Polymers with bio-inspired strength

Biopolymers, ingeniously designed by nature, can combine different mechanical properties and even adapt to changes in their environment. By imitating the structure of a protein, chemists have now made a strong, tough polymer that also exhibits elastic properties.

Stuart J. Rowan

As in many other areas of science, polymer chemists have been drawing inspiration from nature since the dawn of the field; for example, Carothers invented nylon while trying to mimic the properties of silk. More recently, scientists have been inspired by a diverse range of animals and plants, such as the gecko foot, the sea cucumber dermis and the lotus leaf, resulting in new materials that imitate these natural models.

In most of these cases, the synthetic materials mimic the structural characteristics of the natural systems in an attempt to bestow them with the desired properties and/or function of these biosystems. Now, in Journal of the American Chemical Society, Zhibin Guan and his colleagues at the University of California, Irvine, introduce a new synthetic polymer inspired by the protein titin, which shows a rare combination of mechanical properties.

Titin, a very large protein found in muscles, combines strength (how much stress the material can be exposed to before it breaks), toughness (how much energy the material can absorb) and elasticity (the ability to recover its original size and shape once the stress is released). In general, polymers do not possess such a combination of properties. For example, rigid plastic polymers (such as polycarbonates) are generally very strong but also tend to be brittle, whereas a flexible plastic such as polyethylene does not show the strength of a rigid plastic but will deform under stress, thus absorbing more energy, which makes it a tough material. Neither of these materials, however, shows significant amounts of elasticity. So how does titin manage to combine these properties?

Its modular, multidomain structure (Fig. 1a) seems to be key to this ability. At a very basic level, titin consists of over 300 folded (immunoglobulin-like) domains that consist primarily of β-sheet structures. If one imagines stretching such a multidomain polymer, the force on the chain will initially rise quickly with extension, until it reaches a level that breaks the non-covalent interactions within a specific domain. At this point that domain unfolds, thus reducing the force on the chain and preventing the covalent bonds from breaking. This process, which can be repeated until all the domains have been unfolded, makes the polymer both strong and tough. Furthermore, on removal of the force, the unfolded domains will automatically refold, bestowing elasticity on the material. In all, nature has developed a very elegant solution to the problem.

Inspired by this example, Guan and his co-workers designed a synthetic modular polymer that consists of domains made of a dimeric supramolecular motif — the quadruple-hydrogen-bonding 2-ureido-4[1H]-pyrimidone (UPy) dimer — constrained within a macrocycle (Fig. 1b). The concept here is that any stress on the polymer will result in decomplexation of the supramolecular dimer (Fig. 1c), similar to the unfolding of the protein domain. The supramolecular dimer was constrained within a macrocycle to encourage the reformation of the same intra-macrocyclic complex after removal of the stress — as opposed to the formation of dimeric complexes between the UPy units of adjacent polymer chains — thus enhancing the ability of the material to recover to its original state.

The resulting synthetic polymer shows very interesting mechanical properties. It is a relatively strong material (Young’s modulus of around 200 MPa) and undergoes large plastic deformations (maximal strain greater than 100%) with only a relatively small increase in stress, confirming that the material is also tough. Furthermore, the plastic deformation is not permanent. The material shows a gradual self-recovery over time (>18 h) at room temperature and a much faster, more complete recovery at higher temperatures (around 30 s at 80 °C). The researchers propose that on strain-induced breaking of the macrocyclic UPy dimer, intermolecular UPy supramolecular crosslinking dimers are formed, temporarily fixing the materials in the elongated state. This temporary ‘fixing’ behaviour is similar to that shown by shape-memory polymers, however, in this case the material is not permanently fixed at room temperature. Instead, it slowly reverts to the preferred intramacrocyclic UPy complexes, resulting in the recovery of the film’s original, pre-stressed dimensions. This interesting mechanical behaviour is directly related to the supramolecular motif placed along the backbone. When the UPy units were protected — which in essence prevents the formation of the supramolecular dimer — major differences in the mechanical properties were observed; the material obtained was...
brittle (it fractured at 7% strain) and showed no recovery abilities.

