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Role Of Serine In The Structural Modifications From Silk I To Silk II

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ABSTRACT

We have examined the role of serine, essentially oxygen atom belonging to serine, in the Crank-shaft structure of silk I and β-pleated structure of silk II by studying the intra-and inter-weak hydrogen bonds. We observe that the presence of serine in the structural refinement does increase the crystalline order and hence the stereo-chemical energy in silk I phase making it an unstable phase which on a slight mechanical pretex, changes over to silk II modification.

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KEYWORDS

Bombyx mori;
Dipeptide;
Hexapeptide;
LALS;
WAXS;
β-pleated.

INTRODUCTION

Silk fibroin of Bombyx mori has two crystalline modifications namely silk I and silk II. Crystal and molecular structure of silk I has been reported by Loth and Keitz[1,2] and also recently by Kenji Okuyama, Somashekar, Naguchi and Ichimura[3] , wherein they report the unstable Crank-shaft molecular model (Space group $P2_12_12_1$ L-form). Crystal and molecular structure in silk II(Space group $P2_1$ D-form) of raw silk fibre has been recently reported by Sangappa, Mahesh and Somashekar[4] and in earlier paper by Marsh, Corey and Pauling[5]. We have examined the detailed structure of silk I and silk II using the available X-ray data using both dipeptide (Ala-Gly) and hexapeptide $(Ala\text{-}Gly)_2$-Ser-Gly sequence of molecular model. The corresponding (ϕ,ψ) angles of Ala and Gly in dipeptide and hexapeptide sequence of silk I and silk II are given in TABLE 1. In hexapeptide sequence, the other atomic co-ordinates of serine is the same as that of alanine except that of oxygen. Using fractional co-ordinates of atoms obtained from dipeptide and hexapeptide sequence of both silk I and silk II, and employing PLATON[6] we have simulated the x-ray powder patterns and they are given in figures 1, 2. In these figures we have also presented the experimental WAXS patterns of silk I(Cp fraction)[7] and silk II(a single degummed Bombyx mori fiber)[8]. A comparison of both peak positions and peak intensities with the hexapeptide and dipeptide simulated patterns, indicates that, in both the cases, the hexapeptide model gives a much better agrement. In addition to this, a comparison of simulated patterns for silk I and silk II

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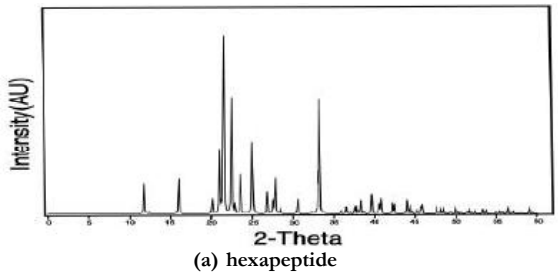
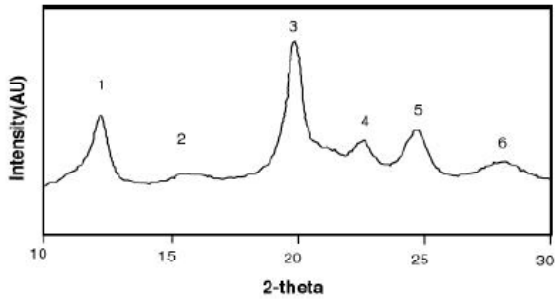
TABLE 1 : Refined details of silk I and silk II with hexapeptide and dipeptide repeating units

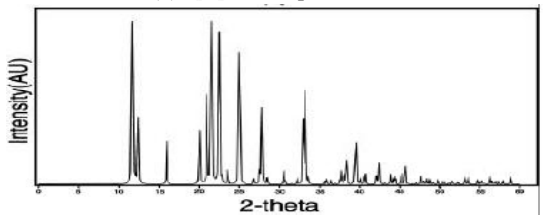
Refined parameters	Silk I(Hexapeptide)	Silk I(Dipeptide)	Silk II(Hexapeptide)	SilkII(Dipeptide)
Torsion angle(^{0})				
ϕ_{Ala}	-112.09*	-109.91	-147.99*	-147.07
ψ_{Ala}	-5.55*	-2	143.68*	143.16
ω_{Ala}	179.23*	173.41	178.62*	179.91
χ_{ser}	174.71	------	79.76	------
*ϕ_{ser} , ψ_{ser} , ω_{ser} same as Alanine				
ϕ_{Gly}	71.39	73.3	-144.64	-145.34
ψ_{Gly}	-98.66	-101.76	146.48	146.21
ω_{Gly}	-172.1	179.9	178.19	179.91
R-factor				
R_c	0.07	0.12	0.17	0.17
R_w	0.08	0.14	0.17	0.17
Stereo-chemical Energy(σ)	8.25E+003	2.00E+004	2.35E+003	1.35E+003
Hydrogen bonds(Inter) Between anti-parallel chain Distance(Å) angle(^{0})	N(Ala)...O(Gly) (2.98,76.9)	N(Ala)...O(Gly) (2.87,77.7)	----------	----------
Intra-molecular Distance (Å) angle(^{0})	N(Gly)..O(Ala)(3.13,125.6) N(Ala)..O(Ala)(2.88,86.4) O(Ser)..O(Ala)(2.65,88.5)	N(Gly)..O(Ala)(3.02,123.7) N(Ala)..O(Ala)(2.84,83.6)	N(Ala)..O(Ala)(2.74,165.2) N(Ala)..O(Ser)(3.1,136.0) O(Gly)..N(Gly)(2.7,161.5) O(Ser)..O(Ala)(2.8,89.5)	N(Ala)..O(Ala) (2.75,164.63) N(Gly)..O(Gly) (2.74,162.24)



