

Molecular motion in poly(amino acid)s: 7. Molecular motion in the β -form crystal of silk fibre

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Molecular motion in the β -form crystal of fully annealed silk fibre was investigated by means of an X-ray diffractometer, an infra-red spectrophotometer, and thermal and viscoelastic measurements. There was ordinary thermal expansion in stable sheets up to 250°C, in which chains were bound side by side with intermolecular hydrogen bonds. It was shown that the slip motion between the sheets started at about 200°C, accompanied by active motion and/or slight scission of the side chains packed in the intersheets. Melting of the crystal occurred due to scission of the intermolecular hydrogen bonds above 260°C in the sheets. Melting was accompanied by degradation of the molecular chains.

Keywords Molecular motion; β -form crystal; silk fibre; slip motion; hydrogen bond; melting; degradation

INTRODUCTION

Magoshi¹ observed dispersion with a maximum at about 240°C in the temperature dependence of the dynamic loss tangent ($\tan \delta$) for degummed silk fibre. He proposed without any direct evidence that the dispersion was due to molecular motion in the crystalline phase.

In preceding papers^{2,3}, the temperature dependence of the spacings for unannealed silk fibre was studied. It was proposed that the molecular motion in the crystal occurred with weakening intermolecular hydrogen bonds.

Natural poly(amino acid) such as silk fibroin is polymerized from only the L-type amino acids⁴. Thus if silk fibre is fully annealed, the silk fibroin chains will fall into a stable and dense packing and only vibrate thermally in the crystal, especially in the sheets.

This paper considers the molecular motion in the β -form crystal for fully annealed silk fibre.

EXPERIMENTAL

In order to anneal the degummed silk fibre of *Bombyx mori*, it was gradually heated up to 200°C at a heating rate of 0.5°C min⁻¹ and held at this temperature for 1 h *in vacuo*.

X-ray measurements were performed on a Rigaku Geigerflex 2028 diffractometer equipped with a scintillation counter and a pulse height analyser, using Cu K α radiation. The temperature was controlled within an accuracy of $\pm 0.5^\circ\text{C}$ under N₂ gas flow.

Infra-red measurements were made on a JASCO A-302 infra-red spectrophotometer equipped with a heating device. The i.r. spectra were measured by the KBr tablets method in dry N₂ gas atmosphere.

The temperature dependence of stress was measured by a Shinko Tsushin strain meter at a heating rate of 2°C min⁻¹ in a silicone oil bath.

Thermo-mechanical properties were measured on a

Rigaku thermo-mechanical analyser (t.m.a.) at a heating rate of 10°C min⁻¹ in N₂ gas atmosphere.

The temperature dependence of $\tan \delta$ was measured by a Rheovibron DDV-IIC dynamic viscoelastometer at a frequency of 110 Hz and at a heating rate of about 2°C min⁻¹.

RESULTS AND DISCUSSION

It is important in investigating the molecular motion in the β -form crystal of silk fibre that one observes the temperature dependence of the interchain and intersheet periodicities. The spacings for the 002 and 400 reflections observed on the equatorial X-ray diffraction intensity curve correspond to the intersheet and interchain periodicities. Since the diffraction intensity of the 400 reflection, however, was very weak, the spacing for 201 reflection was used as the interchain periodicity. *Figure 1* shows the temperature dependence of the spacings for the 201 and 002 reflections. The interchain periodicity for 201 reflection increases linearly and slightly up to 250°C. This result indicates ordinary thermal expansion of the lattice in stable sheets up to 250°C. The slope of the temperature dependence of the intersheet periodicity for the 002 reflection increases above about 210°C. This increase of the slope implies active motion and/or slight scission of the side chains packed in the intersheets and weakening of the interaction force between the sheets. Consequently the stable sheets will slip past each other in the crystal above 210°C. The linear thermal expansion coefficients (α) were calculated from the slopes of the lower line in *Figure 1*: α_{201} and α_{002} are 2.0×10^{-5} and $7.4 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$, respectively. The thermal expansion is found to be anisotropic, which means that the interaction force between the sheets is weaker than the intermolecular hydrogen bonding force within the sheets. This result supports the appearance of slip motion between the sheets, as de-

