FANTASTIC PLASTICS

Polymers have infiltrated almost every aspect of modern life. Now they are being stretched to their limits.

BY MARK PEPLOW

NIK SPENCER/NATURE

Hermann Staudinger was a pacifist, but this was one fight he was determined to win. In 1920, the German chemist proposed that polymers — a broad class of compounds that included rubber and cellulose — were made of long chains of identical small molecules linked by strong chemical bonds[1]. Most of his colleagues thought this was arrant nonsense, and argued that polymers were merely looser aggregations of small molecules. Staudinger refused to back down, sparking feuds that spanned a decade.

Eventually, laboratory data proved that he was right. He won the 1953 Nobel Prize in Chemistry for his work, and synthetic polymers are now ubiquitous: last year, the world produced about 300 million tonnes of them. The molecular chains that Staudinger hypothesized have entered almost every aspect of modern life, from clothes, paint and packaging to drug delivery, 3D printing and self-healing materials. Polymer-based composites even make up half the weight of Boeing's most recent passenger aeroplane, the 787 Dreamliner.

So where will polymers go next? Some answers will come this week, when a once-per-decade workshop organized by the US National Science Foundation attempts to survey which new areas are emerging.

"The general trend — still continuing — is the expansion of polymers into applications that have not been traditionally theirs," says Tim Lodge, a polymer chemist at the University of Minnesota in Minneapolis and editor of the journal *Macromolecules*. That expansion has been driven by advances in every aspect of polymer science, he says. Researchers have developed new methods to synthesize and analyse molecules, improved theoretical models and created mimics of polymers found in nature. At the same time, says Lodge, attitudes to the science have changed. No longer do universities dismiss polymer science as too dirty, practical and industrial for academia. "Just about every chemistry department has someone doing polymer stuff now," he says, and frontier work on polymers is increasingly interdisciplinary.

It will need to be. Researchers have a growing toolbox of techniques with which to craft the chemical architecture of polymer strands, but they are often unable to predict whether the resulting compound will have the particular properties needed for, say, a membrane or a drug-delivery system. Meeting that challenge will demand a much deeper understanding of how the chemical structure of a polymer determines its physical properties, at every scale from nanometres to metres.

POLYMERS FOREVER

Polymers are everywhere — and therein lies the problem. "Most polymers we use in everyday life are from petroleum-based products, and although they're durable in use, they're also durable in waste," says Marc Hillmyer, director of the Center for Sustainable Polymers (CSP) at the University of Minnesota. An estimated 86% of all plastic packaging is used only once before it is discarded[2], producing a stream of waste that persists in waterways and landfill, releases pollutants and harms wildlife (see page 263).

That is why the past decade has seen an explosion of interest in polymers that are made from renewable resources and biodegrade easily and harmlessly. Polymers based on natural starch are already on the market; so too is synthetic polylactide (PLA), which is made from lactide or lactic acid derived from biological sources, and which is found in products from tea bags to medical implants.

But sustainable polymers still make up less than 10% of the total plastics market, says Hillmyer. One hurdle is that they cost too much. Another is that the monomer building blocks of natural polymers tend to contain more oxygen atoms than are found in the fossil hydrocarbons of petroleum. This affects the polymers' properties — stiffening the materials, for example — which can make it difficult for them to directly replace cheap and flexible plastics such as polyethylene and polypropylene. Turning natural polymers into exact molecular matches for conventional ones takes some sophisticated chemistry.

One alternative approach is to beef up sustainable polymers such as PLA by blending them with conventional polymers. This route typically has downsides, such as rendering some plastics less transparent. But CSP researchers have got around that problem by adding just 5% by weight of a low-cost, petroleum-derived polymer that contains some sections that are hydrophobic — water-insoluble — and others that are hydrophilic, or water-soluble[3]. These additives cluster together to create spherical structures, which render PLA substantially tougher without reducing its transparency.

Hillmyer's team has also made[4] a partially recyclable form of polyurethane foam, which is found in a host of products, including insulation, seat cushions and gaskets. The recipe for this polyurethane includes a low-cost polymer called poly(β-methyl-δ-valerolactone) (PMVL), based on monomers made by modified bacteria. Heating the foam to above 200 °C breaks down the polyurethane so that the monomers can be extracted and used again.

It remains to be seen whether these sustainable polymers can be commercialized. "Often the biggest challenge is to do it at scale, which requires favourable economics," says Hillmyer. He thinks the field needs to establish general design rules that predict how a monomer's chemical structure affects the rate, temperature and yield of polymerization reactions, and how the resulting polymers will interact with other materials. His team has developed such guidelines for PMVL's constituents[5], and last year formed a spin-off company at the CSP called Valerian Materials to exploit these principles.