(a) hexapeptide

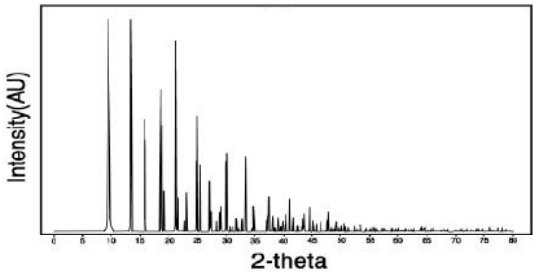


(b)dipeptide sequence

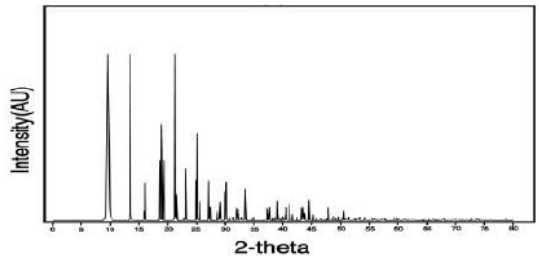


(e) Tetsuo Asakura et al (2001)[7]

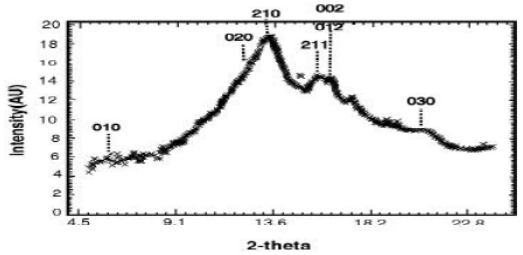
Figure 1 : Simulated X-ray powder patterns of silk I using (a) hexapeptide (b)dipeptide sequence and (e) Tetsuo Asakura et al (2001)[7]



(c) hexapeptide



(d) dipeptide sequence



(f) Manfred Rossle et

Figure 2 : Simulated X-ray powder patterns of silk II using (c) hexapeptide(d) dipeptide sequence and (f) Manfred Rossle et al.(2004)[8]

with hexapeptide model indicates that the presence of serine increases crystalline order in silk I phase and decreases the crystalline order in silk II phase. In silk I phase, the increase in intensity is observed in the Bragg planes(011),(020) and in silk II phase the decrease in intensity is observed in (200),(301) and(302) planes. These changes in intensity of certain Bragg planes are due to concentration of oxygen(Ser), which results in additional inter-and intra-weak hydrogen bonds. In dipeptide model of silk I phase, such interactions lead to significantly better ordered polymer network and hence increased intensity of(020) reflection. The same description cannot be attributed to silk II phase wherin we have energeticaly favourable β-pleated structure. Addition of serine in the refinement procedure does not alter polymer chain ordering/conformation which is already in low energy state. Further we would like to recall the observation made by Kratky and Schauenstain[9], that there is spreading of low angle X-ray diffraction patterns due to a periodic distortion of the pseudo structure associated with the occurence of serine residues at regular intervals in the sequence. It is also found that[11] with increase in fiber diameter, the crystallinity decreases and viceversa. From our computation of simulated pattrens, we observe that the presence of serine, essentially oxygen atom of this amino acid, in the molecular model for refinement does increase the crystallinity and hence leads to decrease in the fiber diameter. Also, stereochemical energy expressed as the contact σ in LALS[11] (Linked Atom Least Squares) decreases considerably in silk II(β-pleated structure) phase with the presence of serine when compared to silk I(Crank shaft structure) showing that the silk I is less stable than silk II.

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