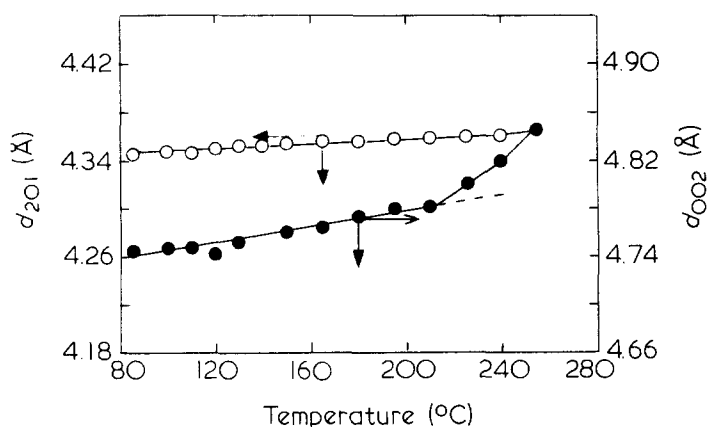


Figure 1 Temperature dependence of spacings of 201 and 002 reflections for the β -form degummed silk fibre

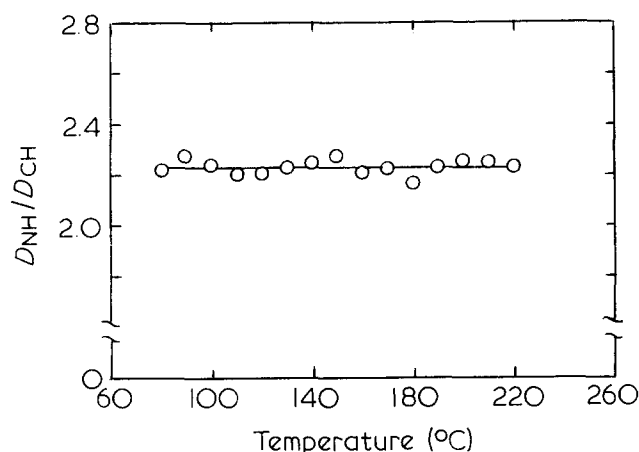


Figure 2 Temperature dependence of the absorbance of NH stretching band of hydrogen-bonded NH groups normalized to that of CH stretching band for the β -form degummed silk fibre

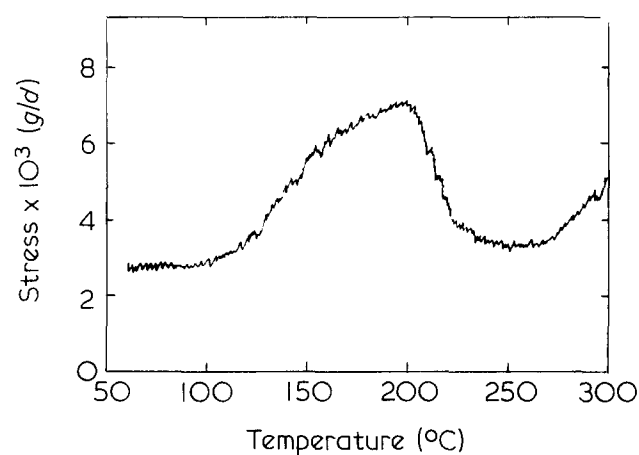


Figure 3 Temperature dependence of stress parallel to the fibre axis for the β -form degummed silk fibre

scribed above. The diffraction intensities of the 201 and 002 reflections are constant up to 210°C and decrease above 210°C. The decrease of the diffraction intensity of the 002 reflection means that the β -form crystal is disordered in the direction of the intersheet periodicity as it expands when the temperature rises above 210°C, and affects the diffraction intensity of the 201 reflection.

