A review of ILL research into complex everyday materials

Neutrons and soft matter

ILL
NEUTRONS
FOR SCIENCE

This booklet is part of a series devoted
to the application of neutron techniques
in different research areas.

We have already published:
Exploring matter with neutrons (May 2000)
Neutrons and life (May 2001)
Neutrons and new materials (May 2002)
Neutrons and the Universe (May 2003)
Neutrons and magnetism (May 2004)

The next one, to be published in 2006, will focus on
the complementarity of neutrons and synchrotron
X-rays to study materials.

Foreword

Many of the objects that we employ everyday – the tools that we use, the clothes we wear, and the food and health products that we consume are made of soft materials with highly complex structures. They are frequently assembled from simple building blocks, using the techniques of synthetic chemistry, and comprise polymeric and other large molecular architectures arranged to give a specific set of useful properties. The natural soft-matter systems found in biology are even more complex and are often constructed by Nature using the principles of self-assembly. Nevertheless, they share many of the same characteristics as synthetic soft matter, which is often designed to emulate biological materials. The components can arrange themselves in many different ways, and exist in many forms that, in general, feel 'soft' and are highly sensitive to external conditions.

Understanding these properties and mastering the procedures to arrange the building blocks are essential for developing smarter materials and more efficient products for tomorrow. This requires a wide range of experimental techniques and analytical tools. Neutrons here play a crucial role, and three properties of neutron methods are commonly exploited: the range of length and time-scales that can be accessed experimentally; the contrast-variation methods (as described in the Introduction); and finally the combination of neutron experiments and computer simulations.
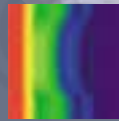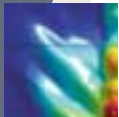
This booklet presents some of the advances made at the Institut Laue Langevin (ILL) using neutron instruments in the field of soft matter. They demonstrate that neutrons are unrivalled in providing answers to an extremely wide range of problems related to materials of everyday importance.

However, scientists are continually faced with new challenges relating to the design of even more elaborate materials with predictable properties. This requires further progress in instrumentation, data-handling and interpretation. The ILL has undertaken an ambitious programme to renew its instruments and infrastructure – the Millennium Programme – to meet the needs of its users; it also includes exploring the benefits of combining the latest sophisticated neutron scattering techniques and advanced computational methods such as molecular dynamics calculations.
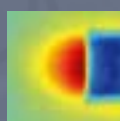
We wish to ensure that chemists and other scientists coming to the ILL can benefit from the appropriate neutron methods and tools to investigate all the complex systems that are currently being developed, and which, for some of them, are very close to technological applications.

Dr Christian Vettier
Associate Director
Head of Science Division

Contents

Investigating soft condensed matter with neutrons

>> PETER LINDNER AND RALF SCHWEINS

Although the study of soft matter is now a frontier subject, it has a long tradition at the ILL

Peter Lindner and Ralf Schweins

Soft condensed matter comprises a wide range of materials found everywhere – both naturally-occurring and manmade. Examples include polymers (plastics), surfactants such as soaps and detergents, the liquid crystals found in electronic displays, and biological matter such as cell membranes. One important class of soft materials includes fine suspensions of one material in another, perhaps in a different phase. They are called colloids, and can have intriguing bulk forms such as gels or foams.

These kinds of matter all have complex, and often highly ordered, structures at the scale of 10 to 100 nanometres. They may comprise large molecules such as polymers, molecular assemblies as found in biological systems, or minute particles of matter suspended in a complex medium. The forces acting between these structures are quite weak, and have energies associated with ambient temperatures. This means that, under everyday conditions, they readily respond to external influences such as pressure (which is why they are soft), shear forces, or small amounts of heat.

Not surprisingly, research into soft matter is of interest to a wide range of scientists – chemists, physicists, biologists and material scientists. Many of these researchers work in industries that manufacture or process familiar products such as household cleaning materials and cosmetics (which are often in the form of complex, highly structured fluids), plastics (increasingly built from several types of polymer building blocks), paints and other coatings, pharmaceuticals and foods.

Researchers studying soft materials are interested in relationships between their structure and the properties that control their behaviour. Although many of these materials, for example soap, have been around for a long time, it is only in the past few decades that the analytical techniques have been available to investigate their structure in detail. For 30 years, neutron scattering has been the most powerful tool for studying soft matter (see opposite).

Today, scientific interest in soft matter has undergone an enormous revival with the burgeoning development of 'nanotechnology'. New methods of constructing complex forms of matter organised at the molecular and supramolecular level are now allowing scientists to create materials with highly tailored properties that are underpinning technological innovations. The ILL, with its dedicated and unique suite of state-of-the-art instruments, is ideally placed to continue to play a major role in this exciting area of science. ■

The ILL site

The D11 team. From the left: Ralf Schweins, Peter Lindner and David Bowyer

THE POWER OF NEUTRONS

Many studies of soft matter could not have been carried out without the intense neutron flux provided by the ILL which has developed a suite of techniques specifically suited to studying the properties of matter at the nano-scale.

Like X-rays, neutrons can scatter off the arrays of atoms in materials to produce a characteristic diffraction pattern. However, rather than interacting with the electron clouds of the atoms in a sample (as in the case of X-rays) neutrons are scattered by the atomic nuclei. The neutrons may penetrate quite deeply into a material before actually hitting any nuclei, so relatively thick samples can be studied – neutrons can 'look' inside the material. This is particularly useful for studying 'real' objects of commercial interest such as plastic bottles.

Another characteristic relevant to soft-matter systems, which can be used to great advantage, is that isotopes of the same atom may have very different scattering strengths. In particular, hydrogen (with a nucleus containing just a proton) scatters quite differently from its isotope containing an additional neutron, deuterium. In fact, the difference is the largest between any two isotopes of an element in the Periodic Table. The elaborate structures that typify soft matter usually include a large number of hydrogen atoms, as do water or the organic solvent hosting them. Judiciously substituting deuterium for some or all of the hydrogen atoms (which does not alter the chemical properties) increases the scattering 'contrast' for selected components in a soft-matter system, so they are more 'visible' to neutrons. For example, ordinary water can be partly replaced with deuterated water so its scattering matches that of one of the components, rendering it 'invisible'. Another component then stands out. This is called 'contrast variation'.

A third advantage is that neutron beams can be prepared with a wavelength that matches the length-scales associated with nano-sized architectures, so making them a highly effective probe of soft matter. The scattering angles are very small (the angle of diffraction decreases as the distance between nuclei increases), and to measure them, detectors must be placed far away from the sample. The ILL has two dedicated small angle neutron scattering (SANS) instruments, D11 and D22, used for soft matter. These instruments can be combined with special equipment to study, for example, the flow of material under a force, which is important in many practical applications. Another technologically important method is reflectometry (carried out with the reflectometer D17) whereby neutrons are reflected off a surface or interface to give information about thin films or layered structures.

Finally, the motions associated with soft matter structures – movements of various molecular components or vibrations of layers, for example – can also be studied with neutrons, by measuring the small exchanges of energy resulting from interacting with moving atoms – inelastic scattering. A remarkable technique called neutron spin echo, pioneered at the ILL by a Hungarian physicist, Ferenc Mezei, offers a highly sensitive method for following very slow dynamic processes in soft matter. It takes advantage of another important property of neutrons – their spin. The neutrons are first polarised so that their spins are all in the same direction and then passed through a magnetic field. This causes the spins to wobble, or precess (like a spinning top). The number of precessions depends on the time each neutron takes to traverse the field, which in turn depends on its energy. After being scattered by the sample, the neutrons pass through a second magnetic field, which winds back the spins through the same number of precessions (a sort of 'echo') over the same period of time so that the spins achieve their original orientations. If, however, some of the neutrons have lost or gained energy by interacting with the sample molecules, they will not all end up with the same spin polarisation. This deficiency then provides a neat way of measuring tiny energy changes associated with slow movements such as that of a polymer chain sliding through the tangled chains in a melt. The ILL has several instruments for measuring inelastic scattering including IN5, IN6, IN11, IN15 and IN16 used in soft-matter studies.

A spherical polymer brush
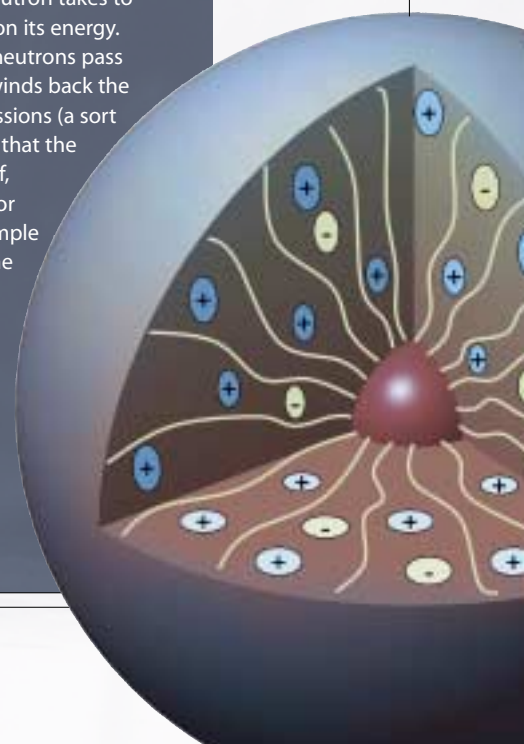
Will the real dendrimer structure step forward?