Some researchers are pursuing another trick: rather than stringing together bioderived monomers, they are learning to use natural polymers directly. Cellulose, for example, consists of glucose molecules strung together into chains, which in turn line up to form strong fibres, or fibrils, that make up the stiff cell walls of plants. In many places, the cellulose chains form crystalline chunks that are up to 20 nanometres wide and hundreds of nanometres long, and that can be chemically extracted from cellulose pulp. Proponents say that these crystals could be used for applications such as strengthening composites, forming insulating foams, delivering drugs and providing a scaffold for tissue repair[6].

Cellulose nanocrystals and longer nanofibrils are now produced on a commercial scale, but the commercial applications do not yet go much beyond stiffening paper or thickening fluids. Christoph Weder, director of the Adolphe Merkle Institute for nanoscience at the University of Fribourg in Switzerland, says that it will take a lot more work to reduce costs and demonstrate unique advantages for sustainable polymers. "We really need a road map for biobased polymers," he says.

> ***"Just about every chemistry department has someone doing polymer stuff now."***

SKIN IN THE GAME

In a mixed-up world, polymers can restore some order. Polymer membranes already serve as molecular sieves for separating gases, desalinating seawater and keeping molecules apart inside fuel cells. But they could have a much bigger impact in the future, says Lodge. "There are so many problems that could be solved by better membranes."

Separating mixtures with membranes takes a lot less energy than does distillation, in which a liquid is heated to evaporate its components at different temperatures. It also requires much less space than using scrubbers, devices in which pollutants are trapped by chemical reactions. Membranes made from polymers are not only cheap to make at large scale, but can cover large areas without acquiring structural defects that let the wrong molecules pass through.

Gas-separation membranes are already used industrially to tease hydrogen and carbon dioxide from natural gas. But improved membranes could tackle harder tasks, such as distinguishing between the very similar hydrocarbons propane and propene. Tougher, chemically robust membranes could operate at higher temperatures to remove carbon dioxide from hot flue gases.

Membrane chemist Benny Freeman of the University of Texas at Austin is hoping to improve the treatment of waste water from gas fracking operations, in which water is forced into rock to split it open and release natural gas. After use, the water is so dirty that standard filtration membranes quickly get clogged, so the water must be put under high pressure to push it through, and the membranes must be cleaned with chemicals that shorten their lifespan. But Freeman has found a way to sidestep that problem by giving the membranes a gossamer-thin coating of polydopamine, which mimics the waterproof glue used by mussels to cling onto rocks. Piloted at a fracking water-treatment facility near Fort Worth, Texas, the polydopamine coating halved the pressure needed to push water through the membrane, which could result in smaller, more efficient treatment systems[7]. The team has already used these membranes to build units for the US Navy, so that ships can purify oily bilge water before dumping it.

In December 2015, the US presidential administration launched a 'moonshot for water' to boost water sustainability, and as part of that effort the US Department of Energy plans to establish a desalination-research hub in 2017. Polymer membranes will have a big role in that effort, says Freeman. "We're slated to see a huge increase in efforts to expand the use of polymers in that space."

To design better desalination membranes, researchers will need to be able to predict how factors such as the distribution of charged chemical groups in a polymer affects its permeability to ions. Earlier this year, Freeman and his colleagues published[8] what he believes is the first model to do just that, which could enable chemists to build particular properties into a membrane by tailoring its chemical substituents and cross-linking the molecules. "I'm on a mission to get people to ask these kinds of questions about structure–property relations, which could really guide synthesis," he says.

The ultimate separation membrane could be just one molecule thick. These 2D polymers are surfing the wave of enthusiasm for single-layer materials that followed the isolation of graphene just over a decade ago.

The flat polymers are not just very thin films of ordinary, linear polymers. Instead, they have an intrinsically 2D chemical structure that looks like a fishing net, with a regular, repeating mesh full of molecule-size openings. They can also carry a wide variety of chemical decorations on their surfaces, so that each opening can be precisely engineered to allow certain molecules through and bar others.

But creating 2D polymers is tough. If just one of the holes in the growing mesh closes up in the wrong way, the membrane could buckle into a 3D mess. Polymer chemist Dieter Schlüter of the Swiss Federal Institute of Technology in Zurich worked on this problem for more than a decade before achieving success in 2014.

His approach relies on coaxing carefully designed monomers to form a crystal. A blast of blue light then triggers a chemical reaction between monomers in the same plane, creating a new crystal made up of stacked polymer layers. These can be peeled off to give individual 2D sheets just one monomer thick (see ‘Chemical peel’).

Using the same approach, Schlüter and Benjamin King, head of the chemistry department at the University of Nevada, Reno, have independently produced different types of 2D polymer[9,10]. Now collaborators, the two researchers hope that they will soon be able to make these sheets in kilogram batches, easily enough to distribute samples to research groups around the world.

Schlüter admits that he has faced scepticism about whether 2D polymers will flourish. “But that’s healthy,” he says. “And I’m very stubborn — I will not give up, I’m convinced of the great potential this development has.”

BOUTIQUE POLYMERS

Widely used polymers such as polystyrene and polyethylene are spectacularly boring in one sense: they repeat the same monomer over and over again. Their one-note tune is especially monotonous when compared with the quadraphonic symphony of DNA, which encodes an entire genome with 4 monomers; or the baroque masterpiece of a protein, drawing from 23 amino acids to build a complex 3D structure.

