Materials science

Synthetic polymer self-assembly

Paul Calvert

THE normal way to make a synthetic fibre is to polymerize material as an emulsion or suspension to form a powder, then to melt or dissolve that powder, squirt the liquid through a spinneret and draw it out into a strong fibre. In contrast, natural fibres such as collagen, cotton and wool seem to associate directly into fibres as they are polymerized. Certainly they are not melt-processed. So far there have really been no synthetic polymers that order in this way, but H.S. Yoon, on page 580 of this issue, now describes such self-association in an aromatic polyamide, a close relative of the commercial fibre Kevlar.

Mainstream polymer science is concerned with the behaviour of linear flexible macromolecules, mostly close relatives of the commercial polymers developed between 1930 and 1960, including polyethylene, polystyrene, aliphatic polyamides (nylons) and a dozen or so others. The molecules are very flexible, with weak forces between the chains, so that the polymer normally has the form of a random walk in three dimensions. To make a strong fibre it is necessary to pull the chains out straight and align them parallel to the fibre axis. This is achieved during drawing when the polymer is warmed and stretched to several times its original length.

During the 1970s the Dupont company developed aromatic polyamides such as poly-*p*-phenylene terephthalamide (see figure) which behave quite differently from the flexible polymers. The chains

Poly-*p*-phenylene terephthalamide.

have very little conformational freedom because both the phenyl group and the amide link are essentially planar and rigid. They can coil up, but only by a series of small changes in direction. It was found that if the solvent conditions are correct, these polymers form liquid-crystalline solutions where the molecules spontaneously align parallel to one another. These aligned solutions can be spun to strong fibres without a separate drawing stage. These and other liquid-crystalline polymers have been the subject of intense investigation over the past few years, but polymer science has not yet absorbed stiff chains and flexible chains into one seamless overall treatment.

Collagen is hydrophilic and bristles with hydrogen bonds that link chains together

into threefold helices, resulting in a very stiff structure. To form fibrous tendons it is necessary to export the polymer from the cell to the deposition site. The polymer is formed as procollagen, a short-chain soluble form with bulky terminal sections that stop the chains aggregating. Outside the cell the end sections are enzymatically removed and the chains form triple-helical rods of tropocollagen, 260 nm long. These rods assemble into rather weak fibres and then crosslink to form strong, high-molecular-weight, collagen fibres.

The significance of the new work of Yoon is then that the fibres form by a process very similar to the self-assembly of natural polymers. The polyphenylene terephthalamide system has much in common with silk or collagen — it is a stiff

chain with strong interactions between chains and strong solvent interactions. Yoon's most important result is that the polymer forms a metastable gel structure when polymerized in dimethylacetamide, and that this then slowly polymerizes further and aggregates into highly oriented fibres.

In discussing natural materials, it is tempting to ascribe all the control and self-organizing effects to powerful enzymatic mechanisms, because similar effects are not usually observed in synthetic materials. It may be that we are often also looking at the wrong types of materials. Flexible-chain polymers are relatively easy to characterize because they can be melted and dissolved. As polymer science spreads out into the less tractable polymers, we may find several phenomena which have previously been observed only in nature. Whether that will teach us more about polymers or more about nature remains to be seen. □

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Superconducting ceramics

Temperatures rise higher still

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IN a recent News and Views report¹, we described the remarkable discovery of superconductivity near 40 K in the oxides (La, X)₂CuO₄ with X = Ba, Sr, Ca. The rapid pace of events made that report obsolete even before it was published: Chu and co-workers had reported² that the critical temperature, *T*_c, had more than doubled to 93 K in another yttrium-based oxide, Y-Ba-Cu-O. Even as that work appeared in *Physical Review Letters* on 2 March, other laboratories had confirmed the results and shortly afterwards it was shown that many other elements could be substituted for yttrium to give values of *T*_c in the neighbourhood of 90 K. Indeed, one of these, La-Ba-Cu-O, contains the same elements as the original material discovered by Bednorz and Müller³, which set this sequence of events into motion. Although this higher *T*_c phase contains the same elements, it has a different composition and crystal structure. A special session devoted to these developments was held on 18 March in New York at the annual meeting of the American Physical Society (see pages 432–433 of last week's issue).

The degree to which these discoveries have excited the condensed-matter physics and materials-science communities was borne out by the extraordinary character of the session, which was attended by a vocal, enthusiastic audience of more than 2,000 scientists, many of

whom viewed the proceedings by closed-circuit television. In an appreciation of the historical significance and wide interest in the proceedings, a videotaped record has been prepared and copies can be obtained from the American Physical Society.

The session consisted of about 60 presentations and lasted from 7.30 p.m. until the early hours of the morning, with some diehards holding out until 6.00 a.m. After introductory remarks, the session began with presentations and discussions by a panel of experimentalist 'pioneers' in the field consisting of K.A. Müller (IBM Zurich), S. Tanaka (University of Tokyo), C.W. Chu (University of Houston), Z.X. Zhao (Chinese Academy of Sciences) and B. Batlogg (AT & T Bell Laboratories). By this time all the groups had prepared the yttrium-containing oxides, and the superconducting phase (the original report of 93 K was for a multiphased sample) had been identified as YBa₂Cu₃O_m with *m* ~ 7. Impressive strides had also been made in fabricating the superconductors using ceramic processing techniques, and Batlogg evoked an enthusiastic response from the large crowd by displaying a roll of pliable tape made from unfired material. The initial presentations of experimental findings were followed by short talks by P.W. Anderson (Princeton University), V. Kresin (Lawrence Berkeley Laboratory), A.J. Freeman (Northwestern University),