Large molecules called dendrimers have elegant shapes on paper but the reality is more messy
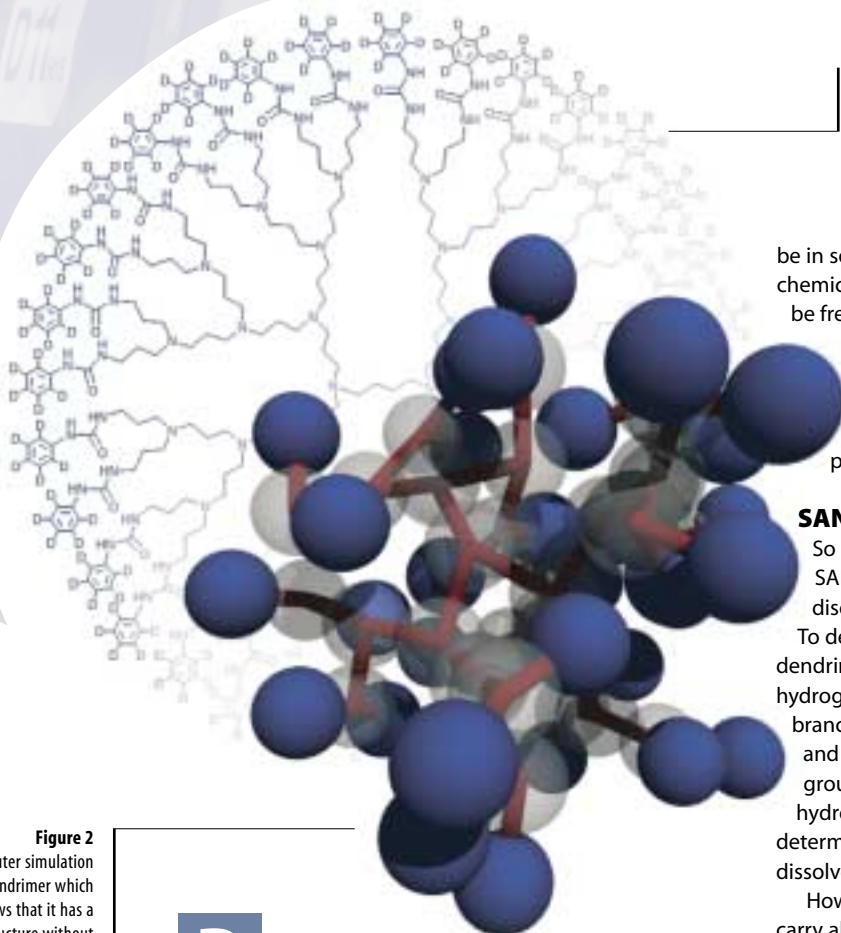
>> **MATTHIAS BALLAUFF AND CHRISTOS LIKOS**

Figure 1
An idealised structure of a dendrimer molecule showing a well-defined 'shell' of end-groups (blue)

Figure 2
A computer simulation of the dendrimer which shows that it has a diffuse structure without a sharp surface and that the blue end-groups are spread throughout the structure

Dendrimers could be used for gene therapy

D endrimers are large organic molecules with a tree-like structure. The word 'dendrimer' derives from the Greek word for tree, *dendron*. Because they are synthesised starting from a central core and then building outwards in all directions by adding on groups of atoms in chains, they are also called 'starburst molecules'. Dendrimers are just a few nanometres across and can be dissolved in suitable solvents.

Research on dendrimers is one of the most active fields in chemistry, and a great number of applications have been suggested. Most of them relate to their chemical structure which suggests a dense ball-like shell of outer end-groups that shelter a void inside – as shown in figure 1 above. The obvious idea is that dendrimers could be used as molecular vehicles in gene therapy or drug delivery – as proposed for surfactant micelles on p.12.

However, the model of a dendrimer with a defined surface and interior turns out to be misleading. The molecular scaffolds of dendrimers investigated so far are flexible. Most applications would require them to

be in solution – an environment in which all the chemical bonds in the dendrimer would, therefore, be free to bend and twist about into many different conformations with widely differing shapes. The result would be a range of somewhat untidy three-dimensional structures rather than the elegant shell-like dendrimer shape presented in figure 1.

SANS seeks out the truth

So what do dendrimers really look like in solution? SANS offers the best way of investigating just how disordered these large polymeric molecules are. To determine how the individual branches of the dendrimers orient themselves, we substituted the hydrogen atoms in the groups at the ends of the branches with deuterium. This allowed us to pick out and measure the scattering intensity due to the end-groups against the background scattering of other hydrogen atoms in the sample (p.5), and so determine the average position of end-groups within dissolved dendrimers.

However, the diffuse scattering pattern does not carry all the information necessary for a full structural analysis of the dissolved dendrimers. Computer simulations (molecular and brownian dynamics) help here. They give direct, realistic information on the various shapes that dendrimers may adopt in solution by predicting the average positions of all units in the chemical structure. The information can then be used to ascertain how the different shapes contribute to the measured SANS intensities.

All results obtained with the help of the D11 instrument demonstrate clearly that dendrimers do indeed adopt a rather disordered structure (figure 2). The end-groups are dispersed throughout the molecule as the branches bend back on themselves. The dendrimer therefore does not possess a defined surface. This is in marked contrast to what many researchers assumed from the chemical structure alone.

This approach revealed the power of modern SANS, especially when combined with molecular dynamics simulations. The techniques developed here can also be used to study other complex molecular or supramolecular structures in solution. ■

>> DRAZEN ZANCHI,
BERNARD CABANE, AND
AUDE VERNHET

Most of us enjoy a full-bodied wine, but what are the physical and chemical processes that contribute to our appreciation?

The secret of a good red wine

One of the main ingredients in red wine, which gives it colour, body and texture, is a group of natural polymers called polyphenols. These molecules, mainly tannins and anthocyanins, are released from grape skins during fermentation. Upon further ageing, the tannins evolve into ever more complex structures until the wine is eventually drunk.

Tannins are responsible for a wine's bitter taste and astringent feel to the tongue (the viscosity of saliva drops suddenly as the tannins precipitate out the saliva proteins). The deep-red and violet anthocyanins endow red wine with its colour. In very young wines, the tannins tend to be sharp-tasting. But as the wine ages, the tannins change and the wine tastes more velvety and smooth, or fine-grained and supple. These are all terms that represent different sensations of astringency and are related to the complex structure of the tannins.

One of the important processes in the ageing of a red wine is that some tannin molecules can aggregate to create a colloidal dispersion of nano-sized particles. The amount, the size and the shape of these particles depend on the chemical composition of the tannin-polymer structures, and this changes as the wine ages. Our aim was to explore this colloidal state and its effect on the quality of a red wine. SANS (p.5) offered a suitable technique.

We first created a model 'wine' using tannins extracted from the seeds of Languedoc-Roussillon grenache grapes. Our tannin fraction had an average degree of polymerisation of 11 units, so we called it DP11. The wine was a fairly awful-tasting solution of tartaric acid in water, with 12 per cent alcohol and 5 grammes per litre of the DP11 tannin. To increase the contrast of the tannin structures we used deuterated water and alcohol.

Shape of tannin structures

We were able to identify both the polymeric tannins and nanoparticles using SANS. What was significant, however, was that the size and internal structure of the tannin particles depended sensitively on how the sample was prepared.

We made two samples with the same chemical composition, but mixed in a different way. Tannins are completely soluble in alcohol and form particles only when water is present. In the first sample, an alcoholic tannin solution was added to the acidic water to give a highly supersaturated solution which then formed small aggregates. These gradually grew into the metastable colloidal state. The SANS spectrum revealed that the nanoparticles were about 600 nanometres across and had a branched, bushy structure.

In the second sample, we gradually added small quantities of acid water to the tannin-alcohol solution, following the SANS spectrum after each addition. The spectrum revealed only small DP11 tannin polymers down to a level of 68 per cent of alcohol, when the colloidal state suddenly appeared. In this case, only the largest particles grew, with the smaller ones re-dissolving, so aggregation did not happen.
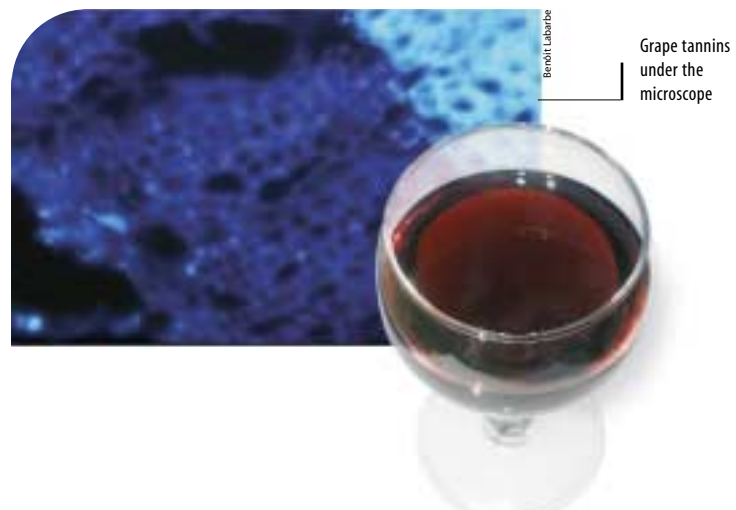
These results show that in making wine, the architecture of the tannin particles and the manner in which the tannins are released from the grapes are just as important as the overall chemical composition. ■

Grape tannins under the microscope

Benoît Labarbe

>> ANDREAS WISCHNEWSKI

Neutron spin echo picks out the subtle motions of polymer chain ends

Polymers make a new move

A polymer chain (red) is confined to a tube by a matrix of other polymer chains

It's hard to imagine life today without plastics. Although they are now common materials, much research still goes on into their structures and behaviour at the microscopic level. Understanding how the long-chain polymer molecules move is particularly important for the industrial processing of plastics at the temperatures at which they melt, when the chains become more mobile.

