The Crystallinity of Solid High Polymers. I. The Crystallinity of Polyvinyl Alcohol Film[*1]

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Introduction

The recent studies on solid high polymers have emphasized that the crystallinity is one of the most important factors to describe the state of them. The crystallinity is generally defined as the weight fraction of crystalline material. This definition is quite distinct if the polymer material is made of two distinct parts perfectly crystalline and perfectly amorphous. However, it is possible that there exist a transitional intermediate zone between these two perfect regions. In fact the same chain molecule may pass continuously from the one to the other region several times through such an intermediate zone. From this point of view the term "crystallinity" will be by nature an approximate one. During the past decade various methods of estimating crystallinity have been devised and developed, such as

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X-ray diffraction[1,2], density[3,4], infrared absorption spectrum[2,5], specific heat[6] etc. On the other hand some authors determine as a measure of this quantity the so-called "accessibility" by making use of the isotope exchange[7], hydrolysis[8] or sorption of water vapor[9,10]. In view of the conceptional limit of crystallinity mentioned above as well as the variety of detailed texture of polycrystalline high polymers, such as distribution of the size and shape of crystallites, their orientation, etc., it becomes of great importance to examine these methods of estimating crystallinity more critically as to what characteristic each of them possesses.

Although there exist a considerable number of reports on the crystallinity for cellulose[1a,3,7,8,9,10], polyethylene[1b,2,4,5a,6a,6b] nylon[2,5c,10], polyethylene terephthalate[2,5] etc., little work has been done with the same samples prepared under the same conditions by the comparative use of various kinds of existing methods estimating the crystallinity. In order to make some contribution to such a problem, we have undertaken to clarify the relationship among density, sorptive power for water vapor and infrared absorption spectrum as the proposed measures of the crystallinity, using the samples of polyvinyl alcohol (PVA) subjected to heat-treatments at different temperatures, each of which was prepared from one and the same source of material.

Experimental

a) Sample.—The powdered specimen of PVA (average degree of polymerization: 1650) was used as a starting material. The method of purification of the sample and the procedure adopted for the preparation of film specimens were the same as those described already in the previous paper[11]. Several large films prepared were all 0.01–0.03 mm. thick and they were cut in pieces of about 5 mm. × 10 mm. These small pieces of films were then divided into four groups, and each group was placed on a paper in an air-thermostat and subjected to the heat-treatments, the conditions of which are given in Table I. A part of the specimens of each group mentioned above were then cut further in smaller sizes of about 1 mm. × 5 mm. and they were used for the density measurements.

TABLE I

Sample	Conditions of heat-treatments	Appearance
I	No heat-treatment	———
II	100°C, 30 min.	Almost no change
III	160°C, 15 min.	
IV	193°C, 2.5 min.	Colored slightly brownish

b) Apparatus and Procedures.—The sorption and desorption[*2] isotherms were measured by the desiccator method and the measurements of the density were carried out by the flotation method. The apparatus and the procedures are essentially the same as before[11], so the description of them may be omitted here. The drying condition was about 60°C under a high vacuum (10^{-4} mmHg or below) over phosphorous pentoxide, the vessel being connected to a liquid air trap. For the attainment of constant weight it took about five days. The experiments of sorption and desorption as well as the measurements of density were all performed at 25°±0.03°C. For the sorption equilibrium it required about three weeks.

Infrared (from 2 μ to 15 μ) and ultraviolet absorption spectra (from 200 mμ to 550 mμ) were also taken for reference to those experiments mentioned above, by using the Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer with sodium chloride prism and the Beckman Model DU Quartz Spectrophotometer with ultraviolet accessaries respectively.

Results and Discussion

a) Density.—The densities of the bone-dry samples at 25°C are given in Table II. They seem to increase with the rise of the temperatures of heat-treatments. In order to evaluate the crystallinity of a sample from the density data, it is necessary to know the densities of crystalline as well as amorphous

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1a) P.H. Hermans and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948); idem., *J. Polymer Sci.*, **4**, 135 (1949). b) S. Krimm and A.V. Tobolsky, *J. Polymer Sci.*, **7**, 57 (1951).

2) J.B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954). (Review about the X-ray and infrared spectroscopic method).

3) P. H. Hermans, *J. Polymer Sci.*, **1**, 162 (1946); idem., "Contribution to the Physics of Cellulose Fibers", Elsevier Publishing Co., Inc., Amsterdam—New York, (1946), p. 70; "Physics and Chemistry of Cellulose Fibers", same publisher, (1949), p. 205.

4) E. Hunter and W.G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).

