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### MATERIALS SCIENCE

# Synthetic polymers with biological rigidity

Brush-like polymers with a rigidity similar to that of polymers in living cells have been synthesized and used to build force-responsive materials. The advance opens the door to applications in drug delivery and tissue engineering. SEE LETTER P.651

#### MARGARET LISE GARDEL

The diverse physiology of cells and tissues is underpinned by materials consisting of macromolecules whose mechanical behaviour allows organisms to control and maintain their shape 1. The construction of synthetic versions of these materials could allow artificial cells and tissues to be made, but preparing such materials has long been a major challenge. On page 651 of this issue, Kouwer et al.<sup>2</sup> report that they have produced the first synthetic polymers whose rigidity can be tuned to mimic that of a wide range of their biological counterparts. The authors' achievement will facilitate the construction of polymer networks that have highly tunable, force-responsive behaviour\*.

Synthetic polymers, such as polyethylene, nylon and silicone, were an important class of material in the twentieth century, finding diverse applications as paints, adhesives, fibres and plastics. But these polymer molecules behave rather like cooked spaghetti, because they have little rigidity along their length. Their flexibility is entirely due to the randomization of the polymer chains' configurations by thermal energy — the energy available to act on molecules at ambient temperature.

Biological polymers, which are formed from amino acids or nucleic acids, are very different. These materials are ubiquitous in nature, and include DNA; cytoskeletal filamentous proteins, such as actin, microtubules and intermediate filaments; and scaffolding molecules in the extracellular matrix, such as collagen and fibrin. Biological polymers are much more rigid than chemical polymers, and so are similar to partially cooked spaghetti. Because of this high rigidity, the energy required to bend biological polymers is comparable to that available from thermal energy,

\*This article and the paper under discussion<sup>2</sup> were published online on 23 January 2013.

such that they bend much less than synthetic polymers at ambient temperature. This inherent rigidity makes the mechanical behaviour of biological polymers at the bulk scale qualitatively different from that of synthetic polymers<sup>3</sup>.

Kouwer and colleagues have discovered that polyisocyanopeptide polymers, grafted with flexible side chains of a different polymer, serve as mimics of a protein structure known as a  $\beta$ -sheet, and self-assemble into helical structures similar to those formed by DNA and actin filaments. Moreover, the authors report that the polymers aggregate into bundles when heated in solution (Fig. 1), similar to the bundles formed by collagen and fibrin.

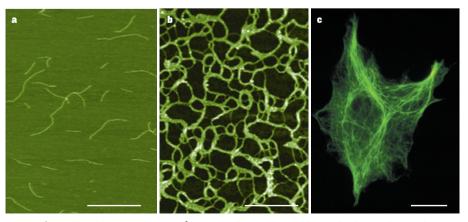
One way to characterize the rigidity of a material is through its persistence length: the higher the persistence length, the more rigid the polymer. The persistence length of biological polymers varies from about 100 nanometres for DNA to 1 millimetre for microtubules; by comparison, the effective persistence length of a flexible synthetic polymer is typically about 0.1 nm. When the authors characterized the

mechanical properties of their polymers using force-spectroscopy techniques, they found that single polymer chains had a sizeable persistence length, 500 nm. They also found that this increased for larger bundles, consistent with the idea that rigidity correlates with bundle diameter. Kouwer and co-workers' materials therefore represent the first semiflexible synthetic polymers to have tunable persistence lengths, and so might serve as building blocks for biomimetic materials.

One of the main consequences of increasing polymer rigidity is that it alters the mechanical response of crosslinked networks of the polymer. The mechanical rigidity of a material is described by a parameter known as the elastic modulus. For networks of flexible polymers (such as rubber), the elastic modulus depends only weakly on the density of the polymers or crosslinker connections. By contrast, in networks of semi-flexible polymers, the elastic modulus depends more strongly on these parameters<sup>3</sup>.

A second characteristic of networks of semi-flexible polymers is that their response to stress is highly nonlinear<sup>3</sup>. Under increasing loads, conventional polymeric materials simply stretch until they break. Networks of semi-flexible polymers, however, stiffen under increasing load and have an elastic modulus that increases dramatically at a critical strain. Both of these distinctive properties of semi-flexible networks are typical of biological polymers, and are also found in Kouwer and colleagues' synthetic polymers.

Because of their unusual mechanics, the authors' materials are highly responsive to applied stress: as the applied stress increases,



**Figure 1** | **Bundling fibres.** Kouwer *et al.*<sup>2</sup> report the first synthetic polymer that has rigidity similar to that of biological polymers such as DNA. Single chains of the polymers (a) form bundles (b) when heated in solution. The polymers most resemble those found in intermediate filaments (c) inside cells. Scale bars:  $\mathbf{a}$ ,  $\mathbf{b}$ , 250 nm;  $\mathbf{c}$ , 85  $\mu$ m.

the elastic modulus also increases to minimize changes in deformation. This suggests that the materials will maintain their shape when subjected to a wide range of externally applied stresses. What's more, the polymers' highly tunable rigidity means that tiny quantities of polymer could be used to make materials that have a wide range of stiffnesses.