The basic theory of polymer dynamics was proposed by the Nobel prize-winner Pierre-Gilles de Gennes as long ago as 1971. Known as the reptation model, it imagines each polymer chain slithering like a snake through an entangled mass of other polymer snakes. The adjacent chains confine the snake's motion to create a virtual tube. The snake wriggles within the tube while slowly sliding out of it.

Neutron spin echo (NSE, p.5) has provided an excellent way for probing the dynamics of polymer chains. Although the creeping of the chain out of the tube happens too slowly to be seen by this technique, it can detect the faster, lateral fluctuations of polymer segments within the tube confines. Over the years, the de Gennes reptation model has been confirmed as the right approach.

However in 2002, using the ILL's ultra-high resolution NSE spectrometer, IN15, we found evidence for an additional type of movement.
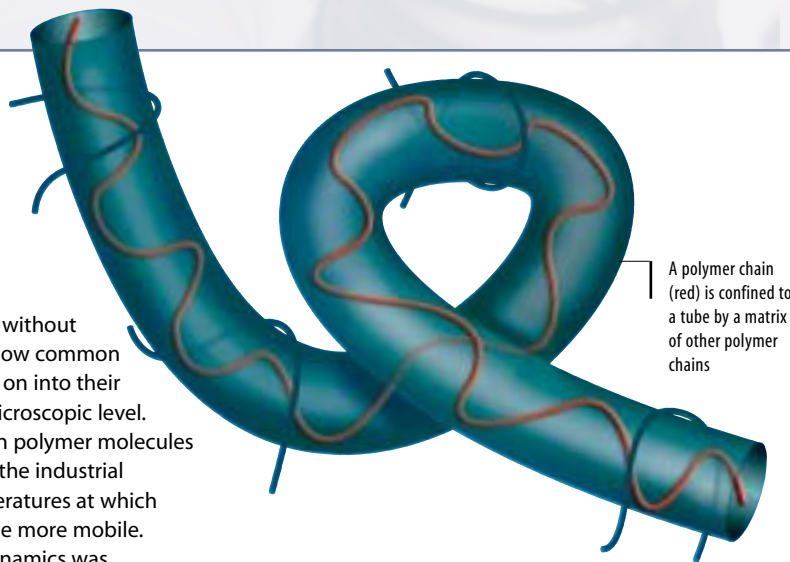
Contour length fluctuations

We explored the chain dynamics in melts of polyethylene (at temperatures of around 500K) over a wide range of molecular weights and therefore chain lengths. For very long chains, the results fitted the reptation picture well but for increasingly shorter chains the data indicated they were less confined, and the tube size was bigger than predicted by the model. We suggested that this was because the chain ends can retreat back into the tube, thus shortening it, and then re-emerge in an arbitrary direction. These so-called contour length fluctuations are more easily observed, and have a more significant effect, in the shorter chains.

This picture has recently been substantiated with further NSE experiments which separated the two kinds of movements: reptation and contour length fluctuations. We replaced the hydrogen atoms in 90 per cent of a polymer melt (at 509K) with deuterium so that we could see just the movement of the 10 per cent of chains containing hydrogen atoms (equivalent to observing a single chain in a tangled matrix).

We carried out another experiment where the end parts of these chains were also deuterated so that they too became 'invisible' against the polymer matrix and just the middle part could be observed with NSE. The experimental results for the whole chain and then just the centre part of the chain could be compared.

We found that the NSE data for just the centre part of the chain fitted the calculated confinement parameters – the tube diameter – expected from the reptation model; in other words, it behaves like an infinite chain. In effect, what we were doing was masking out the effect of the contour length fluctuations associated with the chain ends seen for increasingly shorter chains. We concluded therefore that the loss of confinement seen with decreasing molecular weight indeed starts from the chain ends, and thereby unambiguously corroborates the concept of contour length fluctuations. ■

Nobel prize winner Pierre-Gilles de Gennes (1991)

The large time-range of the IN15 instrument (up to several hundreds of nanoseconds) allowed us to investigate how contour length fluctuations affect the confinement of polymer chains

Hidden strength of dancing rings

Plastics used as building and engineering materials owe their unique qualities to some delicate dynamics

>> SILVIA ARRESE-IGOR
AND JUAN COLMENERO

P. Hodkinson

Plastics are light, durable and cheap, and have replaced traditional wood, glass and metal in many everyday items such as packaging, furniture and even car components.

Engineering thermoplastics like polycarbonate or polysulfone are extremely strong and resilient. Their mechanical properties are, of course, related to their chemical structure. They possess carbon (phenylene) rings spaced along the polymer chains. The rings themselves contain strong double bonds so remain stiff. However, they can still rotate about the polymer axis – although there will be some obstruction from neighbouring groups of atoms (see graphic below).

These microscopic motions are the origin of dynamic behaviour known as secondary relaxations and are thought to be responsible for the mechanical properties in polymers. Subtle ring movements allow the polymers to absorb energy, say, from applying stress, without any bonds actually breaking. Furthermore, they also permit the chains to slide smoothly against each other imparting a degree of flexibility to the plastic.

Rock and roll

Secondary relaxations have been studied using spectroscopic techniques that provide information mainly about their energies. Inelastic neutron scattering (p.5), however, can determine the energies of the motions while pinpointing the molecular structure responsible.

We applied the technique to samples of polysulfone well below the temperature at which it softens (more accurately called the glass transition). The polysulfone was partially deuterated so as to highlight only the scattering from the hydrogen atoms in the phenylene rings. In that way we could follow the motion of the rings over time in a range of temperatures 2 to 450K (the glass transition for polysulfone is at 460K). We used both the IN6 and IN16 instruments to observe a wide range of dynamics from fast to slow.

We found that at temperatures above 200K, the data (mainly from IN16) revealed that the motion of the hydrogen atoms in the ring corresponded to a jump of 0.43 nanometres between two equivalent positions differing by 180°. In other words, the main secondary relaxation process was indeed the flip of the phenylene ring – rather like flipping a pancake or tortilla. At the lowest temperatures (using IN6), however, we got completely different results: the dominant movement is a small, fast rocking of the rings of about 0.15 nanometres about the polymer axis.

We conclude that both types of dynamics contribute to the secondary relaxations seen in spectroscopic investigations. Our results are supported by theoretical (molecular dynamics) calculations for a disordered, glassy polymer which predict the occurrence of both kinds of motions.

The picture we have is that the phenylene ring undergoes rapid oscillations probably in concert with rotations of the adjacent groups of atoms. The oscillations increase in amplitude with temperature until the ring overcomes an energy barrier due to obstructing neighbouring atoms and flips over.

These experiments not only answer the fundamental question about the origin of secondary relaxations in polymers but also provide useful information for designing new plastics with tailor-made mechanical properties. ■

Polysulfone unit (repeated 50–80 times in the polymer chain)
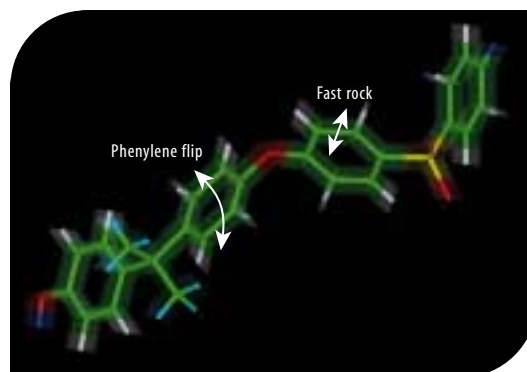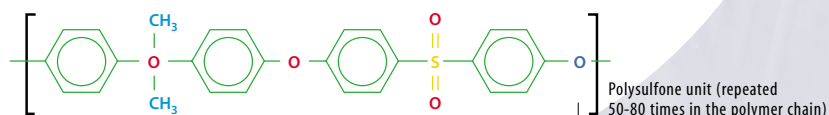
The phenylene rings in polysulfone chains rock rapidly at low temperatures, eventually completely flipping over at higher temperatures

Fast rock

Phenylene flip

Neutron scattering shows how the structure of surfactant bilayers can be controlled by applying a shear force

>> **WALTER RICHTERING**

The tailor-made shear cell developed at ILL

Going with the flow

H ousehold detergents may look like simple water-based liquids but they have highly complex structures. The main ingredient is a surfactant (pp. 12, 22) whose molecules line up and self-assemble into stacks of double layers. The alignment of stacks may extend over several micrometres, leading to a patchwork of domains with different orientations.

However, the structure may change radically when the detergent is poured, or pumped through a pipe, resulting in accompanying changes in viscosity. Understanding these transitions is therefore extremely important for industrial processing.

We used SANS (p.5) to investigate what happens to the structures of various surfactant solutions when subjected to a shear force – which is what the detergent experiences when flowing down a narrow pipe.

