Small angle X-ray scattering patterns in silk fibres

Silk fibroins are known to give excellent wide-angle X-ray patterns[1–6], but till date, small angle long-spacing patterns have not been reported. Using synchrotron radiation and 2D imaging plate system we have recorded small angle patterns for six different varieties of silk fibres.

Silk fibres are of importance in view of their extensive use in the textile industry. Cocoons of the silk worm (*Bombyx mori*) are the raw product to reel silk fibres. First the cocoons were cooked in boiling water for two minutes to soften the sericin and later transferred to a water bath at 65°C for two minutes. Then the cocoons were reeled in warm water with the help of a reeling equipment known as Epprouvite.

X-ray patterns were recorded at the DND-CAT Synchrotron Research Center, Advanced Photon Source, Argonne National Laboratory, USA. The energy of the X-ray beam from an insertion device (ID) was tunable from 7 to 18 keV. The ID, double crystal monochromator, first, second, third set of adjustable slits, and the sample were located at 0, 30, 35, 54, 66 and 68 m respectively, along the X-ray beam path from the synchrotron orbit. The size of the square beam was defined at the first and second sets of the slits, which were both sets of 100 μm. The 2-D CCD (Mar) detector had 2048 × 2048 pixels with a 16-bit intensity scale and a circular active area of 133 mm diameter was used. In all cases the detector was used in a 4 × 4 binning mode at a resolution of 512 × 512, with an effective pixel size of 258 μm. The detector was placed at the end of an evacuated 8-inch pipe fitted with Kapton® windows on both ends. The sample to detector distance was adjustable from a few cm to 8.5 m. The detector was placed at a distance of 722 mm away from the sample and the ID was tuned to an energy of 8.048 keV, corresponding to the wavelength 1.541 Å At this distance the detector covered a scattering angle 2θ corresponding to the range in the scattering vector magnitudes $5 \times 10^{-3} < q (< 4\pi \sin\theta/\lambda) < 4 \times 10^{-1}$ Å^{1}. The recordings corresponding to 10 s exposure time are shown in Figure 1 *a–f* for all the samples. The patterns are close to the four-point pattern. After correcting for the air scattering, the meridional scattering profile has been used to obtain the radius of gyration, correlation length and the invariant[7,8] (Q).

