Hydrogels – smart materials

In this series of activities students investigate hydrogels, a type of polymeric smart material. Hydrogels are found in many commonly available products, including disposable nappies, cheap hair gel and plant water storage crystals. The practical work (Experiments with a smart material – hydrogels) – is fun to do and the results are clear and easy to see (in two cases, they are both sudden and dramatic). This is followed by written work (Hydrogels and how they work). Information is provided on the structure of hydrogels and students consider how this structure relates to the properties they have observed. Finally, a possible future use for very small particles of hydrogel (microgels) in drug delivery systems is introduced (Drug delivery and smart materials). This material could be used to enhance teaching of ionic and covalent bonding or equilibrium. Alternatively, hydrogels could be considered as interesting polymers and as an example of smart materials and nanotechnology.

Prior knowledge required

Students will need to have some knowledge and understanding of:

- Ionic and covalent bonding
- Reversible reactions
- Acids and bases
- Rates of reaction and particle size – for Drug Delivery and smart materials only.

Hydrogels – background information

Hydrogels are polymers that can retain many times their own weight in water. They are often polymers of carboxylic acids. The acid groups ionise in water, leaving the polymer with several negative charges along its length. This has two effects. Firstly, the negative charges repel each other and the polymer is forced to expand. Secondly, polar water molecules are attracted to the negative charges. This increases the viscosity of the resulting mixture because the polymer chain now takes up more space and resists the flow of solvent molecules around it.

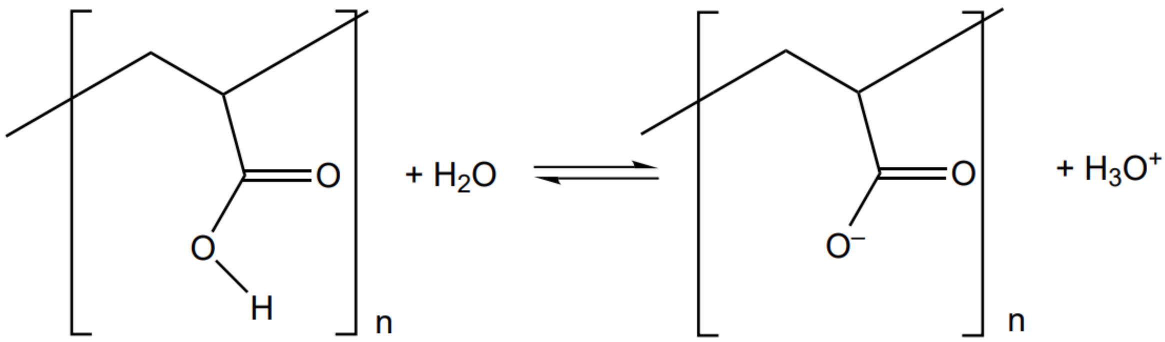

Figure 1 Carboxylic acid groups on the polymer ionise in water

The polymer is in equilibrium with the water around it, but the equilibrium can be disturbed in a number of ways. If the ionic concentration of the solution is increased, for example by adding salt, the positive ions attach themselves to the negative sites on the polymer, effectively neutralising the charges. This causes the polymer to collapse in on itself again. Adding alkali removes the acid ions and causes the position of equilibrium to move to the right; adding acid has the opposite effect. There are a large number of hydrogels and they expand and contract at different pH values, temperatures and ionic concentrations. By using a mixture of monomers to create the polymer these characteristics can be fine-tuned.

The commonly available hydrogels that are suggested for use in this practical activity are sensitive to salt concentration but do not show much change across the pH range which can be investigated readily in the classroom. They lend themselves very well to a range of investigative practical work. For example, their volume in different amounts of water or in different salt concentrations could be measured.

Equipment required

Do not be put off by the long list of requirements given below; many items are needed for all the experiments. The equipment is listed separately for each experiment so that just one or two parts of the activity can be prepared if preferred.

Plant water storage crystals

This experiment is referred to in the worksheet Drug Delivery and smart materials. If this worksheet is to be used, then tea must be included in the experiment. If you do not intend to use the worksheet, the water crystals can be coloured with a few drops of food colouring (for wonderful, lurid colours) or not at all (but they look great when coloured).