Shear genius
The surfactant solution was placed in the 1-millimetre gap between two concentric cylindrical cups. One of the cups was allowed to rotate to create a velocity gradient across the gap – the shear flow. The neutron beam can pass either along the gap between the cylinders in the direction of the flow, or through the middle of them across the flow. The scattering patterns were collected every few seconds for an hour. Parallel optical measurements of the sample with a laser completed the observations, while measurements with a rheometer revealed changes in viscosity.
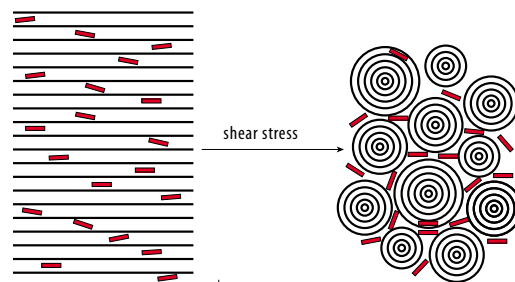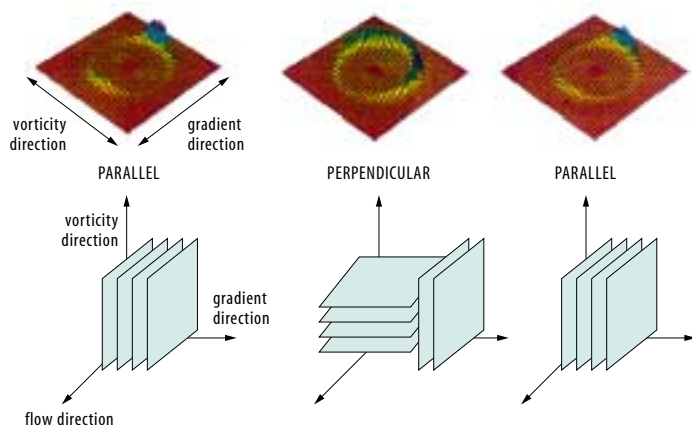
Figure 2
Shear-induced phase separation of the lamellar phase doped with clay particles. A vesicle contains several hundred bilayers

We found that the surfactant bilayers became more orderly under shear stress. The domains disappear and the layers all align in the direction of the flow. With increased shear rate, they then flip to a perpendicular orientation, and at high shear rates they reverse back to the parallel orientation (figure 1). At the same time the viscosity drops with each transition. We still don't understand all the underlying processes.

In some materials, the increasing shear force causes the layers to roll up first into cylinders and then into relatively stable multi-layered spheres, or vesicles. They organise into an orderly, densely-packed arrangement, eventually squeezing together into a polyhedral foam-like structure. The viscosity rises considerably – this is called 'shear thickening'. The actual size and numbers of shell-like layers in the vesicles can be usefully controlled by the shear flow, and they are potential vehicles (liposomes) for transferring drug molecules or DNA into cells.

The effects of adding nano-scale particles which can squeeze between the layers or fit into the vesicles is also of interest – for example, cleaning products often contain mineral abrasives. We carried out the same experiments adding flat clay particles and found that they were not incorporated inside the vesicles. Instead the stiff platelets suck water out of the surfactant solution causing the layers to squeeze together (figure 2).

Another possibility is to add polymers to surfactant solutions. Polymers are interesting not only because they could be used to stabilise drug-containing liposomes but also because their interaction with the surfactant bilayers is a good model for understanding how proteins (also long-chain molecules), embedded in the phospholipid bilayers of cell membranes, control their elasticity. Shear SANS experiments throw light on this crucially important area of biological research, and represents an exciting area for further investigation. ■

Figure 1
Shear-induced reorientation of surfactant layers

vorticity direction

gradient direction

PARALLEL

vorticity direction

gradient direction

flow direction

PERPENDICULAR

PARALLEL

Neutrons reveal for the first time the microscopic structural changes during shear-thinning of thick complex liquids

>> STEPHAN FÖRSTER

What makes tomato ketchup flow?

A micrograph of the worm-like micelles used in the experiment

P. Hodkinson

M any everyday fluids such as face creams, shampoos and sauces flow in unusual ways. Their viscosity may drop drastically when stirred or shaken, a phenomenon called 'shear-thinning' or thixotropy. For example, tip a bottle of ketchup upside down and the sauce hardly moves; shake it and the liquid pours out. Cosmetics such as liquid foundation rely on thixotropy to give an even spread on the skin – the fingers supply the shear force.

Such unusual flow properties derive from the behaviour of long chain-like molecules in the material. They obstruct movement of the liquid because they form networks, either as a result of becoming entangled or of being held together by weak attractive interactions. In household products, the chain structures are mostly polymers or surfactant micelles (p.12). However, solutions of carbon nanotubes (minute cigar rolls of graphitic carbon) or various nanofibres used in high-performance materials also behave in this way. Understanding their flow properties during processing and manufacture is of considerable technological interest.

Surprisingly, until recently, the shear-thinning behaviour of these materials was little understood. It seemed likely that the forced flow induces changes in the orientation of the chain-like molecules and the network structure, but no decisive experiments had been performed.

Measuring shear-induced structures

We addressed this question with a new device recently developed at the ILL. It consists of a high-precision rheometer that can be set up and aligned in the neutron beam (p.10). It allows us to probe changes in molecular orientation and network structure using SANS (p.5) while simultaneously shearing the fluid and measuring the shear viscosity. We could therefore relate the viscosity – a bulk property – to the structure and orientation of the network strands – a molecular property.

We employed 'model' solutions of worm-like micelles of varying thickness and stability. Depending on their chemical structure, they have diameters between 4 and 40 nanometres. The image above taken with an atomic force microscope shows a typical micellar network. Solutions with concentrations between 1 and 10 per
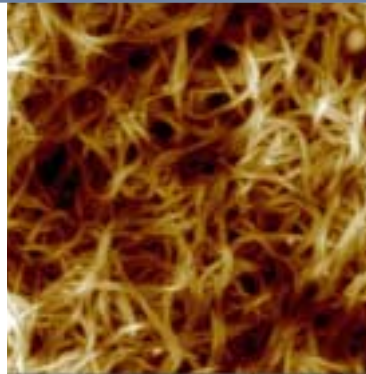
cent show pronounced shear-thinning.

We found that when such a solution was sheared above a certain rate it started to shear-thin, and the neutron scattering pattern became less symmetrical, stretching in one direction (as shown below). This is what we would expect to see as the micelles begin to orient in the direction of the flow. As the shear rate is slowly increased, the viscosity gradually drops and the stretching pattern becomes even more stretched out, thus confirming that shear-thinning is directly related to the orientation of the chain molecules in the flow direction. Furthermore, to see shear-thinning in liquids containing thin micelles, they had to be sheared much faster than those containing thicker micelles.

The quality of the data allowed us for the first time to establish a clear relation between shear viscosity and the orientational order of the chain molecules. The scattering patterns could be analysed quantitatively using theoretical predictions for the distribution of orientations of the worm-like micelles. We were surprised to find a simple exponential relationship between the decrease in shear viscosity and the degree of orientational order – irrespective of micellar thickness and concentration.

These results considerably deepen our understanding of thixotropic fluids, allowing us to predict and tailor their flow properties for particular applications. ■
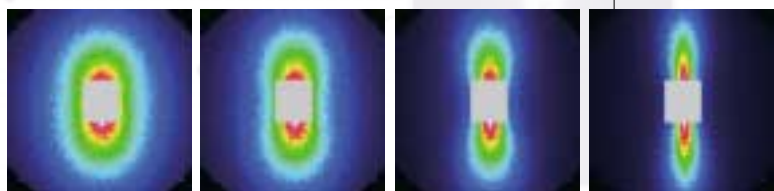
Figure 2
The SANS patterns obtained with decreasing shear viscosity as a result of increasing shear rate

A smart route to nano-structures

>> **JEAN-FRANÇOIS BERRET**

A wide variety of molecular components can be self-assembled using controlled electrostatic forces

Figure 1
Spherical micelles made from surfactants

micelle → 4 nanometres

Figure 2
New architectures for polyelectrolyte-neutral copolymers

di-block copolymer   tri-block copolymer   polymer star   comb polymer
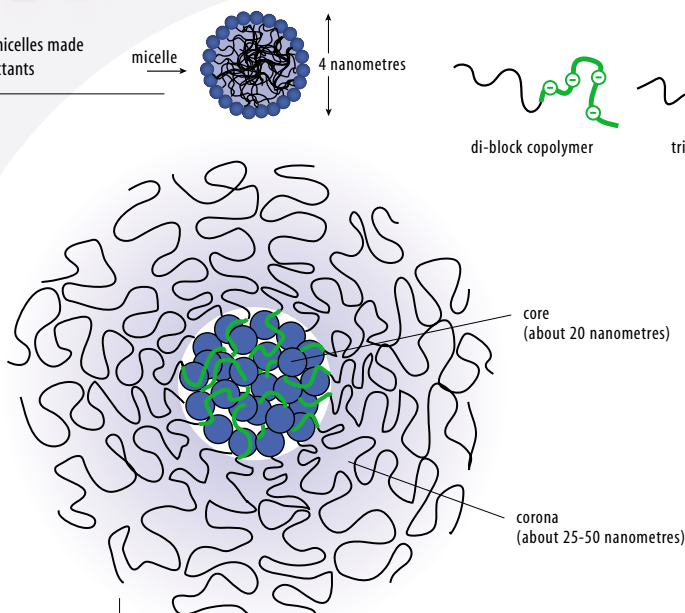
Figure 3
A mixed polymer-surfactant complex

core
(about 20 nanometres)

corona
(about 25-50 nanometres)

M olecules that spontaneously assemble themselves into complex structures at the nano-scale offer exciting prospects for creating new materials with specific functions. The simplest model are surfactants – long-chain molecules with a water-loving (hydrophilic) 'head' and a water-repelling (hydrophobic) 'tail'. In water they collect into tiny cells – micelles – so as to minimise contact between their hydrophobic tails and the water molecules (figure 1). These nano-structures can be globular, cylindrical or planar.

