preparing part of the charts of the infrared absorption spectra, and to Kurashiki Rayon Co., Ltd. for kindly giving him the PVA samples.

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[33] H. C. Haas, *J. Polymer Sci.*, **26**, 391 (1957).