DISCUSSION

In modelling band thickening, boundaries between bands are allowed to disappear with time. A physical representation of this model is the coalescence of two bands. We treat the boundaries as planes including many defects rather than as an amorphous region. The hexagonal phase contains many chain defects[8]. Therefore when a crystal transforms orthorhombic to hexagonal phase, the boundary defects can easily migrate through the crystals along the chain axis. Eventually the defect will be excluded from the crystal to the surface, i.e. another boundary; thus the two bands coalesce. Although the diffusion along the chain is fast in the hexagonal phase, a defect can be trapped in the lamella. With a mean path between trapping sites, λ, and trapping energy, E, the rate at which defects vanish, R_D, is as follows:

$$R_D \propto \exp(-LE/\lambda kT) \quad (4)$$

where k is the Boltzmann constant and T is the absolute temperature. The thickening rate of the band, $\mathrm{d}\bar{L}/\mathrm{d}t$, is then given by:

$$\mathrm{d}\bar{L}/\mathrm{d}t = R_D \cdot \bar{L} \propto [\exp(-\bar{L}E/\lambda kT)]\bar{L} \quad (5)$$

A neighbour vanishes when a distance between boundaries, $\bar{L}$, exists, and thus the contribution to the thickening rate $\mathrm{d}\bar{L}/\mathrm{d}t$ is approximately proportional to $\bar{L}$. It is easily shown that equation (5) is essentially a straight line for the curve $\bar{L}$ against log t. The essential point in equation (4) is that a factor proportional to L is included in the exponent; this is the reason why the probability for vanishing of a defect is weighted by m^{-n} in the simulation: $L = n\bar{L}_0$. Comparing m obtained from the simulation with the experimental curve, we obtain $2.3kT$ for the value of $(E/\lambda)\bar{L}_0$. For $T \approx 500$K, $(E/\lambda)\bar{L}_0$ is about 2.3 kcal mol^{-1}. This value is not surprising though its validity is open to discussion. For annealing in the orthorhombic phase, the value of E/λ is much larger, presumably due to both smaller λ and larger E.

Thus it has been shown that band structure can be formed by annealing through the coalescence of lamellae. Even annealing in the orthorhombic phase for a long period would give the band structure.

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Stability of the crystal structures of poly(vinyl alcohol) (PVA) by CNDO/2 calculations

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CNDO/2 calculations using the tight-binding approximation for polymers was applied to poly(vinyl alcohol) (PVA). The calculations were performed assuming several crystal structures. The stability among the structures was explained by using the calculated results in connection with the hydrogen bonding involved.

Keywords Stability; crystal structure; poly(vinyl alcohol), CNDO/2 calculations; semi-empirical MO; MO procedure; hydrogen bonding

We have previously presented[1] the results of the CNDO/2 calculations[2] on poly(hydroxymethylene) (PHM) and poly(vinyl alcohol) (PVA) using these molecules as models of the poly(saccharide).

The relative conformational stability among four forms of PHM and between two forms of PVA can be reasonably explained by these calculations, and we have obtained information about the stability of the ring part of the saccharides.

However, we were unable to obtain information on the crystal structure of PVA, because we were considering only a single polymer chain.

Several models for the PVA crystal have been proposed and investigated[3-7]. Among these, Bunns[3a] and Sakurada's [3b] models are well documented.

Here, we investigate which model is most suitable in describing the crystal structure of PVA, using CNDO/2 methods in conjunction with the tight-binding approximation[8].

We designate Bunn's model as Model I and Sakurada's model as Model II. Calculations were carried out on an isotactic form of PVA. Numerical calculations were performed as in the previous papers[9,10]. Geometries used for the calculations are listed in *Table 1*. Distance a (*Figure 1*) was allowed to take values 2.8, 3.0, and 3.2 Å.

Two structures were studied for each model: in the first, the group O–H...O was assumed to be straight; in the other the angle φ(COH) was taken to be 105.937°[11]. The

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Table 1 Geometries of PVA

r(C–H), Å	1.09	a
r(C–O), Å	1.40	a
r(C–C), Å	1.55	a
r(O–H), Å	1.01	b
ϕ(CCC)	109.47122°	a
ϕ(COH)	105.937°[c]	a
ϕ(CCH)	109.332°	d
ϕ(CCO)	110°	d