Longer-chain molecules comprised of blocks of hydrophobic and hydrophilic polymers behave similarly, and are extensively used in applications such as drug delivery, catalysis and the stabilisation of colloids and emulsions.

More recently, researchers have sought to extend the concept of self-assembly by exploiting the more general principle of electrostatic attraction and repulsion to bring together diverse molecular components. This approach is set to have a huge impact on applications in material science, nanotechnology and in biology.

Controlled electrostatic self-assembly needs two ingredients to be successful. The first is a pair of oppositely charged molecules such as a polyelectrolyte which carries negative charges along its backbone and a suspension (colloid) of, say, protein particles or micelles carrying a positive charge. The polyelectrolyte will strongly adsorb onto the particles. However, if its chains are long enough, it will attract several particles simultaneously, leading to a catastrophic result: the
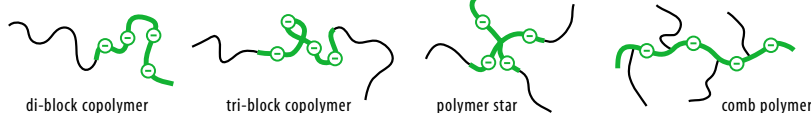
particles aggregate and precipitate out of the colloidal suspension. This destabilisation indicates that in fact the electrostatic attractions are too strong. Some repulsive forces are needed to counter-balance them.

This is where the second ingredient comes in. Polymer scientists have recently found new ways of binding a second chain to the end of the polyelectrolyte chain to form a di-block copolymer. This second component is both neutral and water-soluble and is designed to soften the strong attraction mediated by the charges. A third or more copolymer blocks can even be added to form unusual star and comb-like architectures (figure 2).

Opposites attract

During the past 3 years, our research group has been investigating how these neutral-polyelectrolyte block copolymers interact with oppositely charged micelles, (multiply-charged) ions and inorganic nanoparticles. In the three cases, we have established the various conditions in which they form complex nano-structures via electrostatic self-assembly.

Earlier research suggested they have a core-shell configuration (figure 3). However, their inner structure was unveiled by us only recently, using a combination of light, X-ray and neutron scattering experiments. The SANS technique (p.5) is crucial in determining the microstructure in a quantitative way.

The copolymer used was a poly(sodium acrylate)-*b*-poly(acrylamide) di-block, where the poly(sodium acrylate) is negatively charged in water and poly(acrylamide) is neutral. For the micelle-forming surfactant, we used the C12-cationic dodecyltrimethylammonium bromide. The SANS results showed that the core consists of densely packed micelles and is connected by the polyelectrolyte blocks. The outer shell, or corona, is made up from the neutral chains and insures the stability of the whole aggregate. Similar types of core-shell structures were obtained with the multivalent ions and the inorganic nanoparticles. In the three cases, the mixed aggregates form spontaneously and have a remarkable long-term stability. We anticipate that the process of electrostatic self-assembly could have a large impact in material and biological sciences in the future. ■

>> **IAN HAMLEY**

Dynamics of hair gels

The gels comprising many everyday products have complex dynamic structures as revealed by neutrons ■
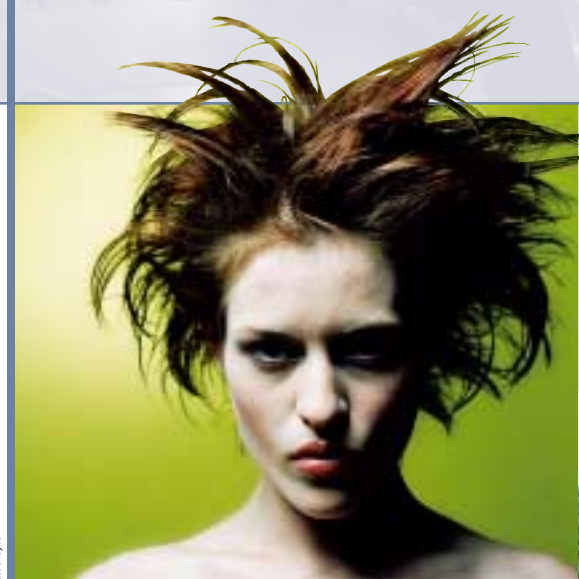
Stockbyte

S pikey hairstyles are the current fashion – achieved by combing through specially-designed gels with a consistency something between a liquid and a solid. The stiffening ingredient may well be a so-called block copolymer built from segments of two kinds of water-soluble long-chain molecules. Indeed, these materials are incorporated into many household and personal-care products to give the required effects. And because the molecules also tend to self-assemble in water into spherical clusters called micelles, there is a great deal of interest in using them to deliver drugs. Not surprisingly, therefore, people are keen to understand how block-copolymer gels form and behave.

Gelation is a complex process. As the temperature is lowered, or concentration increased, the rapid movements associated with molecules in a liquid state suddenly decrease as the polymer chains become entangled. In the case of block copolymer micelles, the chains radiate from the micellar core to form a corona, and they gradually interpenetrate the coronae of neighbouring micelles so that the movement of the micelles is blocked, causing a microscopic 'traffic jam'.

A polarised neutron beam – with the neutron spins all in the same direction – offers an excellent tool for studying the detailed dynamics of this process. The sophisticated technique of 'neutron spin echo' (NSE, p.5) uses magnetic fields to control the orientation of the neutron spins and measure any changes in orientation caused by the absorption of tiny but precise amounts of energy associated with micellar motion, as the beam passes through the sample.

Jellyfish dynamics

We used NSE to study the gelation of a block copolymer consisting of 92 repeats of oxyethylene and 18 of oxybutylene ($E_{92}B_{18}$). This compound forms quite large micelles with coronae of long dangling chains, which move slowly and are therefore easier to study. We investigated the 'hard-gel' phase (doesn't flow under its own weight), the soft-gel state produced by partly melting the gel, and the liquid solution, over a range of temperatures and concentrations. In all cases, we discovered that there were two types of dynamics – slow and fast. By comparing the data with those from experiments on other polymers, we believe that the slow mode represents the micelles squirming past each other, while the fast mode is the result of the dangling polymer chains on each micelle expanding and contracting like the legs of a jellyfish.

The slow mode also gave us a measure of the 'hydrodynamic' radius of the micelles – the size of the micelle given by its movement in a liquid – which agreed with that obtained with light-scattering measurements. This gave us the confidence to use the neutron data to measure the hydrodynamic radius of micelles at high concentrations, not obtainable using light scattering.

We hope to probe the fast mode in more detail in further experiments and perhaps make measurements of the coronae using contrast matching (p.5) . ■
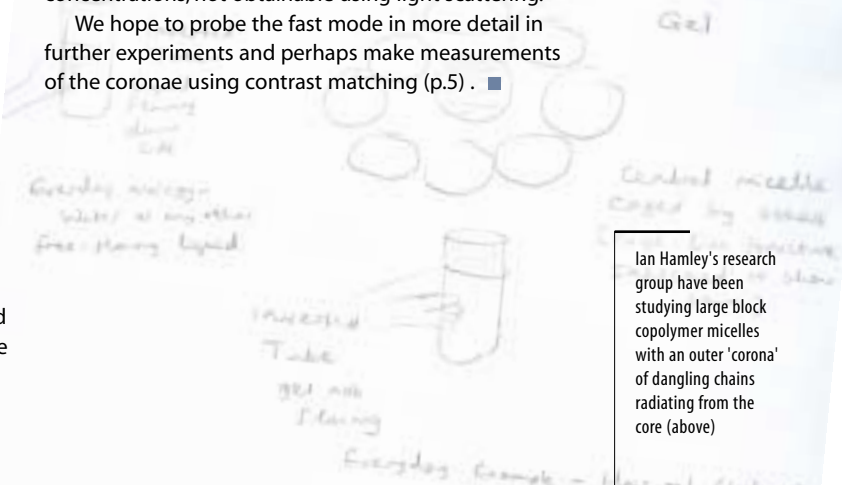
Ian Hamley's research group have been studying large block copolymer micelles with an outer 'corona' of dangling chains radiating from the core (above)
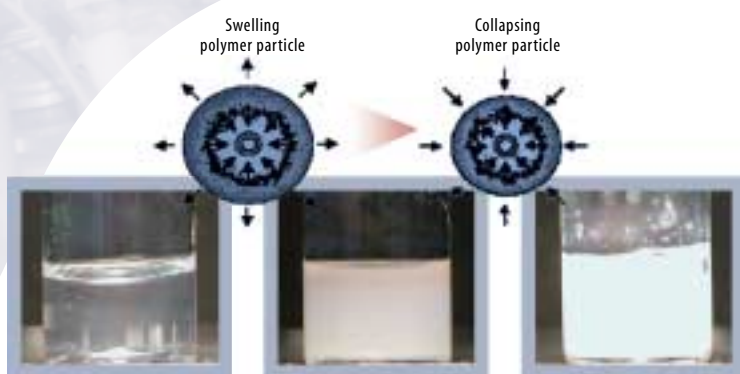
Incredible shrinking gels

Unusual structural changes are revealed in 'smart' microgels which rapidly inflate or shrivel when disturbed by a weak external stimulus

>> ENRIQUE LOPEZ CABARCOS

Swelling polymer particle

Collapsing polymer particle

Bernhard Frick working with the IN10 instrument

A microgel that shrinks when heated, becoming cloudy as the suspended particles become compacted

Gels are usually formed by networks of interconnected polymer chains in a solvent, usually water. Smart gels are a spectacular class of these materials which swell or shrink in response to minute changes in their environment – for example, acidity, temperature, light intensity, solvent composition, or electrical or magnetic fields. This reversible change opens up some exciting applications. The expanding gel could be used to absorb materials such as pollutants, and to encapsulate drugs or perfumes which could then be released by a change in pH. Smart gels could even be incorporated in artificial muscles.

