Polymer Nanotechnology: the Quest for Motility

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We ask the question "what will a realistic nanobot look like?". The answer is something like a bacterium (such as e. coli) or a sperm. Both of these have a propulsion mechanism (a flagellum), a capsule containing a chemical payload and a system of sensors to detect food or the target for the payload. It is be soft and wet, just like biology, and to exemplify this we have built a series of biomimetic devices. Our progress in the development of responsive polymer-based molecular devices is be discussed with examples of vesicles of controlled size, synthetic muscles & flagella, and microparticles fitted with a jetpack.

1. INTRODUCTION

The first wave of nanotechnology has concerned itself with what is in effect an incremental continuation of long-existing trends in materials science, in which ever-greater control over the nanoscale structure of materials leads to better properties and more functionality. Modern materials rely on being able to control both interfacial structure and grain boundaries in order to develop improved properties. Functional materials for electronics and photonics are changing the way we live and modern materials can enhance our lives further through medical applications of nanotechnology. What is now at issue is the form a second wave of nanotechnology might take – one in which attention is focused, beyond simple materials, to fully functional nanoscale devices.

What might such functional nanoscale devices look like? There are (perhaps unfortunately) plenty of futuristic science-fiction visions of nano-assemblers and nanoscale submarines to be found in newspapers and on television, but what these have in common is a total neglect of the way the laws of physics work at the nanoscale and the constraints this puts on the design of devices. (For a gallery of rather more realistic nano-images and short films which aim to explain nanotechnology to a broad audience**,** see [1])**.**

One piece of classic nanotechnology iconography seems unshakeable in its appeal: the tiny submarine that first appeared in the film *Fantastic Voyage*. But why is this dream so enduring? Obviously human beings are captivated by the idea that they can live long and healthy lives, and science, technology, and medicine mean that people are living longer. There is something very attractive about the science-fiction story of a device that swims around the body with the capability to do cell-by-cell surgery. Of course, the science-fiction vision remains entirely unrealistic, but the creation of a device that is able to propel itself is a very attractive target for experimentalists. Here we summarize work at The University of Sheffield that aims to create such a device.

1.1 Motion at the cellular length scale

Firstly, you have to consider the size of the device. It would have to be about the same as a red blood cell to get around the vascular system. So what is different about a swimmer that is 7 μm across (like a red blood cell) compared to one that is 2 m high? The laws of physics are the same for both; the difference is how those laws are applied [2, 3]. For an object moving in a fluid, the Reynolds number determines the mechanisms by which the fluid resists its motion. A small object has a low Reynolds number; resistance is dominated by the fluid's viscosity, not its momentum. Such an object sees the water as we would see treacle – viscous and gooey. A small swimmer effectively has no momentum; unlike a big swimmer, it cannot stop swimming and just coast along – it comes to a dead stop within less than 1% of its body length. This means that you cannot use the same design rules to make a small swimmer as you would to make a large one. A human that was a million times smaller than us would just rock backwards and forwards in water if it tried to swim, and a submarine that was the same size as a red blood cell would not get very far.
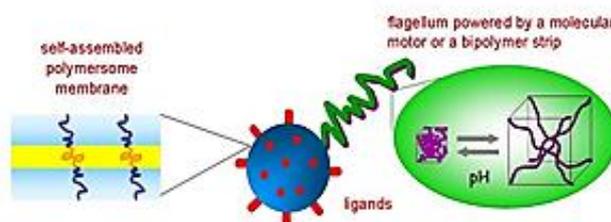

Fig. 1 – A nanobot we might be able to see?

Just a few moments' thought will lead you to the conclusion that a good starting point for designing a nanobot would be to take something like a bacterium (such as *Escherichia coli*) or a sperm as a prototype. Both of these have a propulsion mechanism (a flagellum), a capsule containing a chemical payload and a system of sensors to detect food or the target for the payload. So if we are to build a nanobot what do we need in the nanomechanical toolbox? One potential solution is given in Fig. 1.