For each pair or group:

Part 1

- 1 teaspoon water crystals – available from garden centres and sold under various names, eg Phostrogen Swellgel
- Large (at least 1 dm^3) beaker or plastic tub – ice cream or similar tubs are fine
- 500 cm^3 strong tea – use 1 tea bag per 500 cm^3, pour on boiling water and leave to brew overnight (this tea will stain some containers).

Part 2

- Sieve (plastic ones are fine) or large funnel lined either with paper towels or with filter paper – groups will be able to share these
- 2 x 250 cm^3 beakers
- 200 cm^3 very concentrated or saturated sodium chloride (table salt) solution
- 200 cm^3 distilled water
- Dessert spoon or similar – plastic disposable spoons are fine and could be re-used
- White paper (to place under beakers to make it easier to see the results)
- 2 x stirring rods
- Sieve or tea strainer – if a funnel was used earlier, tea strainers are needed now; the same sieves could be used throughout
- 2 petri dishes – lids not required.

Hair gel

For each pair or group:

- Approx 1 large teaspoon hair gel – the cheaper and nastier the better
- Salt
- Petri dish or lid
- Teaspoon or similar – an ordinary spatula is a bit small.

Disposable nappies

For each pair or group:

- A disposable nappy – the ultra-absorbent type
- Scissors
- A large ice cream tub or similar container for collecting the inside of the nappy – this is safer than using newspaper or similar; if tubs are in short supply, large ziplock

bags could be used (students put the nappy in the bag, zip it up and manipulate it until all the hydrogel has been extracted)

- Approx 500 cm^3 distilled water – tap water can be used but the results are not as spectacular.
- Salt
- Dessert spoon or similar measure
- Stirring rod
- Large beaker or plastic tub – at least 600 cm^3
- Eye protection
- Plastic gloves for those with sensitive skin.

Note: As an alternative to using nappies and extracting the hydrogel, sodium polyacrylate can be ordered from Sigma-Aldrich.

Hydrogel and sugar

Students are asked to predict the outcome of this experiment towards the end of the worksheet Hydrogels and how they work, and then to test their prediction. The experiment should be carried out in the same way as part 2 of Plant water storage crystals but using sugar instead of salt solution.

- Remaining hydrated plant water storage crystals
- Sugar or sugar solution in distilled water
- Distilled water – it is important that distilled water is used, both in the sugar solution and as the 'plain' water in this experiment
- 2 x 250 cm^3 beakers
- Tea strainer or sieve.

Timing

It will take over an hour to do all the practical work at once. If lessons are shorter than that then part 1 of Plant water storage crystals can be done in a separate lesson before the rest of the experimental work. The crystals will keep for a few days in the tea solution, although the tea may stain some types of container. The remaining practical work should fit into an hour if students are organised. They should set up the parts of the experiments that need to be left then do the rest of the work while they wait.

The time required for the written work will depend on the ability of the group. The Hydrogels and sugar experiment is best done part-way through the written work. The hydrated crystals can be kept for a few days if covered with water.

Answers

Experiments with a smart material – hydrogels

Students should make detailed notes on their experiments. They should record changes in volume, colour and any other observations they make. Some expected observations are described below.

Plant water storage crystals

The crystals swell up from about 5 cm^3 to about 500 – 600 cm^3. They take on the colour of the tea, which shows that the tea has also been absorbed.

The hydrated crystals swell up more when added to distilled water than in salt solution. In distilled water, the tea remains absorbed in the crystals and the water does not change colour. In salt water, the crystals begin to shrink and the water changes colour as the tea is released.

It is possible to measure the approximate size of individual pieces of the hydrogel and to show that the pieces have swollen or shrunk.

Hair gel
The hair gel shrinks very quickly when salt is added. After a couple of minutes only liquid is left in the petri dish.