For the gel to expand or contract, the solvent has to diffuse through the polymer network, and this takes time if the gel dimensions are large. However, it is possible to prepare gels consisting of a suspension of tiny polymer particles containing cross-linked chains. Solvent can diffuse in and out of these 'microgels' in seconds, or even milliseconds, rather than minutes, which makes them an attractive prospect as switchable or intelligent materials.

Negative thermal expansion

One type of microgel based on NIPAM, poly(N-isopropylacrylamide), shows fascinating behaviour. Unlike most materials, it actually shrinks when heated from 15 to 50°C, the polymer particles compacting to one-tenth of their original volume. The effect is readily visible: at low temperatures, the swollen particles have a similar refractive index to the surrounding water so the microgel suspension is clear. As the temperature rises, the denser, compacted particles start to scatter light diffusely so the suspension looks milky.

We decided to look at the microscopic changes within the polymer particles, and how the particles interact, as they shrink or swell. A SANS study (p. 5) with instrument D11 shows that the particles have a highly cross-linked core surrounded by a shell of less-connected, and therefore more elastic, polymer segments. The two regions respond differently to temperature. As the gel cools, the shell region expands and solvent is absorbed, exerting additional pressure on the core which collapses (if the polymer chains were not cross-linked they would dissolve in the solvent). At higher temperatures, measurements of the surface roughness of the particles shows their surfaces become smoother and more compacted. The solvent filling the space between the chains is expelled as the microgel contracts at a precise temperature – within about one-tenth of a degree.

The molecular motions of the polymer chains are also very different in the swollen (17°C) and in the collapsed (54°C) microgels. We investigated these states using incoherent elastic and quasielastic scattering experiments on the neutron backscattering spectrometer IN10. At low temperatures, when the microgels are swollen, the polymer chains are under tension and vibrate with harmonic motions like the strings of a guitar. From the neutron data we could calculate the amplitude of the vibrational motion, and we found that it oscillated as the microgel heats up and shrinks. The lack of tension in the polymer chain during the microgel collapse is similar to that of a slack guitar string, and the gel vacillates between more and less compact structures. At low temperatures, the microgel behaves as a polymer in solution, whereas at high temperatures it is more like a solid polymer.

We suspect that heating destroys electrostatic screening effected by water molecules between the charged polymer chains, causing them to collapse. We hope to test this idea with neutrons in the future. ∎

Interactions between polymers and membranes are
of key importance in many biological processes

Of micelles and membranes

>> PETER GRIFFITHS AND ALISON PAUL
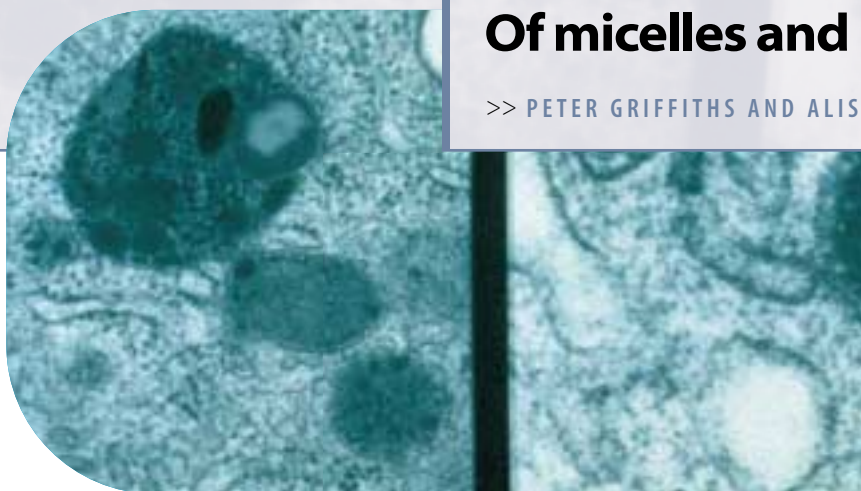
M any everyday products – paints, cosmetics and detergents – are complex suspensions of polymers and surfactants which interact to provide a particular set of properties. Using a combination of analytical techniques including SANS (p.5), we have been probing interactions between polymers and micelles comprising more than one surfactant, to see how the structure of the surfactants and polymers affects the binding process – as well as concentrations and surfactant proportions.

We are now applying the same approach to biological systems. Fats (lipids) taken in as food are first emulsified by natural surfactants – bile salts from the liver. They form mixed micelles which can then interact with, and be broken down by, digestive enzymes produced by the pancreas; for example, phospholipids are broken down by phospholipase in this way. We were interested in characterising the structure of these micelles as an important aspect of the micelle-enzyme interaction (enzymes are essentially polymeric molecules).

Using SANS, we examined two model mixed-surfactant systems, each composed of a phospholipid, diheptanoylphosphatidylcholine, and a synthetic surfactant – one anionic (sodium dodecyl sulfate) and one cationic (dodecyltrimethylammonium bromide). We found that while the structure of the micelles was largely insensitive to their composition, the amount of water that could squeeze into the shell depended on the size of the headgroups of the three surfactants. The shape of the micelles was elliptical so as to accommodate the longest hydrophobic tails.
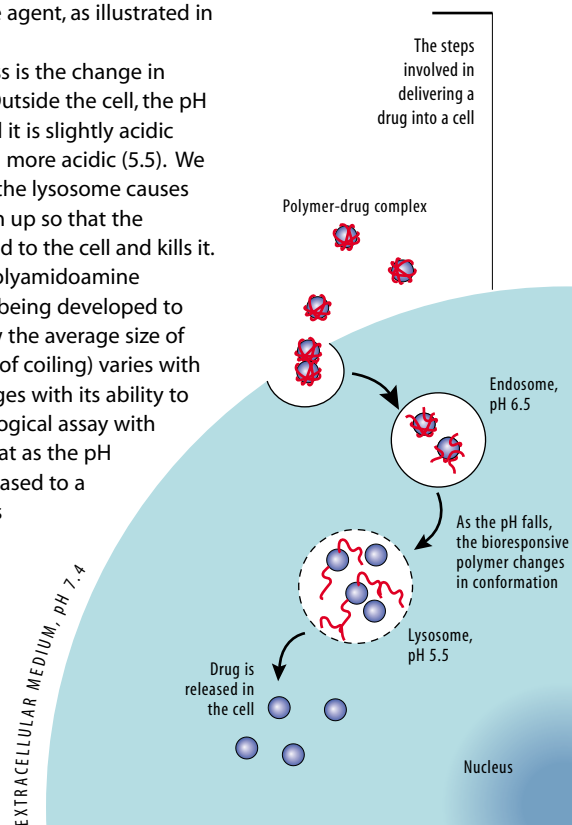
Drug delivery

Cell membranes also share the same characteristics as these mixed micelles, being composed of phospholipids and other molecules. A key area of interest in life science is finding optimum ways of permeating such membranes to deliver drug molecules, genes and other therapeutic agents.

One approach is to harness the kind of membrane interactions described above. For example, a water-soluble polymer can be coupled via a biodegradable linker to, say, an antitumour molecule. The polymer coils itself around the antitumour molecule, acting as a shield while it circulates in the blood. Normally the polymer-drug agent would be too large to pass through a blood vessel wall, but fortunately tumour blood vessels are porous enough to allow it to pass through so that it selectively reaches tumour cells. The agent is taken into the cell via a micellar unit called an endosome. Intracellular, single-membraned units called lysosomes then engulf the agent, as illustrated in the figure below.

A crucial aspect of this process is the change in acidity across the membranes. Outside the cell, the pH is slightly alkaline (7.4), in the cell it is slightly acidic (6.5), while the lysosome is much more acidic (5.5). We speculated that the lower pH of the lysosome causes the coiled polymer chain to open up so that the anticancer drug becomes exposed to the cell and kills it.