Figure 2 shows the temperature dependence of the absorbance of NH stretching band for hydrogen-bonded NH groups normalized to that of CH stretching band (D_{NH}/D_{CH}) for a deuterated sample. The hydrogen atoms in the NH groups in the amorphous phase are so easily deuterated that the undeuterated NH groups are in the crystalline phase. D_{NH}/D_{CH} is almost constant up to 220°C. This indicates that the hydrogen bonding force and the number of hydrogen-bonded NH groups in the crystal do not change; in other words, the sheets are very stable.

The crystal in the silk fibre is oriented parallel to the fibre axis and the orientation coefficient is 88%⁵. Thus if the silk fibre is stretched statistically and dynamically parallel to the fibre axis, the stress will relax by slip motion between the sheets above 200°C. There was a stress relaxation at about 200°–250°C as shown in Figure 3. A dispersion also appeared at about 190°–250°C in the temperature dependence of $\tan \delta$ as shown in Figure 4. Thus it is reasonable to suppose that slip motion between the sheets causes the relaxation phenomena above 200°C. Furthermore, the slip motion appeared at about 190°–250°C as an elongation parallel to the fibre axis when the temperature rose under small load (Figure 5). According to Kajiyama *et al.*^{6,7}, slip motion between the α -helical chains appeared above 140°C. On the other hand, the α -form crystal of silk fibroin (helical chains form sheets by intermolecular hydrogen bonds just as does the β -form⁸) was disordered in the direction of the intersheet per-

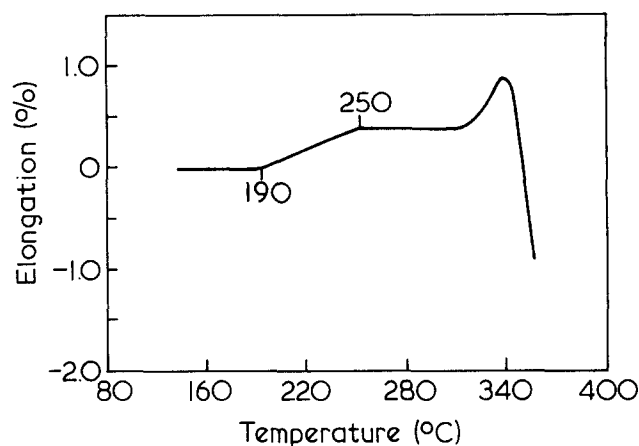


Figure 4 T.m.a. thermogram for the β -form degummed silk fibre

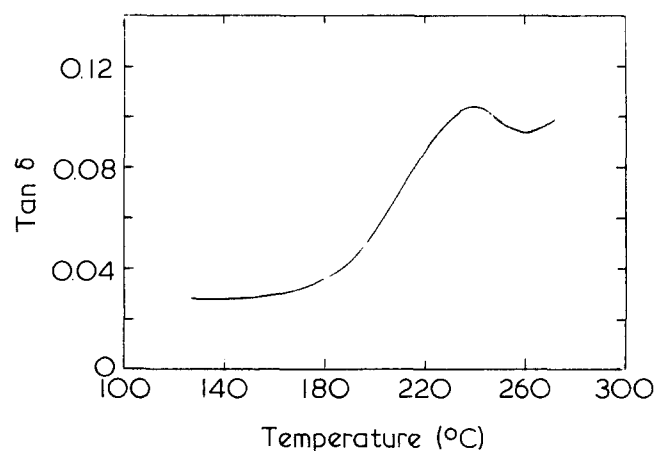


Figure 5 Temperature dependence of $\tan \delta$ for the β -form degummed silk fibre