Disposable nappies
About 10 cm^3 hydrogel can be extracted from the nappy core (the exact quantity depends on the make and size of the nappy used). The hydrogel absorbs water and swells up far faster than the plant water storage crystals. It will absorb about 500 cm^3 distilled water. A very viscous mixture results. On adding salt, the viscosity is immediately reduced and the mixture becomes easier to stir. The hydrogel releases the water and settles on the bottom of the beaker.

Hydrogel and sugar
For the best results, be sure to use distilled water for this experiment.
The hydrated crystals in the sugar solution have the same volume as those in the distilled water. If they are left to stand, the tea is not released for about 15 minutes. (After this time, the water in the hydrated crystals is in equilibrium with the water in the beaker and some tea may begin to be observed.)

Hydrogels and how they work

1. The volume should increase from about 1–2 cm^3 to about 500 cm^3, ie by about 500 times. Exactly how much the hydrogel expands depends on the make of water crystals and the tap water used. Students' results with the nappies may differ from those with the plant water crystals. This is partly due to the difference in the hydrogels but is also a result of the use of tap water in one experiment and distilled water in the other.
2. In the presence of salt the volume of the hydrogel decreases dramatically and the water is released again.
3. The hydrogel is a smart material because it changes shape when a change occurs in its environment – in this case, a change in the concentration of ions.
4. The negative charges will repel each other.
5. This will force the polymer chain to open up and take up more space to allow the negative charges to move apart.
6. The water molecules (the positive ends) will be attracted to the negative charges on the polymer molecules.
7. $NaCl(s) \rightarrow Na^+ (aq) + Cl^- (aq)$
8. The Na+ ions will be attracted to the polymer chain.
9. This will neutralise the charges on the polymer chain.
10. This will cause the molecule to collapse back to its original shape.
11. The symbol means the reaction is reversible.
12.
    a. If you add acid the equilibrium moves to the left in order to remove H_3O^+ ions (ie acid) from the solution.
    b. If you add alkali it reacts with the acid on the right hand side of the equation and removes it. The equilibrium will move to the right, forming more acid.
13. Yes, the hydrogel would be expected to show smart behaviour in response to changes in pH.

14. The shape of the hydrogel does not change when it is placed in sugar solution. Sugar is a covalent molecule and will not be attracted to the hydrogel, nor will it react with any of the molecules in the polymer/water equilibrium. Hydrated hydrogel crystals in a solution of sugar in distilled water should be the same size and take up the same volume as hydrated hydrogel crystals in distilled water.
15. The nappy hydrogel will probably absorb about 500 cm^3 distilled water.
16. The nappy will absorb less urine than distilled water. Urine contains dissolved salts, which will reduce the amount of water the hydrogel can absorb.
17. Manufacturers might put hydrogels in hair gel to increase its volume and make the product look good. The main ingredient of many hair gels is water.
18. BARRICADE® gel contains a large quantity of water. The water removes the heat from the fire before it can get to the coated item. Without heat, the fire triangle is broken and the fire cannot burn.

For further information on BARRICADE® gel, see http://www.barricadegel.com (accessed December 2005).

Drug delivery and smart materials

It may be a good idea to allow students to discuss questions 1 and 2 in groups then talk them through the answers and the following paragraph. They can then complete the written work on their own.

1. Methods currently used to get drugs into the body include swallowing, injection or drip, inhalation (eg asthma drugs), patches placed on the skin (certain bandages and nicotine patches), slow release implants (used for some contraceptives such as Norplant), topical creams placed on the skin. Where the target site is external, such as the skin or eyes, it is relatively easy to deliver the drug selectively to the target. If the drug is required internally it is harder to make it site-specific.
2. Most pills enter the digestive system, pass into the blood stream and then travel through the whole body.
3. The tea is the drug and the hydrogel the carrier.
4. When the hydrogel is soaked in tea, both water and tea enter it. The gel changes colour so you can see that it has absorbed the tea as well as the water. The water is absorbed because the hydrogel has many negative charges on its molecules. Water molecules are polar (they have small charges on them) so they are attracted to the negative charges on the hydrogel polymer.
5. In salt solution, the tea is released from the hydrogel; in distilled water, it is not released. The salt causes the hydrogel to change shape and release some of the water it has absorbed. As it does so, the tea is also released. In distilled water, the hydrogel does not release any of its bound water and so the tea also remains bound.
6. If the particles are very small the overall surface area is very large. This will increase the rate at which the drug is released when the conditions are right.