We tested this idea using a polyamidoamine (PA ISA 23) – a class of polymers being developed to deliver drugs. We measured how the average size of ISA23 (and therefore the degree of coiling) varies with pH, and correlated the size changes with its ability to break up cells (done using a biological assay with rat red-blood cells). We found that as the pH was lowered, the ISA23 size increased to a maximum at around pH = 3, thus confirming for the first time the proposed mode of action for these polymers. ◼

The steps involved in delivering a drug into a cell

Polymer-drug complex

Endosome, pH 6.5

As the pH falls, the bioresponsive polymer changes in conformation

Lysosome, pH 5.5

Drug is released in the cell

EXTRACELLULAR MEDIUM, pH 7.4

Nucleus

SANS reveals how metal ions can make electrically charged polymers coil into transient beaded structures

>> **KLAUS HUBER**

P. Hodkinson

Polymer pearl necklaces

T here is enormous interest in polyelectrolytes – polymers with negatively charged groups of atoms along their chains. A typical example is sodium polyacrylate which has a regular array of carboxylate groups. These groups of atoms can usefully attach themselves to metal ions with two or more positive charges, such as those of calcium, magnesium or a heavy metal. For example, by binding to the tiny crystals of calcium carbonate that deposit in hot-water pipes, the polyelectrolyte inhibits scaling by blocking further deposition. Polyelectrolytes are also incorporated in detergents to prevent calcium and magnesium carbonate crystallites precipitating onto laundry and turning it grey. And they can stabilise calcium carbonate suspensions employed as fillers in paper production and in paints containing metal pigments.

Biopolymers such as proteins represent another important group of polyelectrolytes. Their role in the body often involves interacting with metal ions, for example, in the formation of bone (calcium phosphate) or shells (calcium carbonate). By understanding these biological processes better, it might be possible to mimic them to make new materials.

Exploring how polyelectrolytes behave in the presence of these metals is therefore extremely important. We know that their three-dimensional structure changes as more metal ions are added. For example, in a sodium polyacrylate solution, the chains are quite spread out as the negative carboxylate groups repel each other. Gradually introducing positive calcium ions reduces the electrostatic repulsion and the chains coil tightly together. Eventually, as the respective positive and negative charges cancel out, the hydrophobic polymer chain is no longer soluble in water and it collapses into balls of material which precipitate out of solution.

We were interested in determining how this coil shrinking and precipitation happens. Theoreticians had suggested that the polymer coils first collapse into cigar or beaded chain-like shapes. Several research groups had tried to unravel the mechanism but without clear-cut results.

The first thing to do was to establish the concentrations of calcium ions needed to precipitate a corresponding amount of the polyelectrolyte, and plot a graph showing threshold concentrations for precipitation. We could then explore the behaviour of the polymer chains in the region of the graph just below the threshold concentration divide. This involved starting with a fixed amount of calcium ions and gradually lowering the relative proportion of polyelectrolyte (see figure below).
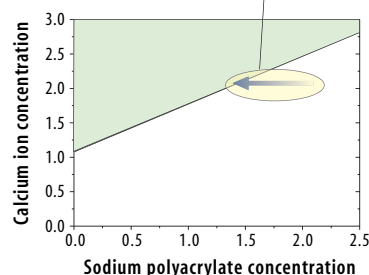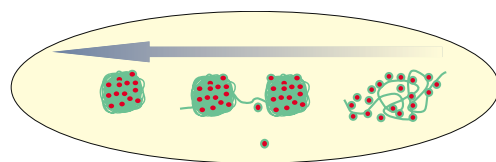
Observing polyelectrolyte collapse

Light scattering was then used to follow the behaviour of the congealing polymer chains ever closer to the precipitation threshold. This allowed us to pick out four consecutive, distinct intermediate states for further examination with SANS (p.5).

We found that the SANS data or the intermediates did not quite fit theoretical curves of fluffy coils or compact cylinders or spheres, which are often used in polymer and colloid research as models. Instead, the scattering curves matched what would be expected for dumbbell shapes. This led us to believe that a series of beads formed, connected by chains, before the final collapse into a globular state.

Neutral polymers may also behave similarly when dispersed in a poor solvent, but the intermediate pearl-necklace structure is not stable enough to observe. However, our results with polyelectrolytes stabilised by charged groups do indeed confirm theoretical predictions. ■

Polyelectrolytes are used to prevent build-up of limescale

A graph showing the threshold amount of calcium ions needed to precipitate a given concentration of polyelectrolyte. The arrow indicates the concentrations at which the polyelectrolyte chains start to collapse

Calcium ion concentration

Sodium polyacrylate concentration

Spherical polyelectrolyte brushes

Polymeric brush-like micelles show some remarkable properties

>> **JOHAN VAN DER MAAREL**

Photodisc

P olyelectrolyte brushes consist of charged polymer chains attached to a substrate. They have huge technological potential in controlling processes such as gelation, lubrication, and flow behaviour, so have found wide-spread application – from stabilising colloidal suspensions in cosmetics and food products to encapsulating and delivering bioactive agents to living cells.

These systems can be prepared by anchoring the polyelectrolyte chains at an interface, or more interestingly, through the self-assembly of di-block copolymers (p.12). These comprise two linearly attached polymer chains – in this case, a polyelectrolyte, which is hydrophilic, and a neutral, hydrophobic polymer. In aqueous solvents, the copolymers arrange themselves into micelles so that the hydrophobic components are hidden from the water. The micelles thus comprise a core of self-assembled neutral chains (typically about 100), surrounded by a polyelectrolyte 'coronal brush' (see figure below right).

These micelles offer an excellent model system for investigating how spherical polyelectrolyte brushes behave, provided that their neutral cores are dense and stable (for example, sodium polyacrylate-polystyrene). Because the coronal brush is ionic, the micelles readily form dispersions in water. The polyelectrolyte dissociates into small positive counterions, and the negative polymer chains stretch out into the aqueous environment – unlike neutral brushes which coil up. Since technological formulations and biological environments usually contain other small ions, a significant aspect is the effect of adding salt (sodium and chloride ions). The addition of extra ions might be expected to screen the electrostatic repulsion between charged segments in the polymer chain, making it behave more like a tightly coiled neutral brush.

The key approach in understanding the behaviour of polyelectrolyte brushes under various conditions is to look at the structure of the micelle, going from the core outwards, in terms of polymer and ion density. We measured these density profiles using SANS (p.5), applying solute and solvent contrast variation techniques (p.5) to highlight or blank out the various components in the complex mixture of copolymer, salt and water.

For a highly charged polymer and no salt added – so with minimal screening – we found that the corona chains are almost fully stretched and the density profile of the counterions follows that of polymer corona. But even when quite a lot of salt was added, the brush did not shrink much. This suggests that the stretching is primarily controlled by the counterions trapped in the corona, which draw in water osmotically, rather than by electrostatic effects.

High concentrations

We then extended our experiments to micelle concentrations high enough to cause the coronal brushes to shrink or interpenetrate. This is significant because many of their technological applications are derived from the fluid properties of dense micelle systems, and yet not much is known about how the brushes behave.

We were able to measure the sizes of the core and corona which gave the overall spread of the micelle; we also ascertained what the effective size of the micelles would be, packed as hard spheres in the solution. The difference between these two values gave the degree of interpenetration of the brushes.

The results showed that the polyelectrolyte brushes do shrink as the micelles are squeezed together. However, at high charge and minimal screening conditions – when the polyelectrolyte chains remain almost fully stretched – they start to interpenetrate above a certain concentration. Flow measurements showed that the viscosity increases by 1000 times, resulting in a gel. We conclude, therefore, that tuning the properties of the brush is of paramount importance in developing formulations with the right flow properties. ■

A spherical micelle with a neutral, solvent-free core and a polyelectrolyte coronal brush
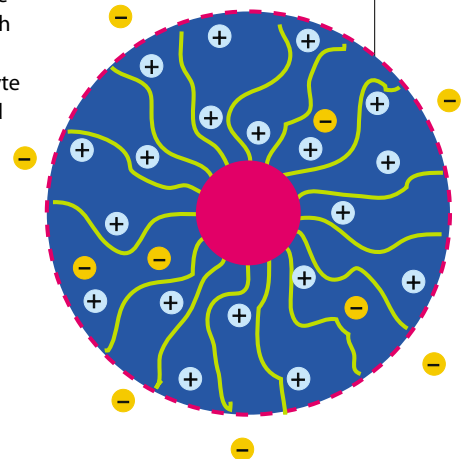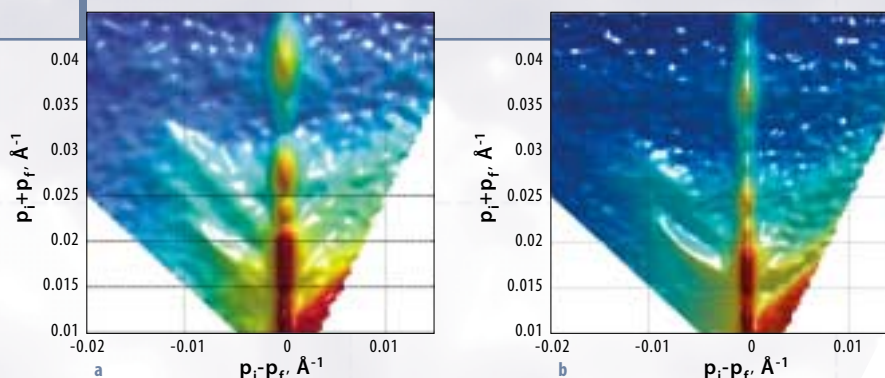
Nano-composites made to order

Neutron studies investigate how to organise complex materials at the nano-scale

>> **VALERIA LAUTER-PASYUK**

Figure 1
Experimental two-dimensional intensity maps of neutrons scattered by PS-PBMA lamellar films with 0 (a) and 13 (b) per cent of nanoparticles

There is great interest in engineering novel, high-performance composite materials and devices that are organised at the nano-scale. Many of these composites consist of a block copolymer matrix (p.12) hosting small metallic or inorganic particles.