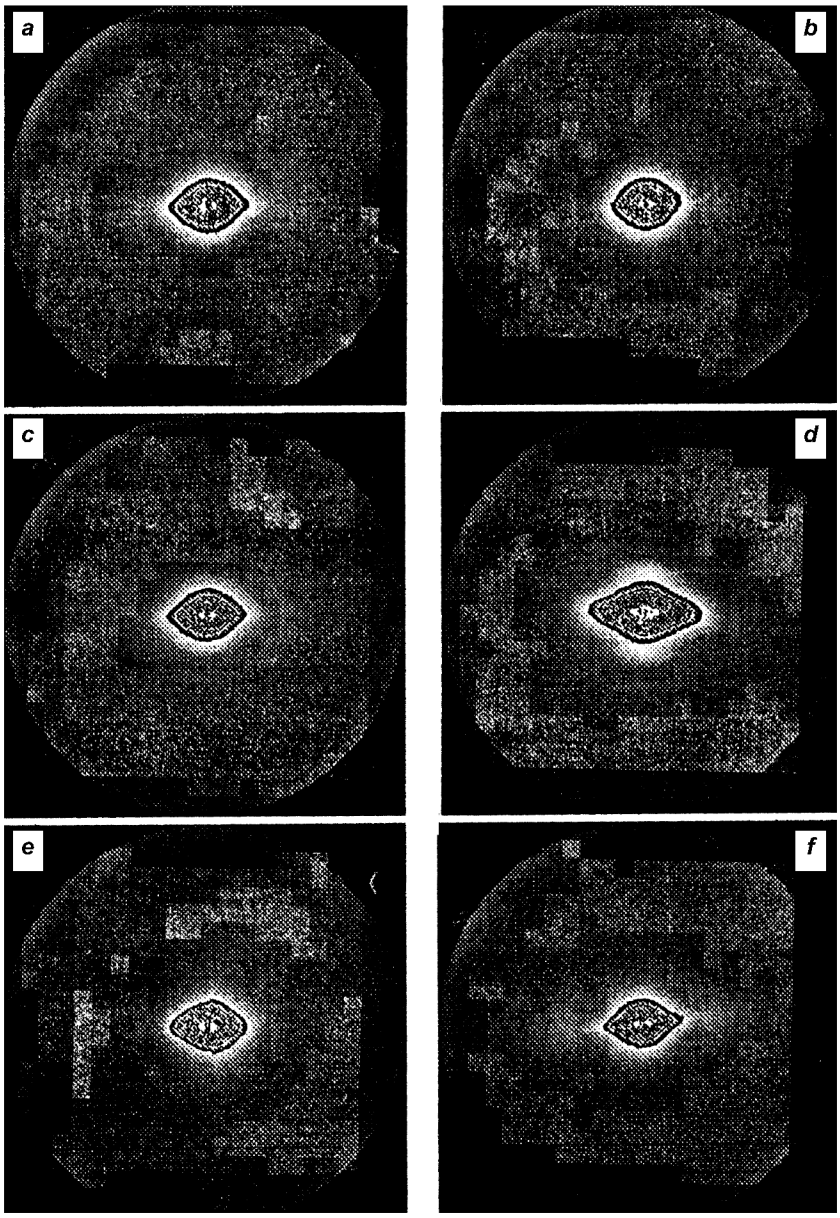

Figure 1. Small angle X-ray scattering pattern with an exposure period of 10 s of ***a***, Pure Mysore silk; ***b***, Bivoltine; ***c***, Nistari; ***d***, Muga; ***e***, Tassar; and ***f***, Multivoltine.

Normally one observes a four-point pattern when the layer normal is inclined to the fibre axis. The fact that we do not have a clear four-point pattern indicates that layer-like arrangement of alternate amorphous and crystalline regions is not an ideal lamellar morphology.

Radius of gyration has been estimated using Guinier's plot and it is a measure of the size of the silk polymer molecule. Correlation length is the mean width of the correlation function which is computed by taking the Fourier transform of the given SAXS curve.

The invariant Q is the second moment of the observed SAXS curve and it

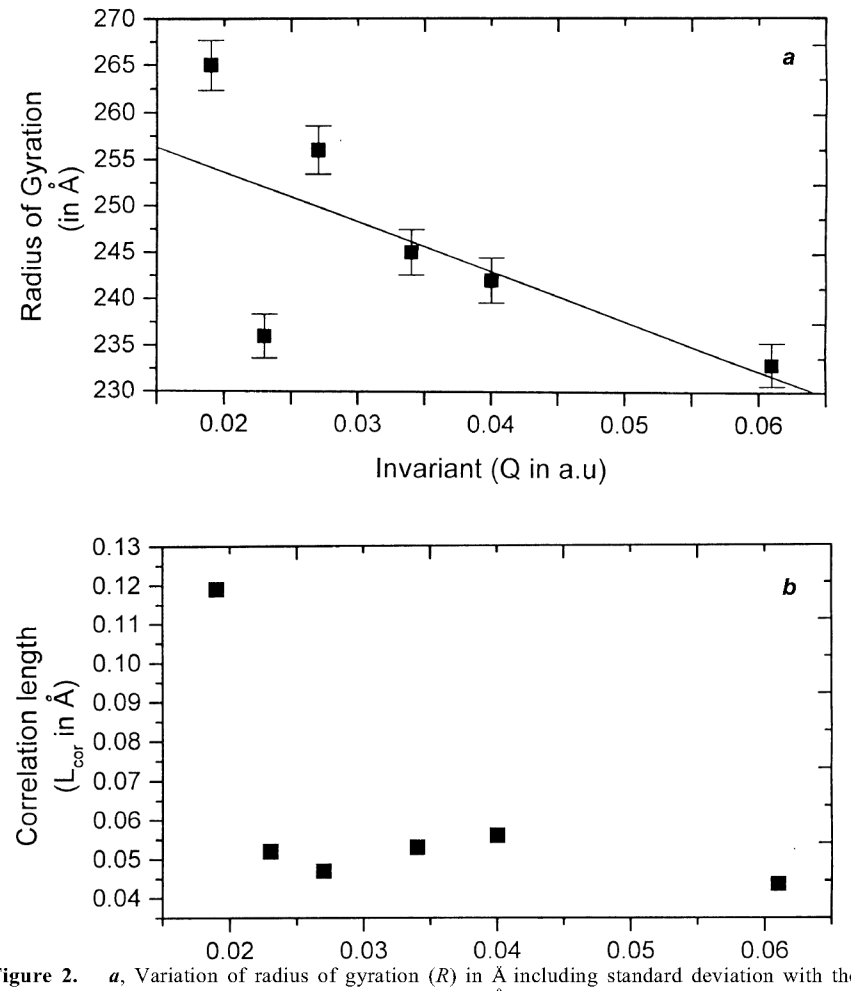

Figure 2. ***a***, Variation of radius of gyration (R) in Å including standard deviation with the invariant (Q). ***b***, Variation of correlation length (L_{cor}) in Å with the invariant (Q).

is a measure of the electron density contrast.

Figure 2 *a* indicates that with increase in Q, there is a general trend of decrease in the values of radius of gyration, whereas in Figure 2 *b* the correlation length initially drops to 0.05 and then there is no significant variation with Q in these silk fibres. This is in contrast to observed increase in lamellar value in $Nylon_{6,6}$ with increase in the invariant[9]. This is due to change in volume fraction of the crystalline lamellae and also the change in electron density contrast between the crystalline and amorphous regions of silk fibres.

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