5a) R.B. Richards, *J. Appl. Chem.*, **1**, 370 (1951). b) W.H. Cobbs, Jr., and R.L. Burton, *J. Polymer Sci.*, **10**, 275 (1953). c) G.B.B.M. Sutherland and A. V. Jones, *Discussions Faraday Soc.*, **9**, 281 (1950). d) J.T. Maynard and M.B. Hall, *J. Polymer Sci.*, **12**, 235 (1954). Even in the case of ionic crystals this method can reveal the difference of the states of aggregation which cannot be differentiated by the X-ray method. (G. Chaudron, H. Mondange and M. Pruna, *Proc. Inter.n. Symposium Reactivity of Solids, Gothenburg* (1952) 9. *Chem. Abst.*, **48**, 13314a (1954).).

6a) H.C. Raine, R.B. Richards and H. Ryder, *Trans. Faraday Soc.*, **41**, 56 (1944). b) M. Dole, W.P. Hettinger, Jr., N.R. Larson and J.A. Wethington, Jr., *J. Chem. Phys.*, **20**, 781 (1952). c) R.C. Wilhoit and M. Dole, *J. Phys. Chem.*, **57**, 14 (1953). d) J.D. Hoffman, *J. Am. Chem. Soc.*, **74**, 1696 (1952).

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

8) H. Maeda, *Chem. and Engineering (Japan)*, **4**, 429 (1951). (Review of the chemical methods).

9) J.A. Howsmon, *Text. Res. J.*, **19**, 152 (1949).

10) A.J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, **42B**, 84 (1946).

11) H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **27**, 451 (1954).

[*2] The details of our desorption experiments will be reported in the next paper.

TABLE II

Sample	Density at 25°C. (g./cc.)	Crystallinity (From density and X-ray data)	$R/44$
I	1.291_0	0.29	5.7
II	1.294_6	0.34	5.9
III	1.300_7	0.42	5.9
IV	1.306_6	0.49	4.7

regions. The density of the former was calculated to be about 1.34 g./cc. from the lattice constants determined by X-ray investigation[12-15]. On the other hand, that of the latter cannot be measured directly, since the preparation of completely amorphous PVA has not yet been successful. By assuming that the ratio of the density of the amorphous to that of the crystalline state for PVA is of the same order of magnitude as that for other organic hydroxyl compounds, such as butyl alcohol (0.94)[16], as P. H. Hermans did in the case of cellulose[3], the density of the amorphous part was estimated to be about 1.26 g./cc. Recently I. Sakurada and his coworkers found that the crystallinity estimated by the X-ray method for the PVA film specimens, prepared under various conditions of heat- and stretching-treatments, shows an approximately linear relationship with their densities[17]. By extrapolation to zero for the crystallinity they found the density of the amorphous part of PVA to be 1.27 g./cc. This value coincides with that derived above by Hermans' method within experimental error. By use of the density values for the four groups of the specimens in column 2 of Table II together with the relationship of Sakurada et al., we can thus calculate their crystallinity, which is shown in column 3 of the same Table.

We measured also the densities of the samples at moist states for reference. As shown in Fig. 1, each density curve showed a conspicuous maximum at about 1.7, 1.5, 1.1 and 0.8% water content for the samples I, II, III and IV, respectively. This tendency is in good agreement with the discussion in the previous paper which indicated that the water content at which the density shows maximum, decreases in the reverse order to the crystallinity[11].

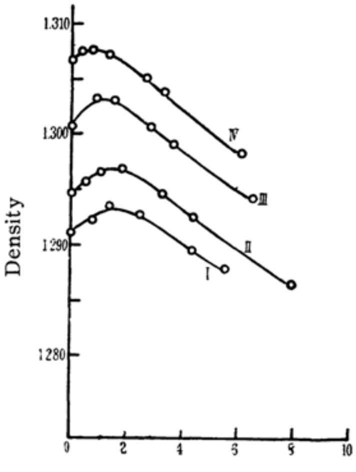

Fig. 1. Density-water content curves.

b) Sorption of water vapor.—The sorption isotherms of water vapor by the PVA films are all given in Fig. 2 and Table III.