Experiments with a smart material – hydrogels

A smart material is one that changes shape in response to changes in its environment. Hydrogels are smart materials and their properties are exploited in a number of products that are currently available on the market. Chemists are working to develop other applications for this unusual type of material.

You are going to investigate three readily available products that contain a hydrogel: disposable nappies, plant water storage crystals ('water crystals') and hair gel. Record detailed observations as you carry out each experiment.

Plant water storage crystals – part 1

You will need

- 1 teaspoon of water crystals
- Large beaker (at least 1 dm^3) or plastic tub
- 500 cm^3 concentrated tea.

What to do

- Estimate the volume of your water crystals.
- Put about 500 cm^3 of the tea into the beaker or tub. Add 1 tsp of water crystals, stir gently and leave for at least half an hour (or overnight).

Plant water storage crystals – part 2

You will need

- Your water crystal and tea mixture from part 1
- Sieve (or a large funnel lined with a paper towel or large piece of filter paper)
- 2 x 250 cm^3 beakers
- Salt solution
- Distilled water
- Dessert spoon
- Piece of white paper
- 2 x stirring rods
- Tea strainer (if you have not got a sieve)
- 2 petri dishes.

What to do

- Sieve your water crystal mixture. It is best to do this over a large tub rather than over the sink in case you drop the sieve. Carefully wash the gel crystals once or twice in water to remove any excess tea. Estimate the new volume of your crystals.
- Place the two 250 cm^3 beakers on a piece of white paper.
- Put two dessert spoons of your gel crystals into each beaker, estimate their volume and then add about 200 cm^3 salt solution to one beaker and about 200 cm^3 distilled water to the other. Label the beakers. Keep the remaining gel crystals.
- Stir the mixtures gently – use a separate stirring rod for each one so that the solutions are not contaminated. Leave for 10–15 minutes, stirring occasionally.
- Place the two petri dishes on the white paper. Pour a little of your solutions into the petri dishes. Use a tea strainer to prevent any crystals getting into the petri dishes. Note the colour of each liquid.

- Sieve each of the remaining mixtures separately, discarding the excess liquid and returning the crystals to the beakers. Estimate the new volume of crystals in each beaker.

Hair gel

You will need

- Hair gel
- Salt
- Petri dish
- Teaspoon or spatula.

What to do

- Put a large teaspoonful of hair gel onto the petri dish lid.
- Gently sprinkle salt from a spatula over the hair gel.

Disposable nappy

You will need

- A disposable nappy
- Scissors
- A large ice cream tub or similar container
- Distilled water
- Salt
- Dessert spoon or similar measure
- A stirring rod or spoon
- A large beaker (at least 600 cm^3)
- Eye protection
- Gloves if you have sensitive skin.

What to do

- Cut the middle section out of the nappy. You want the thicker piece which is designed to absorb urine. Discard the other piece.
- Make sure your ice cream container is completely dry – wipe it with a paper towel if necessary. If there is any moisture in the tub the experiment will not work properly.
- Wear eye protection for the next step. Put the centre piece of the nappy into the ice cream container and gently take it apart. You should start to see small white grains coming away from the nappy and this is what you are trying to collect. Keep gently pulling the nappy apart until you have collected as many of the grains as you can. Do not do this roughly or you will lose your product and put a lot of dust and fluff into the air. Avoid breathing in any dust you do create.
- Remove and dispose of all the fluff and other parts of the nappy, keeping the white grains in the bottom of the tub. The grains are heavier than the other materials and fall to the bottom of the heap, which makes it easier to separate them out.
- Estimate the volume of the grains.
- Pour the grains into the large beaker and add about 100 cm3 distilled water (you can just use the markings on the beaker to measure the volume). Stir the mixture and keep adding distilled water until no more can be absorbed. Stir between each addition of water. Estimate the final volume of the hydrogel.
- Add a dessert spoonful of salt and stir.