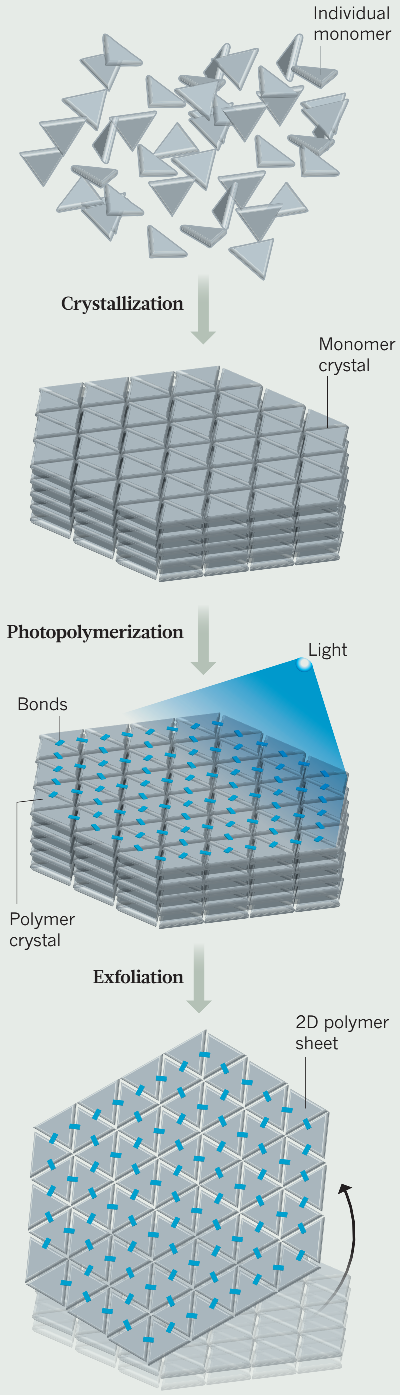
One of the most challenging frontiers of polymer research is to tailor synthetic polymers with the same precision, so that chemists can fine-tune the electronic and physical properties of their products. “It’s become very fashionable in the past five years,” says Jean-François Lutz, a macromolecular chemist at the University of Strasbourg in France. Sequence-controlled polymers would contain monomers in a predetermined order, forming strands of a very specific length.

Last year, a team led by Jeremiah Johnson, a chemist at the Massachusetts Institute of Technology in Cambridge, showed[11] that they could achieve that kind of control through iterative exponential growth — first uniting two different monomers to make a dimer, then connecting two dimers to make a tetramer, and so on. Modifying each monomer’s chemical side-chains between cycles adds complexity, and a semi-automated system can make the process less laborious[12].

Johnson is now studying how his sequence-controlled polymers might be used in drug delivery. A dozen drugs approved by the US Food and Drug Administration use a polymer called polyethylene glycol to shield them from the body’s immune system, improve their solubility or prolong their time in the body. Johnson says that a sequence-controlled polymer could provide a more predictable biological effect, because every strand would be the same length and shape, and its chemistry could be carefully designed to assist its drug cargo in the most useful way.

CHEMICAL PEEL

To make 2D polymer membranes, chemists first coax the monomers to form a 3D crystal, then shine a blue light to link monomers lying in the same plane. This allows them to peel off one sheet at a time.



Sequence-controlled polymers could also store data in a more compact and inexpensive form than can conventional semiconductor technology, with each monomer representing a single bit of information. Last year, Lutz demonstrated[13] a key step towards that goal. He used two types of monomer to represent digital 1s or 0s, and a third to act as a spacer between them. The monomers contained chemical groups that allowed them to connect only to the growing polymer, rather than reacting with each other randomly. The string of 1s and 0s could be read by watching how the polymer broke apart inside a mass spectrometer.

Earlier this month, Lutz showed that a library of different polymer strands could encode a 32-bit message[14]. That pales by comparison with the 1.6 gigabits that have been stored in artificial DNA molecules (see go.nature.com/2b2ve0u). But momentum is growing for polymer data storage. In April, the Intelligence Advanced Research Projects Activity (IARPA), a US agency that funds high-risk research for the intelligence community, drew representatives from the biotechnology, semiconductor and software industries to a workshop on the subject. “There’s a vibrant and growing community of researchers working on this,” says David Markowitz, a technical adviser at IARPA who helped to organize the workshop.

But the approach still faces enormous technical challenges: current synthetic techniques are much too slow and expensive. The key to cracking the data-storage problem — and many other problems at the polymer frontier — will be to develop better ways to predict the properties of polymers and fine-tune their production. That will require a concerted effort. “We need to establish collaborations with physicists, materials scientists, theoretical chemists,” says Lutz. “We need to build a new field.” ■ SEE NEWS FEATURE PAGE 263, AND NEWS & VIEWS PAGE 276

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