As is well known, there are two methods

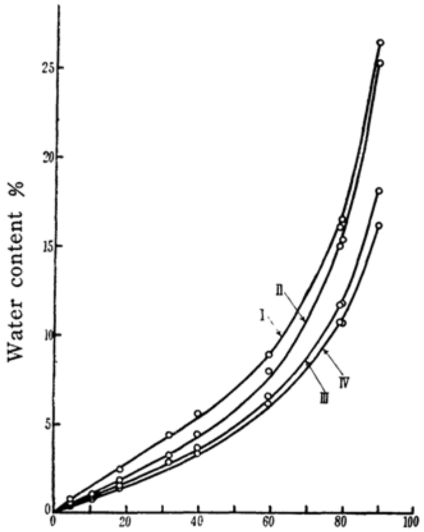

Fig. 2. Sorption isotherms at 25°C.
○ Observed value
— Calculated value

TABLE III

Relative humidity	Water content			
	I	II	III	IV
0.048	0.0079	0.0052	0.0046	0.0036
0.108	—	0.0107	0.0088	0.0075
0.184	0.0247	0.0182	0.0153	0.0132
0.318	0.0431	0.0323	0.0282	—
0.396	0.0553	0.0436	0.0364	0.0330
0.594	0.0890	0.0796	0.0652	0.0610
0.790	0.1606	0,1500	0.1165	0.1070
0,797	0.1650	0.1537	0.1175	0.1067
0.897	0.2640	0.2521	0.1807	0.1617

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[13] C.W. Bunn and H.S. Peiser, *Nature*, **159**, 161 (1947); C.W. Bunn, ibid., **161**, 929 (1948).

[14] I. Sakurada and K. Fuchino, *X-Rays*, **6**, 66 (1950); *Rep. Sci. Res. Inst. (Tokyo)*, **20**, 890 (1941).

[15] I. Nitta and I. Taguchi, *Ann. Report Inst. Fiber Res. (Osaka Univ.)* **6**, 3 (1952).

[16] W. Biltz, *Z. physik. Chem.*, **A151**, 13 (1930).

[17] I. Sakurada, Y. Sone and Y. Nukushina, Annual Meeting of the Chem. Soc. of Japan in April 1954.

of estimating the crystallinity of polymers, in a relative sense, from the sorption data: i) the sorption ratio method⁹⁾ and ii) the Hailwood-Horrobin method¹⁰⁾.

i) Sorption ratio method.⁹⁾—Sorption ratio means the ratio of the water content of a sample to that of a standard sample at the same relative humidity. This ratio is thought to be proportional, in a rough sense, to the fraction of the amorphous region. In the present experiment, sample I was arbitrarily taken as the standard, whereas native cotton has been usually taken as the standard in the case of cellulose.

As for the relative humidity we selected 59.4%, where the swelling is not yet perceptible and the accuracy of the observed data is rather high. Fig. 3 shows the relation between the sorption ratio at this relative humidity and the density.

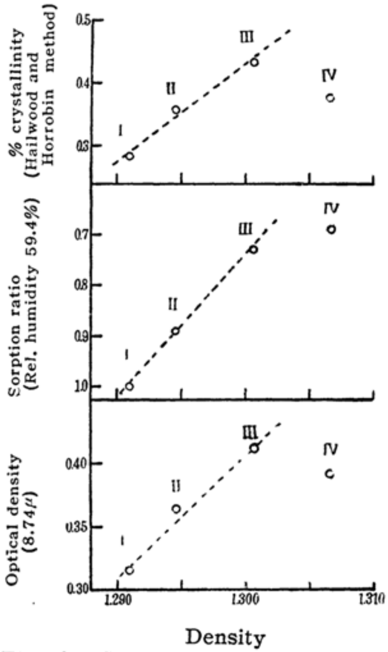

Fig. 3. Crystallinity-density curves (by water sorption and infrared absorption spectrum).

ii) The Hailwood-Horrobin method.¹⁰⁾—Hailwood and Horrobin postulated that moist high polymer is an ideal solid solution of dissolved water, unhydrated polymer molecules, and hydrated polymer molecules, assuming:

$$\frac{W_i}{W_{i-1}a'}=K_i \qquad i=1,\ 2,\ \dots\dots \tag{1}$$

where a' is the activity of the dissolved water in the soild phase, W_i is the activity of the i-th hydrate of the polymer, and K_i is the appropriate equilibrium constant. It follows that:

$$W_i=W_0(a')^iK_1K_2\dots\dots K_i \tag{2}$$

where W_0 is the activity of the unhydrated polymer. Using:

$$a'=\overline{K}x \tag{3}$$

where x is the activity of the water in the vapor phase and $\overline{K}$ is a constant, they then equate the activities of the various species to their mole fractions assuming the formation of an ideal solution. This leads them to the following three-parameter equation, neglecting the second and higher hydrates,

$$\frac{Mr}{1800}=\frac{\overline{K}h}{1-\overline{K}h}+\frac{\overline{K}K_1h}{1+\overline{K}K_1h} \tag{4}$$

where M is the "molecular weight" of the operative polymer unit, r is the regain, i.e. the total grams of water absorbed per 100 grams of bone-dry polymer, and h is the relative humidity. Further (4) can be put into the following form:

$$A+Bh-Ch^2=h/r \tag{5}$$

All the curves shown in Fig. 2 were drawn by using three parameters A, B and C which were calculated from the data of Table III by the method of least squares. We could find that this equation fit the observed values well.