1.2 Separating small volumes

To the combination of a physicist and a chemist, like us, the obvious thing you need is a source of energy. Nature provides energy in the form of separated

volumes with different chemical compositions – these have potential energy that can be used to do work when the chemical potentials run toward equilibrium by either reaction or diffusion. Such chemically different volumes are separated by membranes – so we have to build membranes. The ability of natural phospholipids to assemble into membranes, and specifically into vesicles, has recently been mimicked by synthetic amphiphilic block copolymers, long-chain molecules containing hydrophilic (water-loving and oil-hating), and oleophilic (oil-loving and water-hating) blocks [4, 5] The wholly synthetic nature of these copolymer vesicles, known as polymersomes, allows a wide range of chemistry to be applied in the design of mechanically and chemically enhanced membranes with a range of diameters and
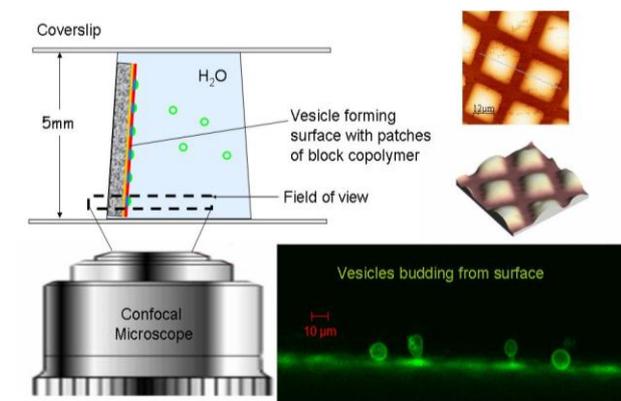

Fig. 2 – Vesicles with a uniform diameter and membrane thickness

membrane thicknesses. We have developed [5] methods for the spontaneous formation of uniform polymer vesicles controlled by the diffusion of water into self-assembled micron-sized patches of block copolymer printed on a silicon substrate (Fig. 2). The resulting vesicle is restricted by the area of the patch from which it is formed. We can thus create single-walled vesicles of a predefined size. Printing on a surface and washing off the block copolymer ink results in the generation of capsules that are all the same size and shape and can be loaded up with whatever you like. And they can carry their own energy supply in the form of different molecules on the inside and the outside.

1.3 Generating Force

How can you make something move? Motility is a nearly ubiquitous feature of living systems and is driven by the ability to directly convert chemical energy into mechanical work. Synthetic polyelectrolytes provide a simple analogy to this through the volume change associated with ionization; this effect was used to build a single-stroke 'artificial muscle' more than 50 years ago by Kuhn [6], Katchalsky [7], and Sussman and Katchalsky [8]. Yoshida [9] more recently demonstrated an elegant system comprising a responsive gel coupled to an oscillating Belousov–Zhabotinsky reaction. Macroscopic applications of such stimulus-responsive gels are limited, however, because the volume change relies on

mass transport of solvent, as shown by Shibayama and Tanaka [10]. For this reason, more recent efforts to make synthetic muscles have concentrated on actuation by temperature, light, or electric fields [11]. Recognizing the fundamental limitation of chemical gel-actuation, we have constructed a scalable, responsive gel from a robust, self-assembled block copolymer comprising hydrophobic, glassy end-blocks and a weak polyacid mid-block [12]. The gels deform affinely in response to a pH stimulus with a volume change of a factor of three. When coupled to a chemical oscillator this provides a free-running chemical motor that generates a peak power of 20 mW/kg by the serial addition of 10 nm shape changes that scales over five orders of magnitude to provide reciprocating macroscopic motion. We have taken another hint from nature and used antagonistic muscles coupled together to make a more efficient device. Thin plates of self-assembled polyacid and polybase triblock copolymer hydrogels have been 'solvent-welded' to produce a pH-responsive bipolymeric strip that is analogous to a bimetallic strip [13].
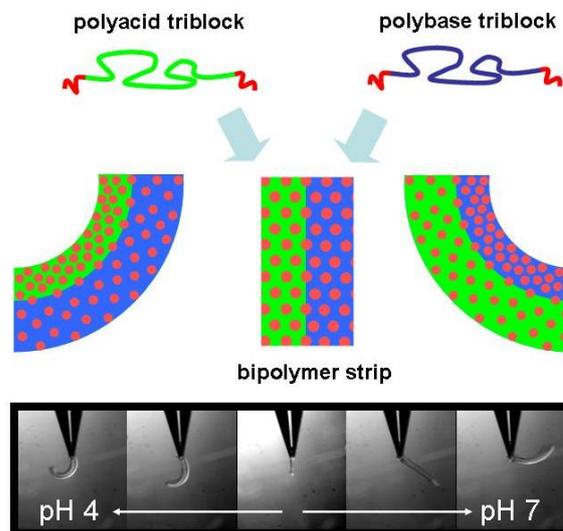

Fig. 3 – A flagellum from a bipolymer strip

When exposed to a pH oscillation, the curvature of the strip depends on the pH. At low pH, contraction of the polyacid gel (and concomitant expansion of the polybase gel) bends the strip in the direction of the polyacid. At neutral pH it bends towards the contracted polybase (Fig. 3). The mechanical advantage of this device compared to a simple linear actuator strip is that displacement of the free end is greater than that of the individual components, a phenomenon well-demonstrated with bimetallic strips, and this one waggles back and forth just like a flagellum. While most bacteria are driven by a rotary motion like a corkscrew, nature uses both rotary and reciprocal flagella to break the balance [2, 3].