Kouwer and colleagues' polymers most closely mimic those found in intermediate filaments (Fig. 1), a class of intracellular polymer that is crucial for cell adhesion and migration and for maintaining cell shape<sup>4</sup>. It will be exciting to see if the authors' approach, or other approaches for making semi-flexible polymers, can be expanded to make synthetic mimics of DNA, actin filaments and microtubules. Another challenge will be to find a way of adding mechanochemically active components<sup>5</sup> — those that transform chemical energy into mechanical work — to the polymer. This would enable filaments to be made that exhibit exotic polymerization behaviour, such as treadmilling (in which one end of a filament grows while its other end shrinks), or which

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For more on synthetic polymers, see: go.nature.com/xbhltj create dynamic instabilities or crosslinks, to form the basis of a molecular motor

The ability to build 'active' soft materials that respond to external chemical and mechanical signals will provide opportunities in the areas of condensed-matter physics and materials science for years to come. Such materials might allow the construction of artificial cells and tissues that are more closely compatible physiologically with their counterparts in humans than currently available materials, so that they might be used in the next generation of drug-delivery and tissue-engineering technologies. Active soft materials might also change the way in which we engage with the physical world, by forming the basis of highly responsive and malleable materials and machines. Kouwer and co-workers' polymers are an exciting first step in these directions. ■

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CONDENSED-MATTER PHYSICS

# Hidden is more

Physicists have puzzled over a hidden electronic order in a uranium-based material for decades. A new theory attributes it to not just a single but a double breaking of time-reversal symmetry. SEE ARTICLE P.621

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magnet sticks to a fridge door, but an aluminium spoon does not. This distinction is well understood in terms of the different ways in which the many billions of billions of electrons are collectively organized inside these materials. In a magnet, the electrons form an order: their tiny spins line up along a particular direction, producing an aggregate magnetic moment, whereas in aluminium these spins are randomly oriented. On page 621 of this issue, Chandra et al. propose a different kind of electronic order, which could resolve a riddle that has confounded physicists for more than a quarter of a century.

Much of the fascination and challenge of condensed-matter physics lies in figuring out how the electrons are organized in their microscopic world to produce the macroscopic properties observed in the laboratory. The tendency of the electrons in a magnet to develop

order is analogous to that of water molecules to form a rigid spatial pattern as the liquid freezes into ice. This electronic order, called ferromagnetism, breaks time-reversal symmetry: if the time direction were reversed, so would be the direction of the magnetic moment.

The condensed-matter system studied by Chandra and colleagues is URu<sub>2</sub>Si<sub>2</sub>. This uranium-based compound is a member of a broad class of materials called strongly correlated electron systems, in which a large Coulomb repulsion between the electrons tends to produce spectacular physical phenomena — such as the high-temperature superconductivity observed in copper-based ceramics. This large repulsion in strongly correlated electron systems contrasts with the weak interactions found in many of the materials used in technology, such as silicon, aluminium or even ordinary magnets.

In the mid-1980s, researchers discovered<sup>2-4</sup> clear signatures of an electronic order in



## **50 Years Ago**

Living with the Atom. By Prof. Ritchie Calder — The author gives his ... contributions to a discussion on responsible reporting. It is difficult for the reporter to steer a course between the attractive liveliness that approaches the sensational, and the dry factual report that few will read ... There is a fear and distrust of scientists, as people who ought to be above human fallibility but unforgivably err like everyone else; and he points out the dangers also of the responsibility for major decisions resting in the hands of men who do not know sufficient about science to be able to challenge with any confidence the advice that comes to them from their experts. There is something in this, although one would feel that a knowledge of men and a flair for consulting the right experts is what brings men to high office. From Nature 2 February 1963

## 100 Years Ago

'Luminous halos surrounding shadows of heads' — The phenomenon referred to ... can also be seen on grass when the sun is low in the sky ... If the grass surface is near to the observer, a faint halo is seen to surround the shadow of his head, and this is more easily perceived if he is moving than if standing still; my attention was indeed first attracted to this phenomenon when bicycling. J. Evershed I happened to be watching our

shadows as we passed along the edge of a field of young green wheat, when, to my surprise, I noticed a halo of light round the shadow of my own head and neck ... The fact that each observer sees only his own halo obviously precludes this phenomenon from having been the origin of the halos recorded in sacred writings round the head of Christ and others. L. L. Fermor From Nature 30 January 1913