Assuming that water molecule is not accessible to the interior of the crystalline region, Hailwood and Horrobin then correlated the constant M in this equation (4) with the accessible fraction θ by the following relation:

$$M\theta=R \tag{6}$$

where R ($\leq M$) is the molecular weight of the "unit" of the polymer molecule which is capable of combining with one molecule of water to form a monohydrate and is equal to M when the polymer is completely amorphous. They assumed further that the value of R is equal to the molecular weight of the unit which contains one characteristic polar group. In our previous paper¹¹⁾, we assumed that the monohydrate consists of one polymer unit -(CH_2CHOH)- and one water molecule according to the method of Hailwood and Horrobin. However, since the value of R cannot be checked as such from the measurement of water sorption only, the crystallinity on the basis of the assumed R would be used at most only as a relative measure. In order to see if the value of R comes out to be corresponding to the monomer unit, we calculated it by utilizing the crystallinity shown in column 3 in Table II and the value of M obtained from A, B and C. In column 4 of Table II, are shown the values of $R/44$ which correspond to the number of monomer units per one monohydrate (molecular weight of monomer unit $=44$). It is rather remarkable that these values for samples I, II and III are nearly constant (5.7–5.9) in spite of the rather naïve and crude theoretical treatment by Hailwood and Horrobin, and at the same time the value for sample IV (4.7) is considerably different from the other three, being parallel to the experimental evidences of sorption ratio and others which will be mentioned below. These results will show that this method may be utilized for estimating the relative crystallinity of this material. However, the questions why these values come out nearly constant and whether their magnitude has a definite physical meaning or not, might be solved first by further experiments; the measurement of the adsorption at very low humidity may be useful in this respect.

By taking $R/44=5.8$ for all samples, the crystallinities are then calculated and plotted against the density in Fig. 3.

c) **Infrared absorption spectrum.**—Fig. 4 shows a part of the infrared absorption spectra of our samples. The curve covering the whole region in this figure is for sample I, while for the other samples only the absorption band at 8.74μ(1146 cm^{-1}) is given by adjusting the intensity of absorption of seven other bands (3.4μ, 7.0μ, 7.40μ, 8.06μ, 9.15μ, 10.9μ and 11.75μ) to fit with those of sample I. Although the optical density of the broad and very strong 3.0μ band changes sensitively with the amount of bound water as some investigators reported[18,19], we have confirmed that those of the above-mentioned seven bonds do not depend on the water content. We have also found that the intensity of the 8.74μ band is not affected by the bound water so long as the water content does not exceed several percent. According to the investigation by A. Elliott et al., this band shows striking effect of dichroism, and they also inferred that this band may be due to a kind of absorption mechanism relating to the presence of the oxygen atoms[20]*3. Recently, E. Nagai and his coworkers found further that this band becomes stronger and stronger as the heat-treatment proceeds until the sample becomes colored[21]. As shown in Fig. 4, the intensity of absorption of this band increases in the order of samples I, II and III, and then decreases in IV. The optical density of this band vs. the density is given in Fig. 3. By the linear relationship of the intensity variation of this absorption band to the density and also by other facts mentioned above, we confirmed that this band is really the so-called "crystallization-sensitive" band[2].

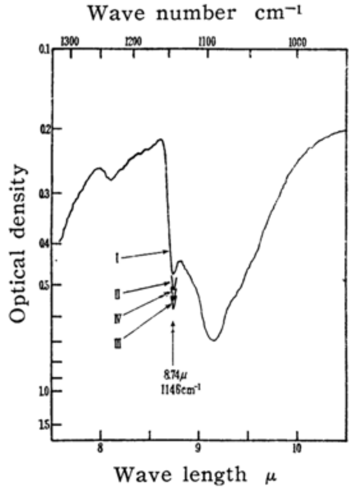

Fig. 4. Infrared absorption spectra of PVA films.

Now we proceed to the relationship among these results obtained above. In Fig. 3 the values given in ordinates for the samples I, II and III lie nearly on straight lines, whereas remarkable deviations are found for the sample IV. As the sample IV was subjected to the heat-treatment at the highest temperature, and got colored considerably, so it may be conceived that such an abnormality is due to the occurrence of some chemical changes.