a, Ref 11; b, Ref 12; c, see test for more details; d, Ref 10

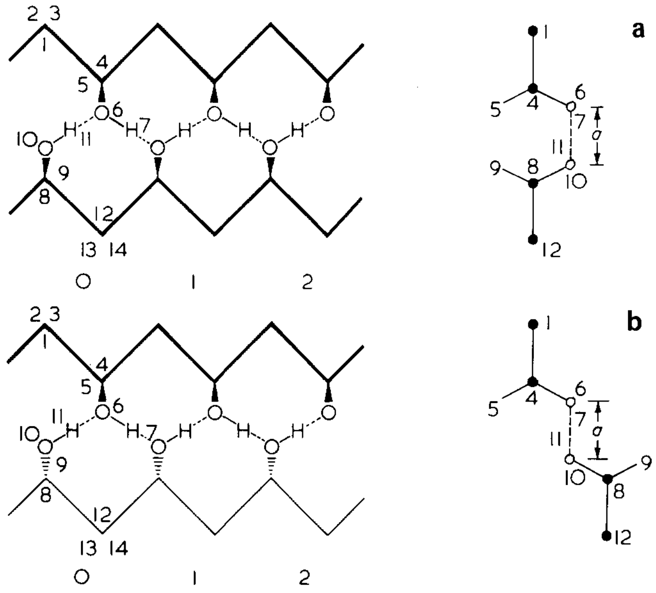

Figure 1 Two schematic models and atom and segment numberings of PVA crystal structures. (a) Bunn's model; (b) sheet structure model

latter model is distinguished by a prime.

RESULTS AND DISCUSSION

Results calculated are summarized in *Figure 2* and *Table 2*. The distance a at minimum energy was 2.8 Å for Model II′. For all the other three models the optimum distance was 3.0 Å, These values correspond well with *ab initio* calculations[12] for hydrogen bonding, and with experimental values[13]. Comparing Models I and II, II is estimated to be slightly more stable than I. Comparing Model I′ with II′, II′ is found to be more stable.

However, comparing Model I with I′, and II with II′, the models carrying a prime are more stable. From these results we can recognize that the model with a straight hydrogen bond for the type O–H ... O is not always the stable structure. Moreover from these results, it is suggested that Sakurada's model is more stable/reasonable than Bunn's.

We attempted to examine in detail the origin of the energy difference between I′ and II′. The energy difference between the two is estimated as 0.09 eV (2.07 kcal), and this is enough to predict the most stable structure for PVA.

As far as the total intrasegment energy is concerned, Model I′ is more stable than Model II′. However, in the case of the intersegment energy, Model II′ is more stable than Model I′.

One centre terms in the intrasegment energy calculations are smaller in Model I′, while two centre terms are smaller in Model II′. In the two centre term, the resonance and electrostatic terms favour stabilization of the II′ form, while the exchange term favours stabilization of the I′ form.

Consider now the intrasegment two centre term. The larger elements contributing to the energy difference between forms I′ and II′ are summarized in *Table 3*. Here the elements which have a plus sign stabilize the II′ form more than the I′ form, while those with minus sign stabilize the I′ form more than the II′ form. First we can consider that the following elements cancel out: (O10,H7) and (H11,H7); H13,H9) and (H14,H9); and (H13,O10) and (H14,O10). Therefore elements (H7,O6), (O10,O6), (H11,O6) and (H11,O10) are retained. The elements (H7,O6), (O10,O6), and (H11,O10) stabilize the I′ form,

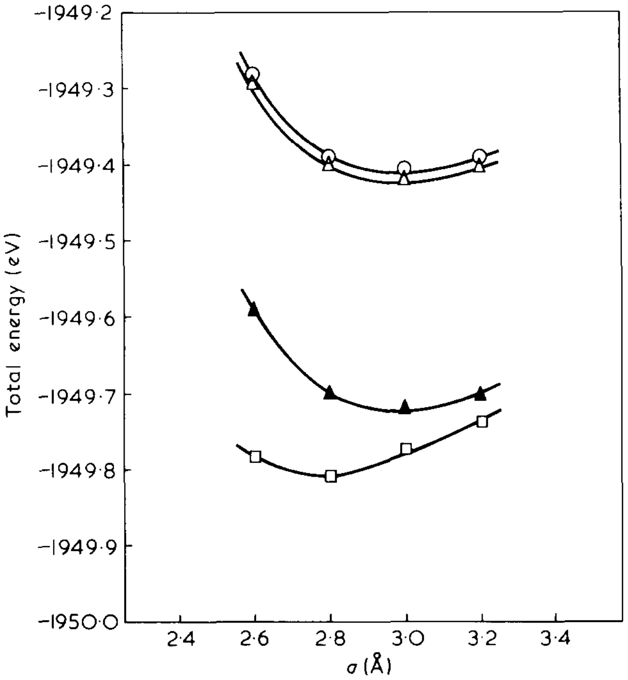

Figure 2 Total energy (eV) as a function of the distance a in the four models. ○, Model I; △, Model II; ▲, Model I′; □, Model II′

Table 2 Total energy (eV) of PVA[a]

