apparently stronger equatorials, and the other weaker visible reflections add nearly as much again. This extra crystalline intensity just happens to be offset by the large integrated intensity of the continuous background, ignored in the simple estimate.

Comparison with Previous Results. Work and Morosoff[13] used X-ray diffraction to determine the orientation distribution of crystals in fibers of spider major ampullate silk. They give values of $\langle\cos^2\phi_3\rangle$ for molecular chain orientation in the crystals of 0.776 and 0.788, with $f \approx 0.67$. This corresponds to fwhm of about 70° for a Gaussian distribution, much larger than our uncorrected result of 20.5° ($f = 0.97$). The silk did come from different species of spiders, but the diffraction patterns (Figures 6 and 7 of ref 13) are very similar to Figure 1. Values of $\langle\cos^2\varphi\rangle$ for (120) are also given in ref 13. They are close to 0.11, and this corresponds to a fwhm of 48° for Ψ, again much larger than the present result (14°, Table 1) and larger than seems possible from the figures in ref 13. If 0.11 is taken as $\cos^2[\text{fwhm}(\varphi)]$, then a more reasonable value of 19° is obtained for the fwhm of Ψ. The overall average orientation was measured for the same fibers using birefringence[32] with results of $f = 0.43$ for *Nephila cruentata* and $f = 0.65$ for *Araneus marmoreus*. The difference is much larger than the difference in crystalline orientations, it prevents useful comparisons with the current result of $f = 0.39$ for *N. clavipes*.

The NMR results for orientation were a fwhm of 5 $(-2 + 8)$° for the alanine crystals, and 75 ± 5° for the remainder of the alanine residues.[10] The deuterated methyl group is perpendicular to the chain, so the comparison to X-ray data should be made with the orientation of the equatorial reflections and not the derived chain axis orientation. These are approximately 11° and 30°, as shown in Table 1. Although the NMR results focus only on the alanine residues, and the X-ray results reflect the entire sample, the NMR-determined fwhm for the crystalline fraction is in good agreement with the present data. One possible interpretation of this agreement is that the crystalline regions are largely comprised of alanine. The second component in the X-ray data, with a fwhm of 30°, is much more highly oriented than the average orientation found by NMR for the rest of the alanines. This suggests that alanine residues make up only a small part of this component.

The crystallinity derived here, 12%, is lower than the usually quoted values of 30−50%.[2] However, these values are often of uncertain origin, deriving from analogy with *B. mori* silk, which is more crystalline than the spider dragline silk. NMR has shown that 40% of the alanine residues in spider dragline silk reside in highly oriented crystalline domains.[10,11] From the chemical composition, this is about 10% of the whole fiber. If the crystals are pure poly(alanine), this is the crystallinity and it is the same as the X-ray result, allowing for the uncertainties of measurement. However, it is easy to explain a greater value for the X-ray crystallinity, since the smaller glycine residues may be incorporated in a crystal with the poly(alanine) structure. This would increase the crystalline content beyond the alanine content. More generally, exact agreement should not be expected because the two methods are sensitive to different things. In a simple model of perfect small crystals of poly(alanine), the regions of three-dimensional spatial order and the regions where the alanines are restricted in their motion are the same. In any more complicated situation, they may be different.

Mechanical modeling of the stiffness of the fibers, either by regarding it as a filled elastomer[2,5] or using a micromechanical composite model[33] requires more than 12% crystallinity. Termonia used 50% volume fraction of crystals, and still needed a surface layer of intermediate mechanical properties around the crystals in order to model the stiffness and strength of the fiber.[33] This indicates that the "oriented amorphous" material must have mechanical properties that are much better than that of regular amorphous material.

Conclusions

A detailed analysis of X-ray fiber pattern from spider silk shows a well oriented crystalline component —orientation function 0.981—which makes up only 12% of the material. Another one third of the fiber material is oriented—orientation function 0.87—but the X-ray reflection from this component is radially so broad that it the material is amorphous by the normal standards of X-ray diffraction. The remainder is amorphous and isotropic. The crystal size obtained by applying the simple Scherrer formula to the crystalline peak widths is approximately 5 × 2 × 7 nm along **a**, **b**, and **c**. These dimensions are lower limits, in that an imperfect crystal of greater size would show similar broadening. The lateral sizes are also the averages of broad distributions.

The crystals clearly re-orient when the fiber is stretched, and the observed change is very close to the prediction of affine deformation. If the material is acting as a filled elastomer, with the crystals as rigid inclusions, then they should reorient in this way. A stretched elastomer should also increase the orientation of the amorphous material, and when it is fully relaxed the orientation should fall to zero. There was some indication of a reorientation of the amorphous material in these experiments, but the scatter was large and the strain range very limited. A larger strain range can be obtained by starting with a fiber fully relaxed by the action of water, and these experiments are in progress.

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