Molecular Modeling for the Crystal Structure of Stereoregular Poly(vinyl Alcohol) (I) - New Crystal Dimension of Syndiotactic Poly(vinyl Alcohol) -

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1. Introduction

Poly(vinyl acetate) (PVAc) from which atactic poly(vinyl alcohol) (PVA) is derived, is always noncrystalline. This was attributed to the irregular steric arrangement of the acetyl groups in PVAc. However, the X-ray diffraction patterns of atactic PVA, a derivative of PVAc, were found to show distinct crystallinity, and to give an identity period of 2.52 Å along the fiber axis, despite the expectation of an irregular arrangement of the hydroxyl groups in atactic PVA, in the same manner as that of the acetyl groups in PVAc. From the fiber period of 2.52 Å, Bunn[1, 2] proposed a concrete model, in which the hydroxyl groups were randomly arranged in the left- and right-hand positions along the chains. The model was based on the fact that the volume taken up by the hydroxyl groups in PVA is so small that the polymer can crystallize despite the stereoirregular arrangement of the hydroxyl groups.

The dimensions of the unit cell of PVA were calculated on the basis of the several models described above from X-ray diffraction patterns. The proposed unit cells are all monoclinic, and despite several later analyses the same basic lattice parameters and molecular configuration are widely accepted up to now.[1-6] Among various models, Bunn's model,[1, 2] in which the steric arrangement of hydroxyl groups is random, has been supported in principle by many authors.[6] The dimensions proposed by Bunn are as follows: $a = 7.81$ Å, $b = 2.52$ Å, $c = 5.51$ Å, and $\beta = 91°42'$.[1]

However, a somewhat different arrangement of the molecular chains in the lattice was proposed by Sakurada.[3] Figure 1 shows the projections of the molecular chains to the (a -c) plane in both models. Two model are different in the azimuthal angle of the molecular plane and hydrogen bonding network. That is, continuous links of intermolecular attraction, due to hydrogen bond formation between two hydroxyl groups of neighboring chains, run roughly along the direction of the a-axis in Sakurada's model, and roughly along the direction of the c - axis in Bunn's model, as shown by the dotted lines in Figure 1. It is noteworthy that all the unit cells described above was obtained from the X-ray patterns of atactic PVA whose syndiotactic diad (S-diad) content is about 47-53%.

Recently, syndiotacticity-rich high molecular weight (HMW) PVA whose mechanical and physical properties are much superior to those of atactic ones has received considerable

attention.[7-10] The commercial and scientific interests in this polymer arise from the fact that crystal lattice modulus of PVA along the chain direction is estimated over 250 GPa. These properties seem to be ascribable to molecular structural characteristics including extended-chain conformation and high molecular orientation due to its HMW, high stereoregularity, and high linearity.

There are many researches in the X-ray diffraction analysis of atactic PVA fibers, films, gels, and crystal mats.[6, 11, 12] And, we have previously reported on the basic structure and properties of the microfibrillar PVA fiber (PVA fibril) prepared from the saponification of PVPi to PVA.[9, 13, 14] Unit cell calculation of highly syndiotactic PVA fibril by X-ray analysis is rare up to now. One of the most interesting problems encountered in the X-ray analysis of PVA may concern the molecular conformation of stereoregular polymer.

So, in this study, unit cell of syndiotactic PVA fibril was determined and compared with that of atactic PVA fiber by identifying the effect of tacticity on the reflections of PVA crystal. Also, the lateral crystallite sizes and paracrystallinity data were determined for PVA fibers having different stereoregularities.

2. Experimental
2.1. Preparation of syndiotactic PVA fibril by in-situ fibrillation
2.2. Preparation of atactic PVA fiber by gel spinning
2.3. X-ray diffraction analysis

The degree of crystal orientation (f_c) was calculated by azimuthal scanning of the (020) reflection (the crystal is monoclinic and the chain axis is parallel to the b axis) at a scanning speed of 2 °/min.

Wide angle X-ray diffraction (WAXD) patterns were obtained by Statton camera with flat-plate geometry using Ni-filtered CuKα radiation at 40 kV and 45 mA. X-ray pattern of the PVA was recorded on Kodak direct exposure film using pinhole collimation under vacuum. The exposure times for WAXD was 12 h. The d-spacings were calibrated using CaF_2 powder. θ/2θ diffractometer scans were recorded using a Phillips PN 3550 diffractometer with scintillation counter in the transmission mode with a constant slit width of 0.1°. These data were collected with increments of 0.02° (Δ2θ) with a counting time of 30 s for each step. CuKα radiation was used in all measurements. The apparent crystallite size D_{hkl} was estimated using Scherrer's eq.

The lateral crystallite sizes and paracrystalline distortion parameters (g) for PVA fibers with different stereoregularities were derived from the integral half-widths of several orders of $h00$ reflections, using the Hosemann equation:

$$\delta^2 = 1/L^2_{hkl} + (\pi g n)^n /d^2_{hkl} \tag{1}$$

where δ is the integral half-width, L_{hkl} is the mean dimension of the crystallite perpendicular

to the hkl plane, d_{hkl} is the mean interplanar spacing, n is the order of the reflection, and g is the parameter of paracrystallinity: $g = \Delta d_{hkl}/d_{hkl}$, where Δd_{hkl} is the standard deviation for the distribution of interplanar spacings.