Energy	I	I′	II	II′
Total	−1949.41	−1949.72	−1949.42	−1949.81
Total intrasegment	−1892.69	−1893.13	−1892.70	−1892.97
Total one centre	−1619.41	−1620.76	−1619.42	−1620.55
Total two centre	−273.29	−272.36	−273.28	−272.43
Resonance	−278.63	−278.06	−278.63	−278.16
Exchange	−65.60	−65.70	−65.60	−65.58
Electrostatic	70.94	71.40	70.94	71.31
Total intersegment	−56.71	−56.59	−56.72	−56.83
0–1 Total[b]	−28.27	−28.21	−28.27	−28.33
Resonance	−29.48	−29.41	−29.48	−29.56
Exchange	−4.72	−4.71	−4.72	−4.73
Electrostatic	5.92	5.90	5.92	5.96
0–2 Total	−0.08	−0.08	−0.08	−0.08

[a] Distance a (see *Figure 1*): I, II, and I′ - 3.0 Å, II′ = 2.8 Å

[b] For simplicity, 0–1 (segments) means the central and the first nearest neighbour segments, 0–2, 0–3, . . . refers to the central and the second, third . . . nearest neighbour segments. In the present article, up to 0–4 segments were taken into consideration for all polymers under study. Energy terms: absolute values less than 0.01 eV are not listed. The meaning of the energy terms is shown in Ref 10

Table 3 Large contribution elements on the energy difference (eV) between the forms I′ and II′ (I′–II′) in the intrasegment two centre term

	O6	H7	H9	O10	Total
Resonance					0.10
H7^{a}	–0.10				
O10	–0.05	–0.01			
H11	0.36	0.03		–0.10	
H13			0.09	–0.07	
H14			–0.09	0.07	
Exchange					–0.12
H7	–0.08				
O10	0.01				
H11	0.03			–0.08	
H13			0.03	–0.02	
H14			–0.03	0.02	
Electrostatic					0.09
H7	0.09				
O10	–0.08	0.05			
H11	–0.02	–0.07		0.09	
H13			0.01	0.01	
H14			–0.01	–0.02	
Total					0.08
H7	–0.09				
O10	–0.12	0.04			
H11	0.36	–0.04		–0.09	
H13			0.12	–0.08	
H14			–0.12	0.08	

Energy terms: absolute values less than 0.01 eV are not listed. (See Ref 10 for more details.)

[a] Atom numberings are shown in *Figure 1*

but the element (H11,O6) stabilizes the II′ form.

Considering intersegment terms, the 0–1 term is dominant in determining the energy difference. In more detail, the 0–1 term (*Table 4*) indicates II′ is more stable than I′. The exchange term is nearly equal both in the I′ and II′ forms. The resonance term stabilizes the II′ form more than the I′ form. However, the electrostatic term is smaller for the I′ form than for the II′ form. As shown in *Table 4*, the elements (^{0}H13,^{1}H9) and (^{0}H14,^{1}H9) cancelled each other out. Therefore elements (^{0}O6,^{1}O10) and (^{0}H7,^{1}O10) are retained. The former element stabilizes the I′ form, while the latter stabilizes the II′ form. This element (^{0}H7,^{1}O10) relates to ^{0}H…^{1}O10 hydrogen bonding. That is, it is easier to form hydrogen bonding in Sakurada's sheet structure than in Bunn's structure.

CONCLUSIONS

In conclusion, present calculations suggest that Sakurada's sheet structure is more stable than Bunn's model. However, the calculated energy differences between the structures considered are not as large as those between the total energies. The conclusion may therefore be ambiguous. Here the dominant elements in stabilizing the sheet structure are the resonance terms, (H11,O6) and (^{0}H7,^{1}O10),

Table 4 Large contribution elements on the energy difference (eV) between the forms I′ and II′ (I′–II′) in the intersegment 0–1 term

	^{1}H9	^{1}O10	Total
Resonance			0.15
^{0}O6^{a,b}		–0.03	
^{0}H7		0.18	
^{0}H13	0.04		
^{0}H14	–0.04		
Exchange			0.02
^{0}O6		0.01	
^{0}H7		0.01	
^{0}H13	0.01		
^{0}H14	–0.01		
Electrostatic			–0.06
^{0}O6		–0.04	
^{0}H7		–0.01	
Total			0.12
^{0}O6		–0.06	
^{0}H7		0.18	
^{0}H13	0.06		
^{0}H14	–0.06		

Energy terms: absolute values less than 0.01 eV are not listed. (See Ref 10 for more details.)

[a] Atom numberings are shown in *Figure 1*

[b] For example, (^{0}O6, ^{1}H9) refers to the interaction element between the O6 oxygen atom in the central segment and the H9 hydrogen atom in the first nearest neighbour segment

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