Biopolymers

Silken spider chains

from Paul Calvert

SILK is best known as the fibre spun by the larvae of many moths to form a protective cocoon for pupation; most commercial silk is from the domesticated larvae of the moth *Bombyx mori* with some 'wild' silk from the Tussah silkmoths *Antheraea*. A great variety of other insects also make silks, fibres of which find uses as supports, shelters and attachments, but the real silk specialists are spiders. Despite the efforts, in the eighteenth century, of M.Bon of Montpellier, who made himself stockings and gloves from spider silk, it has caught on neither commercially nor scientifically. Research papers on spider silk, such as that by Gosline *et al.* on page 551 of this issue, are therefore rare treasures.

Most silks are proteins, containing a predominance of glycine, alanine and serine. For instance, *B. mori* silk is close to a simple repeating (Gly-Ala-Gly-Ala-Gly-Ser) structure. By comparison, spider dragline silk stands out in having 10 per cent each of proline and glutamic acid. In properties and structure, the silks are first cousins to the nylon fibres. Commercial nylons, however, do not have such a high density of amide units as the silks because it makes for strong hydrogen bonding, which results in a melting point too high for processing and a fibre that is too water-sensitive. A shirt that becomes elastic when wet could be a little discomforting; but for animal silk, hydrophilicity is essential as it permits the fibre to be spun from aqueous solution.

The paper of Gosline *et al.* builds on the work of Work and colleagues who showed there to be a 50 per cent contraction, along with a twofold volume increase, when spider dragline fibres are allowed to swell in water (*Textile Res. J.* **47**, 650; 1977 and **52**, 349; 1982). (The Work papers are worth reading at least for the description of how to milk a spider of its dragline.) This water sensitivity is particularly strange in that the dragline must support the falling spider and yet the twinned lines of the garden spider, *Araneus diadematus*, which can weigh 0.65 g, break at 1 g (see F. Lucas *Discovery* **25**, 20; 1964; Lucas & Rudall *Compreh. Biochem.* **26B**, 475; 1968). Such a close strength specification seems to leave little room for rapid deceleration and none for unpredictable properties.

Gosline *et al.* show that the uptake of water converts the amorphous regions of the fibre to a rubbery state. Silks, like synthetic fibres, are composites of small crystalline regions and rigid glassy amorphous regions. For spider silks, no information on the proportions of the two phases seems to have been published, but most natural and textile fibres are at least 50 per cent crystalline. On swelling in water the glassy regions become plasticized so that the chains are mobile, and possibly some of the crystals melt. The result is that the structure relaxes, the chains in the amorphous regions coil up and the modulus decreases by a factor of 1,000. If the fibre is stretched and dried, the original properties return. This process is similar to heat shrinkage of synthetic fibres; for instance, drawn polyester fibres, when heated to 240°C, shrink by 75 per cent and the modulus drops 50-fold (M.P.W. Wilson *Polymer* **15**, 277; 1974).

The size of the modulus drop in spider silk is surprising. The final modulus of 10^7 Pascals is more like that of true rubber than that of a partly crystalline polymer — the modulus of a 50 per cent crystalline polyethylene is 50 times higher. This suggests that the water-resistant crystallinity of spider silk is very low and that most of the dry fibre is oriented glassy material. A reasonable guess would be that the high proline and glutamic acid contents are responsible for preventing much crystallinity developing. This appears strange when the spider could have produced a strong water-resistant fibre of the silkmoth or nylon type. What the spider gains is a fibre that is about twice as strong as *Bombyx* silk and has a very much larger extension (30 per cent) before it breaks. This extension will gradually slow the falling spider rather than there being a thread-breaking jerk. The penalty, apparently, is a rather disconcerting change in behavior in the rain.

Synthetic fibre makers should be impressed by the range of properties attainable within the silk group and spurred in their efforts to control polymerizations to the point where silk-like structures can be duplicated. As a general rule it is very hard to increase the strength of a material without also decreasing the extension to break; the way that both are improved at once in spider silk, compared with silkmoth silk, is impressive. □

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Cell physiology

Cellular site of calcium regulation

from Andrew P. Somlyo

THE concentration of free (ionized) calcium (Ca^{2+}) regulates not only muscle contraction, but also a variety of other cellular processes including glycogen metabolism, secretion, membrane transport and permeability. In muscle, an intracellular organelle system, the sarcoplasmic reticulum (SR), can store and release calcium, and so regulate cytoplasmic Ca^{2+} in the absence of a change in total cell calcium. But what plays the part of the SR in non-muscle cells? The suggestion that it is the mitochondria seems to have stemmed, in part, from the great attention given to mitochondrial Ca^{2+} transport[1,2]. When exposed to high (unphysiological) concentrations of Ca^{2+}, mitochondria can accumulate very large amounts of calcium phosphate salts, nearly enough to be turned to stone. As known since the time of Lot's wife, this is an eye-catching device, but not conducive to much further activity. Here I shall summarize some of the compelling arguments why opinion is shifting strongly away from mitochondria towards the endoplasmic reticulum (ER) as the regulator of cell calcium.

Subcellular fractions containing ER and showing Ca^{2+}-accumulating activity have now been isolated from a wide variety of tissues[3-10]. In some instances, contamination by ER vesicles may account for active calcium uptake attributed to some other organelle, such as synaptic vesicles[11] and, perhaps, vertebrate retinal discs. The ER calcium pump resembles the SR system in using ATP (although other high-energy phosphates can substitute) as an energy source, in being enhanced by calcium-precipitating anions such as oxalate and phosphate and in being inhibited by SH-reactive organic mercurials[10]. Moreover, a phosphorylated 118,000-molecular weight protein, thought to be analogous to the phosphorylated intermediate of the SR Ca-ATPase, has been identified in ER from rat liver[12]. The affinity of several isolated ER preparations for Ca^{2+} is sufficiently high ($K_m \sim 0.2$–$0.6\mu M$) to reduce cytoplasmic Ca^{2+} to the low levels typical of normal resting cells. It has yet to be determined whether there are specialized regions of the ER with a high capacity for storing calcium, like the terminal cisternae of striated muscle SR. The identity of the subfractions of ER largely responsible for calcium-accumulating activity is not known, although it is probably not inherent to the rough endoplasmic reticulum[6].

The introduction of new techniques has greatly advanced the identification of the ER as the source and sink of intracellular calcium in non-muscle cells. For example, whereas squid axons are sufficiently large to permit the manipulation of their intracellular Ca^{2+} by internal perfusion[13,14], for smaller cells, membrane permeabilization by agents, such as saponin, has been used to manipulate intracellular Ca^{2+}. This has allowed investigators to identify the ER as