Summary

Write a summary of what happened in each of your experiments.
What have you learnt about hydrogels?
Can you explain any of their unusual properties?

Hydrogels and how they work

1. How much did the volume of the hydrogel in your experiments increase when it was put into water?

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2. What happened to the volume of the hydrogel when salt was added?

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3. Why is the hydrogel a 'smart material'?

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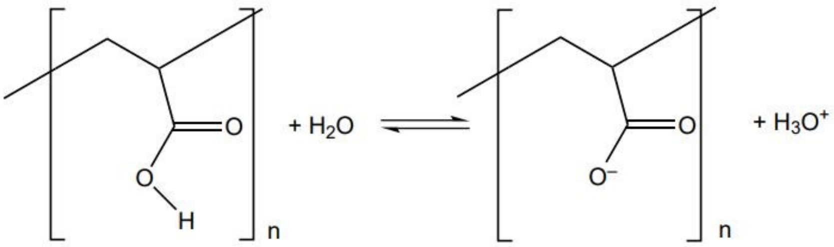
Understanding the structure and bonding of hydrogels helps to explain their properties. This in turn helps chemists to develop new hydrogels and find further uses for them.

Hydrogel structure

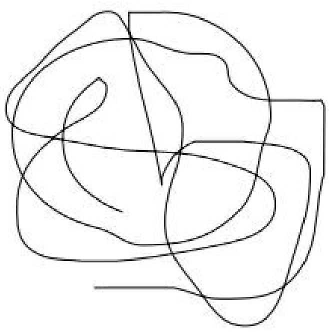
The hydrogel you have used is a polymer of a type of substance called a carboxylic acid. The acid groups stick off the main chain of the polymer, as shown in the diagram below.

When the hydrogel is put into water these acid groups react, the hydrogen atom comes off and the polymer chain is left with several negative charges along its length.

(Note: H_3O^+ is another way of writing H^+ in solution and shows that an acid is present.)



A polymer chain in solution tends to coil up so it looks like this:



However, the hydrogel polymer chain now has several negative charges along its length.

4. What will the negative charges do to each other?

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5. What effect will this have on the polymer chain?

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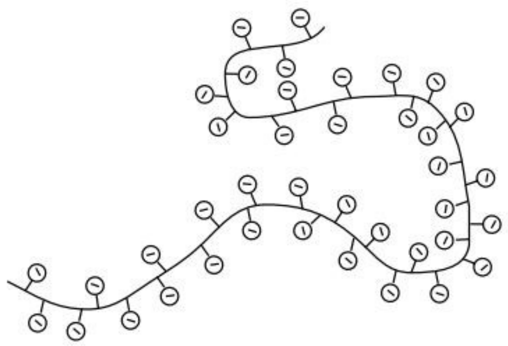
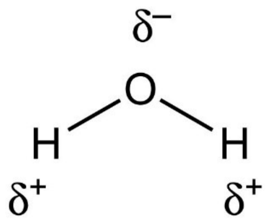
This diagram shows a section of the polymer chain.



Water is a polar molecule, which means that it has an uneven spread of charge over it, even though it is not charged overall. This is because oxygen is better at attracting electrons than hydrogen.



6. What will happen to the water molecules when they get near the polymer?

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Both of these effects mean that the molecules of the polymer get larger as they get wet. This makes the solution more viscous because the polymer resists the flow of the solvent molecules around it. Quite why the polymer absorbs so much water is still not fully understood.

Hydrogels and salt

When salt (sodium chloride) dissolves in water it dissociates (splits up) into sodium ions and chloride ions.

7. Write an equation for this dissociation.

8. Which of the ions will interact with the negatively charged polymer chain? What will happen?

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9. What effect will this have on the charges on the chain?

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10. What effect will this have on the shape of the polymer molecule?

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The polymer changes shape in response to a change in the environment – in this case, a change in the concentration of ions. This is called smart behaviour.

Hydrogels and pH

Look back at the diagram showing the hydrogel polymer and how it reacts when it is put into water.