3. Result and Discussion

WAXD photographs of four PVA fibers with different S-diad contents and similar f_c of 0.985-0.991 maximum drawn at 225 °C show a high crystallinity, a high degree of axial orientation of the crystallites, and a three-dimensional order regardless of syndiotacticity difference. The indicative of narrowness of reflection is the observed splitting of (101) and (10-1) reflections in X-ray pattern of PVA fiber with S-diad content of 63.1%.

Figure 2 presents effect of syndiotacticity on profiles of (100) (A), (001) (B), and (10-1) (C) reflections. Peaks shift to higher angles with increasing syndiotacticity. The spacings decrease linearly with increasing S-diad content without any abrupt change in the slope, indicating some contraction of the lattice perpendicular to the fiber axis. The (100), (001), and (10-1) spacings for PVA fiber with S-diad content of 63.1% are down to 7.63, 5.41, and 4.45 Å, respectively, and these values are much lower than those from Bunn's data. In contrast, the (100), (001), and (10-1) spacings for atactic PVA fibers with S-diad content of 51.2 and 54.5% are about 7.80-7.82, 5.48-5.52, and 4.54-4.57 Å respectively, which are similar to the Bunn's values of 7.81 and 5.51 Å, respectively. This result might be explained by a unit cell compaction to the lateral direction due to a dense packing of chains in the crystal lattice and the tight intermolecular hydrogen bonds for highly syndiotactic PVA. Because PVA fibril in this study was prepared by strong self-packing of highly syndiotactic PVA chains during saponification of syndiotactic precursor, PVPi,[9, 14, 15] this spacing compaction effect is more obvious in PVA fiber with S-diad content of 63.1% than in that of 58.4%.

The unit cell parameters such a, b, c, and $\sin\beta$ of the PVA fibril with S-diad content of 63.1% were calculated on the basis of monoclinic lattice. The calculated unit cell parameters for the PVA fibril with S-diad content of 63.1% are $a = 7.63\pm0.02$ Å, $b = 2.538\pm0.002$ Å, $c = 5.41\pm0.01$ Å, and $\beta = 91.18'\pm12'$. a and c are smaller and b is larger than those reported by other researchers including Bunn. In contrast, in the case of gel-spun atactic PVA fiber having S-diad content of 51.2%, $a = 7.82\pm0.03$ Å, $b = 2.527\pm0.002$ Å, $c = 5.52\pm0.01$ Å, and $\beta = 91.45'\pm15'$ were obtained, which are similar to Bunn's and Sakurada's values.[1-3] Conclusively, it is obvious that syndiotactic PVA fibril in this study have a relatively compact unit cell.