The multiomain supramolecular polymer described here mimics titin very elegantly but, as with most biomimetic systems, there is still a lot to learn. Although the slow recovery is an interesting feature of this system, a better titin mimic would recover its original shape at a much faster rate. As mentioned by Guan and co-workers, an improved understanding of the structure–property relationships of this class of materials is required. What is required structurally to access the desired titin–like properties? How do the size of the macrocycle, the strength and dynamics of the macrocycle, the size and molecular weight of the domains affect the mechanical behaviour of these systems?

Such insights will be essential not only to develop the next generation of titin mimics, but also to find simpler ways to synthesize materials with such properties on the scale required for commercial applications. Biological systems continue to inspire chemists, materials scientists and engineers alike, but of course to be able to mimic them we need to gain a better understanding of how nature achieves the specific materials properties required by the plant or animal. We have only scratched the surface of developing a detailed mechanistic understanding of nature’s solutions to its materials challenges. As this field grows we can expect the development of more biomimetic materials — such as the synthetic titin mimic highlighted here — that have new and unusual properties.

C–H Bond Activation

A radical non-metal solution

Converting methane into more useful and readily transportable compounds has previously required the use of metal-based oxo catalysts, but now sulfur and phosphorus are showing their mettle.

Robert H. Crabtree

The growing concern for energy production with a small carbon footprint has greatly raised the profile of C–H bond activation. A core problem of the field is the conversion of alkanes to any of a variety of more valuable functionalized products. As an example of an energy application, one such problem is the conversion of natural gas, methane, to a more readily transportable form such as methanol or ethane. Natural gas has a favourable carbon-to-hydrogen ratio relative to oil and coal and thus releases less carbon dioxide per unit energy output, but much natural gas is stranded at remote locations and cannot easily be transported to users because its boiling point is so low.

In one broadly useful mechanism for C–H bond activation, a metal oxo species abstracts a hydrogen atom from methane. Unfortunately, methane has unusually strong C–H bonds compared with other hydrocarbons, so it is difficult to persuade it to give up a hydrogen atom and react in a useful way; only very reactive species are so persuasive. If successfully formed, however, the resulting CH⁺ radical can either dimerize to give ethane or abstract an OH group from the metal hydroxy species, formed after hydrogen abstraction, to give methanol. The first pathway is a promising strategy for ethane production and the second has proved important in biological C–H activation as well as in functional synthetic models. Calculations⁴,⁵ suggest that the active form of the metal oxo is not always M=O as traditionally shown in textbooks, but the newly recognized oxyl radical form M·O⁺.

Recent papers by the groups of Giulia de Petris in Rome and Helmut Schwarz in Berlin extend this idea in an important way using gas-phase mass spectrometry data. In these studies, collisions between the reactants are stimulated by causing the charged species to travel through a neutral gas, in this case methane. The products are monitored through their mass using the Fourier transform ion cyclotron resonance (FT-ICR) technique. One advantage of this technique is that highly reactive species can be studied in the absence of complicating effects such as the presence of a solvent.

The workers were able to show that an oxyl group attached to a non-metallic element, sulfur or phosphorus, is just as capable of giving the key abstraction as the classical metal oxos. The specific species studied, SO₂⁺ and P₂O₅⁺ (Fig. 1), are not only radicals but also electrophiles, from the positive charge that they carry.

De Petris and colleagues investigated different pathways available to the reaction of SO₂⁺ with methane. Two were observed, one resulting in the formation of SOH⁺, and one at high pressure in which [CH₃−SO₂⁺] species were observed. A theoretical analysis combined with kinetic isotope studies revealed that the former reaction was a simple exothermic

References

Figure 1 | Ground-state structure calculated for (P₂O₅)⁺⁺ (phosphorus atoms in yellow, oxygen atoms in red). The blue isosurface indicates the spin density. The P–O distances (Å) are compared for the radical cation and the neutral [P₂O₅]⁻ (in parentheses). Reproduced with permission from ref. 4. © 2009 Wiley.