11. What does the $\rightleftharpoons$ symbol mean?

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12. What would happen in the reaction if you added:
    a. Acid

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    b. Alkali

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13. Would you expect the hydrogel to show smart behaviour in response to changes in pH?

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Hydrogels and sugar You have seen what happens to the hydrogel in the presence of water, distilled water and salt.

14. Predict what will happen when you add the hydrogel to sugar solution. Give a detailed explanation for your prediction.

Use your remaining gel crystals to test your prediction by repeating the experiment that you carried out with salt solution, this time using sugar solution. If your results are unexpected, try to explain them.

Using hydrogels

15. What volume of distilled water did the hydrogel from the nappy absorb?

16. How do you think this volume compares to the volume of urine it would absorb? Explain your answer.

17. Why might manufacturers put hydrogels in hair gel?

Fighting fires with Pampers?

Another use for hydrogels has recently been developed by a firefighter in the USA. John Bartlett was at a fire in which an entire house was destroyed – all except a used disposable nappy. He realised that a substance inside the nappy was responsible for preventing it from being burnt and discovered that the material was the hydrogel, which had absorbed liquid. BARRICADE® fire fighting gel was developed as a result. If the gel is sprayed with water onto a house which is in the path of a fire, the house will not burn. This is a major new tool for fire fighters to use when they are battling against the vast forest fires that can burn for days in the USA.

18. Explain how BARRICADE® gel might help prevent something from burning. (Hint: think about the fire triangle.)

Drug delivery and smart materials

Research is currently being undertaken to find out whether it is possible to use hydrogels and similar materials as a drug delivery system – a way to get drugs and medicines to where they are required in the body.

1. What methods are currently used to get drugs and medicines into the body?

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2. If a pill is swallowed, where does it go in the body?

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These methods can cause a number of problems. While all drugs are rigorously tested to make sure they are safe for the vast majority of people, many drugs cause bad reactions in a few people. The negative effects range from an upset stomach to serious allergic reactions.

Chemists are now trying to develop a delivery system that will target a drug at the particular site where it is required. For example, if you have a bad cut on your leg and take antibiotic pills, the drug travels all round your body and not just to your cut leg. This increases the risk that the drug will cause problems. If the drug is only released at the cut then the likelihood of an adverse reaction is reduced. When the drugs are extremely strong, such as those used in chemotherapy to treat cancer, the possible side effects are wide ranging and include hair loss, severe stomach upset and lethargy.

Targeting the drugs so that only the cancer cells are affected is a major goal in current research. Since drugs can be toxic to the body, the aim is to place them in a non-toxic carrier so they can pass through the body without causing any damage. The carrier needs to be smart so that it will release the drug at the required site and nowhere else. Chemists are investigating a wide range of potential carriers, including hydrogels. The experiment you did with tea and hydrogel is a model of this type of drug delivery system. The drug is first loaded onto the carrier and then it is released at the right location.

3. In this model, which is the drug and which is the carrier?

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4. What happens to the hydrogel when it is soaked in tea solution? Give as much detail as you can.

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5. What happens to the tea in the hydrated crystals when they are soaked in salt solution? What happens to it if the crystals are soaked in distilled water? Explain your observations in as much detail as you can.

In this model, the presence of the salt changes the behaviour of the ‘carrier,’ causing it to release the ‘drug.’ As more is understood about exactly how drugs work, research is focusing on how to deliver them in a way that ensures they make their active ingredients available at the time and place required by the body. One type of substance being studied for use in carriers is microgels. These are similar to hydrogels but the particles are far smaller, often only up to 100 nm in diameter. This is an example of nanotechnology.

6. If the particles are very small, what effect will this have on the overall surface area of the carrier and on the rate at which the drug is released when the conditions are right?

Hydrogels and microgels can also change shape and release a drug in response to a change in pH or temperature. Conditions such as temperature, saltiness or ionic concentration and pH can all be different in an infected or diseased area of the body than under normal conditions. If chemists can understand both how the disease operates in the body and how the microgels and hydrogels behave in different conditions it should be possible for them to target drugs accurately at the sites where they are required.