In order to ascertain whether it is really the case or not, the ultraviolet absorption spectra were measured. Our results are shown in Fig. 5, in which the absorption bands at 280 mμ and 330 mμ are particulary distinguished for the sample IV. These two bands are considered to be attributed to carbonyl group and carbon-carbon double bond conjugated with the carbonyl group respectively. This conclusion is also in agreement with the results obtained by J. Ukita and his coworkers using the chemical method[22]. As the occurrence of chemical changes in

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

[19] L. Glatt, D.S. Webber, C. Seaman and J.W. Ellis. *J. Chem. Phys.*, **18**, 413 (1950).

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

*3 The elucidation of the origin of this band seems to have considerable significance for clarifying the nature and structure of the crystalline part. To get further information we are now studying this point by means of deuterium exchange (H. Tadokoro, S. Seki and I. Nitta, *J. Chem. Phys.*, **23**, 1351 (1955)).

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

[22] J. Ukita, S. Usami and T. Kominami, *Chem. High Polymers (Japan)*, **11**, 300 (1954).

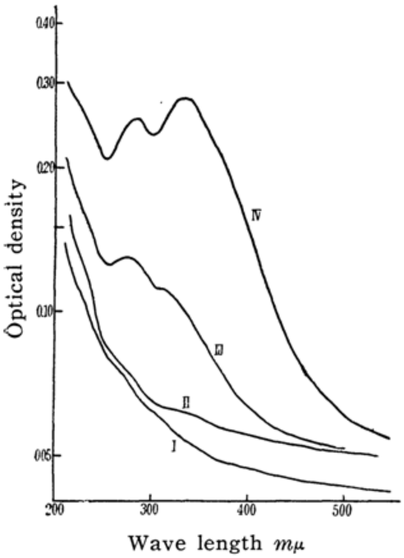

Fig. 5. Ultraviolet absorption spectra of PVA films.

the sample IV were thus ascertained, it may be of less significance to discuss the crystallinity of this sample in comparison with the other three samples on the same grounds. In passing, it may be added here that we found recently the fact that when the heat-treatment was carried out above the temperature of about 180°C, the density-time curve at constant temperature for such a sample shows a maximum in contrast to those treated at lower temperatures*4. This fact may also be explained by the occurrence of chemical changes.

After all, it is ascertained in the present investigation that the crystallinity measured by the X-ray, density, water sorption and infrared absorption methods go approximately parallel with each other as far as chemical change on heating is not appreciable, so the methods we have adopted in the present work may be used for determining the crystallinity.

Although we can correlate the four above-mentioned methods estimating the crystallinity with each other, it would be necessary to carry out further investigation in relation to the detailed texture of solid high polymers in order to obtain deeper insight into the nature of this quantity, "crystallinity". From such a standpoint, we are led to investigate such problems as given below and examine the results with systematical and synthetical criticism:

i) the application of the method for measuring the accessibility, e. g. deuterium exchange*3,

ii) the application of the method for studying the texture, e. g. X-ray small angle scattering*5,

iii) the assignment of the crystallization-sensitive band in infrared absorption spectra*3,

iv) the application of a new method for localizing hydrogen atoms, e. g. proton magnetic resonance absorption, chemical shift,

v) the comparative investigations with other high polymers, e. g. cellulose, nylon, etc.

Summary

i) Densities, sorption of water vapor and infrared absorption spectra were measured on four kinds of PVA films, which were prepared from the same PVA powder specimen and subjected to different heat-treatments.

ii) It was found by the present investigation that the 1146 cm^{-1} (8.74μ) band is the so-called crystallization-sensitive band.

iii) Since the degrees of crystallinity determined by these methods went in parallel, it was found that they may be used as relative measures for the crystallinity.

iv) Samples subjected to the heat-treatment at about 193°C, behave abnormally from the other three groups of samples. This deviation was found to be due to chemical changes occurring in the heat-treatment. This was confirmed by the measurement of ultraviolet absorption spectra.

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*4 Details of this experiment will be published later.

*5 For the elucidation of the texture, the X-ray small angle scattering method seems to be very helpful. For this purpose Dr. M. Kakudo of the Faculty of Engineering of this University is now studying this problem in relation the to same materials we are using at present in accordance with our request.

Note added in Proof: According to Fig. 1 of the paper by E. Nagai, S. Mima, S. Kuribayashi and N. Sagane21) the fourth point (of the specimen of the density 1.306_6) lies on the straight line. This is in contradiction to our result. Such discrepancy might be due to the fact that they have chosen 3.0 μ absorption band as the standard, which does not seem to be adequate judging from our observation.