Up until now, the crystal density of PVA has been known to be 1.345 g/cm^3, which was calculated using Bunn's lattice parameter.[7] However, the measured density of PVA fibril with S-diad content of 63.1% is about 1.38 g/cm^3. Thus we calculated crystal density of PVA by utilizing our a, b, c, and $\sin\beta$. Assuming that the unit cell contains two monomeric units, the calculated crystal density is 1.399 g/cm^3. This is much higher
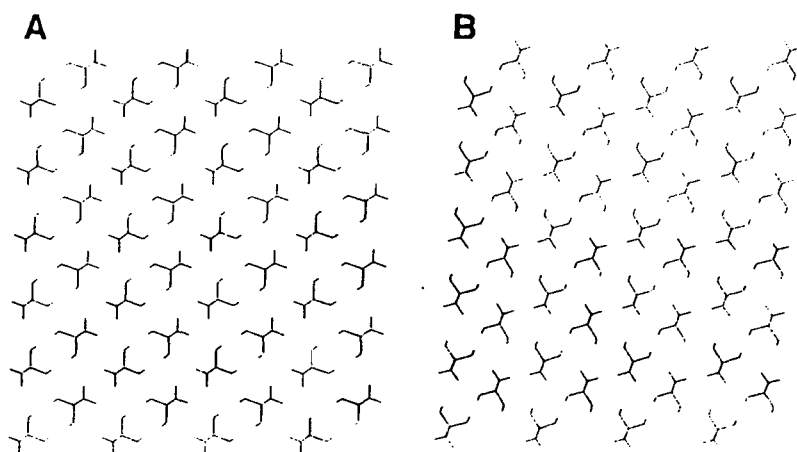
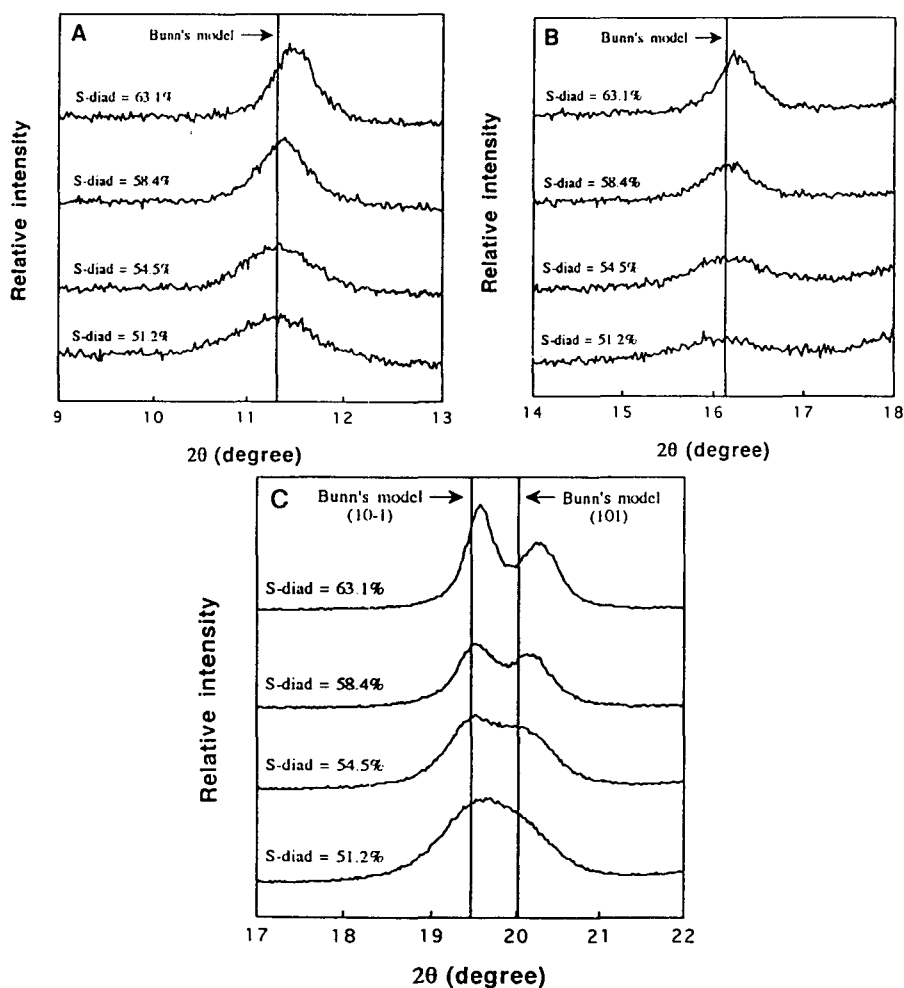**Figure 1.** Crystal sructure models of PVA proposed by Bunn (A) and Sakurada (B).

Figure 2. Effect of tacticity on the 2θ for the (100) (A), (001) (B), and (10-1) (C) planes for the PVA fibers with different stereoregularities and similar f_c of 0.985-0.991.

than reported value. This reason is because previous value was calculated from the X-ray analysis of atactic PVA. From the fact that the PVA fibril with S-diad content of 63.1% have higher crystal density of 1.399 g/cm^3, it is concluded that the higher the syndiotacticity, the more compact and denser the crystal of PVA.

4. Conclusion

X-ray methods have been used to investigate the effect of stereoregularity on the crystal structure of PVA fibers having S-diad content of 51-63%. The (100), (001), and (10-1) spacings decreased linearly with increasing S-diad content, indicating some contraction of the lattice perpendicular to the fiber axis. This lattice spacing compaction effect resulted in modified unit cell parameters for syndiotacticity-rich PVA. That is, unit cell of PVA fibril with S-diad content of 63.1% is monoclinic and dimensions were proposed as follows: a = 7.63±0.02 Å, b = 2.538±0.002 Å, c = 5.41±0.01 Å, and β = 91.18'±12'. In comparison with Bunn's and Sakurada's unit cells, the unit cell in this study has smaller lateral and larger longitudinal lattice parameters. In contrast, unit cell parameters for typically atactic PVA fibers with S-diad content of 51.2% were a = 7.82±0.03 Å, b = 2.527±0.002 Å, c = 5.52±0.01 Å, and β = 91.45'±15' and these data are very similar to Bunn's and Sakurada's values. Based on the lattice parameters of modified unit cell, the crystal density for PVA fibril having S-diad content of 63.1% was calculated to be 1.399 g/cm^3, which is higher than 1.345 g/cm^3 reported in numerous papers as a density of perfect crystalline PVA. This implies that the higher the syndiotacticity, the more compact and denser the PVA crystal. The corrected lateral crystallite sizes and paracrystallinity indices were L_{h00} = 110±5 Å, g = 2.77±0.09% for PVA fiber with S-diad content of 63.1%. As S-diad content increased, L_{h00} and apparent longitudinal crystallite size increased and g decreased. It was concluded that increasing syndiotacticity of PVA is considered to be one of the most effective way to enhance lateral regularity and crystal compactness.

5. References

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