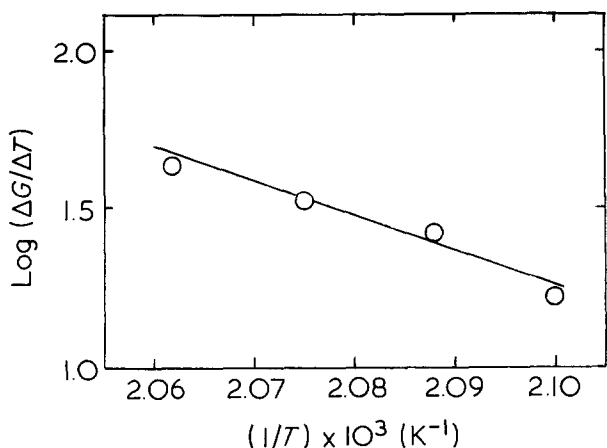


Figure 6 The logarithm of the change of stress with temperature as a function of the reciprocal of the absolute temperature for the β -form degummed silk fibre

iodicity above 210°C and became soft³. Therefore, the slip motion of the α -form crystal of silk fibroin is similar to that of the β -form crystal of silk fibre rather than that of the α -helical chain in poly(γ -methyl-D-glutamate).

To evaluate the transition energy (ΔE) of slip motion, the logarithm of the change of stress (G) with temperature (T), i.e. $\log(\Delta G/\Delta T)$, was plotted as a function of the reciprocal of the absolute temperature (Figure 6). Since $\log(\Delta G/\Delta T)$ decreases linearly, as seen in the Figure, an Arrhenius type equation (1) is assumed:

$$\log(\Delta G/\Delta T) = K - \Delta E/2.303RT \quad (1)$$

where K is a constant and R is the gas constant. The calculated transition energy is 204.2 kJ mol⁻¹, which is similar to the result of a dispersion map of $\tan \delta$ ($\Delta E = 216$ –216.9 kJ mol⁻¹) for unannealed silk fibre².

Stresses were generated above about 120° and 260°C as shown in Figure 3. The first stage of stress generation mainly corresponds to the oriented chains in the amorphous phase shrinking due to the entropic elastic force rather than to water evaporation, because the silk fibre

was used immediately after heating up to 150°C in a silicone oil bath. The second stage of stress generation is attributed to the onset of shrinkage of the sheets in the crystal due to scission of the intermolecular hydrogen bonds, and is with the melting phenomenon. There was a plateau region in the t.m.a. thermogram (Figure 5). The plateau region means that the load balances with the entropic elastic force due to the melting of the crystal.

Weight loss occurred above 215°C, but it was very slight up to 250°C. This implies that the relaxation phenomena appearing in Figures 3 and 4 is accompanied by slight degradation at the side chains which have a large kinetic energy at this temperature. On the other hand, the degradation increased abruptly above 250°C. An endothermic reaction appeared above 260°C on a d.s.c. thermogram. These observed temperatures agree with the onset temperature of the second stage of stress generation as seen in Figure 3. Thus the endothermic reaction corresponds to melting of the crystal and degradation of the molecular chains.

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REFERENCES

- 1 Magoshi, J. *Zairyo* 1973, **22**, 499
- 2 Nagura, M., Goto, K. and Ishikawa, H. *Kobunshi Ronbunshu* 1979, **34**, 389
- 3 Nagura, M. and Ishikawa, H. *Polym. J.* 1980, **12**, 201
- 4 Shultz, G. E. and Schirman, R. H. 'Principles of Protein Structure', Springer-Verlag, New York, 1978, p. 6
- 5 Ishikawa, H. 'ZokuKenshi noKozo', Shinshu University, 1980, p. 213
- 6 Kajiyama, T., Kuroishi, M. and Takayanagi, M. *Chem. Lett.* 1973, 659
- 7 Kajiyama, T., Kuroishi, M. and Takayanagi, M. *Macromol. Sci. B* 1975, **11**, 121
- 8 Hirabayashi, K., Ishikawa, H., Kakudo, M. and Go, Y. *Sen-i Gakkaishi* 1968, **24**, 397