Using a quartz diffraction grating we created a micron-sized periodic structure on the surface of the polybase gel (Fig. 4). The resulting diffraction pattern was used to calculate the swelling ratio of the polymer film in situ, which was compared against small angle X-ray scattering (nanoscopic) and gravimetric studies of bulk

gel pieces (macroscopic). We further proved these motors are affine and scalable, and are capable of working at the molecular, mesoscopic and macroscopic level [14].
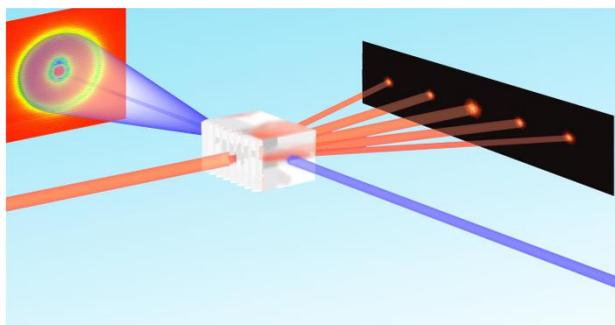

Fig. 4 – An illustration comparing the X-ray scattering (left) and laser diffraction (right) pattern obtained from an imprinted diffraction grating on the surface of a polybase gel

Now we face the problem of joining these devices together – putting the propulsion mechanism into the capsule. And we cannot do it yet! The flagellum is too big for the capsule so we have had to look at other ways of propelling small objects.

1.4 Making objects move

So what other options are there for propelling small particles? One can also try and take advantage of physical phenomena that become predominant at small scales. Interfacial or 'phoretic' effects – such as electrophoresis, thermophoresis and diffusiophoresis – are most promising from this standpoint given the increased surface to volume ratio in small objects. Our colleague at Sheffield, theoretical physicist Ramin Golestanian, and his coworkers [15], have proposed a design for aswimmer that takes advantage of the osmotic pressure gradient that is caused and maintained by a catalytic patch on the surface of a bead. If the surface of a spherical bead is asymmetrically covered with a catalyst, then when the bead is placed in a solution of the molecule that the catalyst breaks up fast, a concentration gradient of excess solute particle will be generated that pushes the bead to one side by way of osmotic forces. Since the gradient is self-generated it will move with the bead, which makes the mechanism highly efficient. It is like fitting a capsule with a jet pack. We have realized their theoretical proposal by taking poly-

styrene spheres and coating one side of the spheres with Pt, keeping the second half as the non-conducting polystyrene [16]. The Pt catalyzes the reduction of a 'fuel' of hydrogen peroxide to oxygen and water, which produces more molecules of reaction product than of consumed fuel. We have followed the motion of the artificial microscale swimmer using particle tracking, and have probed the properties of the motion as a function of hydrogen peroxide concentration (Fig. 5). We show that, at short times, the particles move predominantly in a directed way, with a velocity that depends on the concentration of the fuel molecules, whereas at longer times, the motion reverts to a random walk, in which runs of directed motion are interrupted by random changes of direction – just like a bacterium searching for food.
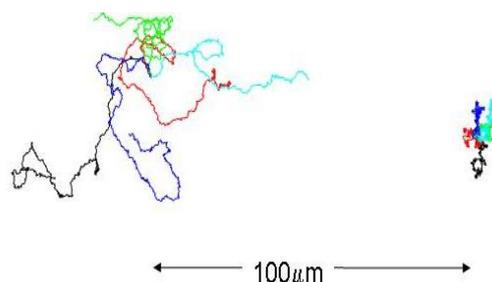

Fig. 5 – Comparing the distance travelled by 5 propelled particles to 5 particles without propulsion

So where have we got to? We have built capsules that are all the same size and we can fill them with stuff. We have built a synthetic muscle that generates forces but we cannot yet fit it into the capsule. So we looked at a different strategy to propel particles – and found something that swims patterns just like a bacteria. We can demonstrate all the features of a nanobot and we are getting closer the the dream that is the *Fantastic Voyage*. But we are still a long way from saving lives!

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