A 'smart' method of making such nano-composites is to use the principle of self-organisation. The copolymer may form cylindrical, spherical or layered (lamellar) structures, depending on its shape and molecular weight. These structures can then act as templates for organising nanoparticles introduced in a controlled way.

We explored how to obtain a highly organised periodic distribution of nanoparticles within the layers of a copolymer film and trace the details of their distribution. A symmetrical di-block copolymer of equal amounts of polystyrene (PS) and polybutylmethacrylate (PBMA) was used.

Coating the nanoparticles with one of the constituent polymers gives them a particular affinity for that polymer in the layered film. We could then produce a nano-composite with, say, the PS-coated nanoparticles in only the PS layers.

The potential of such nano-composite films depends not only on how well the distribution of the nanoparticles in the layers can be controlled, but also on whether the long-range structure of the host matrix can be maintained with increasing concentration of nanoparticles.

Reflections on polymer layers

Neutron reflectivity (p.5) is the ideal method for investigating these issues. By deuterating one of the copolymer constituents to provide scattering contrast, the technique can detect any changes in the thickness (from specular reflections) and roughness (from diffuse scattering) of the layers, as well as changes in the distribution of nanoparticles. The structure of the films is revealed as a 2-D map of the scattering intensity.

We investigated how the particle concentration and size affects the architecture of the composite film. This involved preparing films with nanoparticles 5 nanometres across at five different concentrations from 0 to 13 per cent by volume. The intensity maps for the two extremes of concentrations show the differences due to the presence of the particles (figure 1). Analysis of the maps for all concentrations reveals that all the films are organised into a well-ordered structures with sheets of particles in the PS layers (figure 2a). An important point is that a high contrast in neutron sensitivity between deuterated PS and non-deuterated PBMA lamellae enabled us to quantify the swelling of individual lamellae. The thickness of the PS layers increases with the volume percentage of particles, while that of the PBMA layers remains unchanged.

We also investigated the effect of nanoparticle size on the structure of the multi-layer using larger particles with a diameter of 11 nanometres. We found that for low volume percentages – 5 and 10 per cent – the films are organised into well-ordered lamellar structures, with the particles concentrated around the central part of the PS layers. At 20 per cent, the nanoparticles spread throughout the PS layers – but increasing the concentration to 40 per cent destroys the lamellar structure (figure 2b).

These results show that the nanoparticles can effectively be made to organise into a sequence of sheets by being selectively introduced into one component of a di-block copolymer, thus providing a method of making and fixing tailored nano-structures in protective polymer layers. ■

Figure 2
a) The structure of composite films with increasing concentrations of nanoparticles of 5 nanometres across, along with the neutron scattering length density profile

b) The structure of composite films with nanoparticles 11 nanometres across
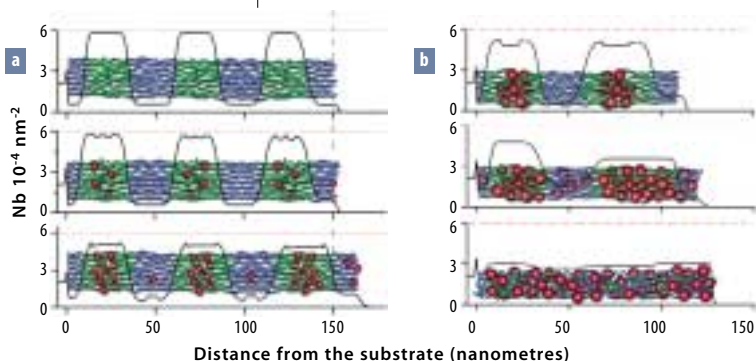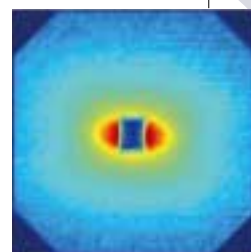
Towards a better tyre

Chemically tailored nanoparticles can be incorporated into polymers to create mechanically superior materials

>> **FRANÇOIS BOUÉ**

Anisotropic neutron scattering from a deformed film containing the nanoparticles

Creating and manipulating minute particles tens or hundred of nanometres across opens up a whole world of technological possibilities. They can be introduced into plastics to create new materials with sophisticated optical or electronic properties – or simply improved mechanical properties. For example, inert particles such as silica, less than a micrometre across, together with carbon black, can be incorporated into rubber to reinforce it for use in car tyres.

You might think that the reinforcement would arise from interactions between the hard particles and the soft polymer matrix. However, in practice, it is the strong contacts between particles that are important. Nanoparticles tend to stick together, and the optimum effect is produced by a network of small clusters, or aggregates, of particles which are pushed together when the rubber deforms.

It is therefore extremely important to be able to control how the nanoparticles aggregate in the polymer. One novel way is first to coat them with polymer chains, which then protect and separate them. This also makes it easier to disperse them in polymer sheets, as well controlling the scale of aggregation.

Clever chemistry

We were interested in finding the best way to graft polymer chains onto 'really nano' silica particles (10 nanometres across). The particles can be suspended in a special solvent that prevents the particles from flocculating. However, attaching chains all over a particle surface is a problem because once one chain is grafted, it blocks access for the others.
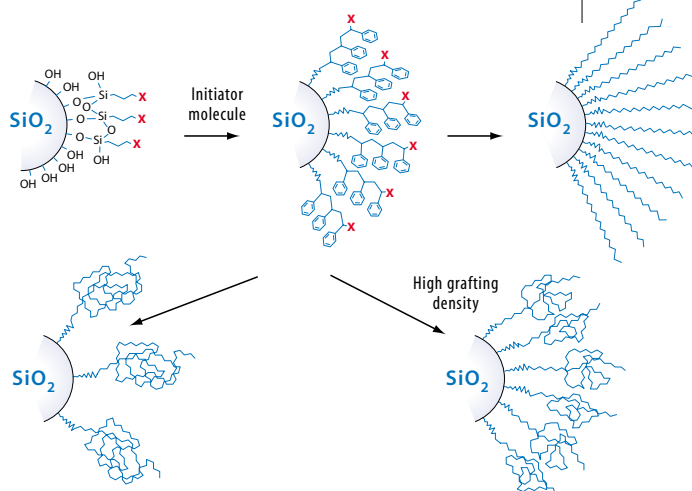
A solution is to grow the polymer chains actually on the particles. A standard method of polymerisation is to start with an 'initiator' molecule with an active site (here, a single unpaired electron or 'radical') which binds a monomer building block. The unpaired electron is then transferred to the monomer which binds another monomer, and so on, to create a chain. By first attaching appropriate initiator molecules to the particle, we should be able to grow many chains around the particle core simultaneously (see figure).

We wanted to observe directly how the chains grow and their effect on aggregation. SANS, with contrast variation using a deuterated solvent (p.5), offers an

effective approach. We could highlight either the silica core or the polymer coating, and we took samples from the reaction batch at successive times for each type of contrast matching,

Highlighting the silica particles revealed that there was some aggregation to start with, which then stabilised. The 'polymer only' scattering profile indicated that a shell of well-defined thickness had grown. The polymer data gave us the polymer mass for an average cluster of particles, while the 'silica-only' scattering revealed the level of aggregation. We could also obtain measurements of single, coated particles by centrifuging and filtering off the larger clusters. Combining these data with measurements of the mass of the grafted chains (made by dissolving the silica particles and retrieving the polymer), we could then calculate the number of grafted chains per particle. This allowed us to monitor the efficiency of the reaction in relation to levels of aggregation and the accessibility of the radicals located at the end of the grafted chains.

We now plan to use SANS further to explore how grafted particles can be dispersed in a film of the same polymer to get improved mechanical properties. An important aspect will be to observe how the coated particles interact when the material is stretched. ▪

Synthesis of polymer-grafted silica nanoparticles

Research team   F. Boué, A. El Harrak, J. Jestin and G. Carrot *(LLB, CEA Saclay, Gif-sur-Yvette, France)*, J. Oberdisse *(University of Montpellier, France)*, and R. Schweins *(ILL)*

How do polymer
latex dispersions dry
into thin films?

Watching paint dry

>> JENS RIEGER

Photodisc

L atices are aqueous colloidal dispersions of spherical polymer particles – typically about 100 nanometres across – used in many products, from paints and printing inks to adhesives and paper coatings. In recent years, there has been increasing interest in exploring how polymer dispersions evaporate to form arrays of close-packed spheres, for example, in paint films. We know from electron microscopy that as the film forms, the polymer spheres start to pack together as shown in the figure below. They are then increasingly compressed, distorting into polyhedra. Eventually they coalesce as the polymer chains from adjoining particles interpenetrate.

However, there are still many open questions about this drying process. What structure do the polymer spheres pack into? Does the temperature at which the film formed affect this structure? How quickly and evenly do the particles coalesce? Where does the water go once the film is exposed to humidity?

SANS (p.5) offers a way of exploring these effects. Our investigations differed from previously published experiments in that we introduced water into samples after the film had formed. The water had been deuterated in order to distinguish its signal from that of the polymer hydrogen atoms.

We used a latex of 50-50 styrene/*n*-butylacrylate copolymer. This was stabilised against coagulation by negative surface charges. The spread of particle sizes was quite narrow with an average diameter of 130 nanometres. Films were prepared by evaporating the water at room temperature, which is the temperature at which the polymer particles readily coalesce into the transparent film. Pieces of film of known mass were packed into polyethylene bags, together with a certain amount of deuterated water, and sealed. We then carried out the SANS on hydrated films.
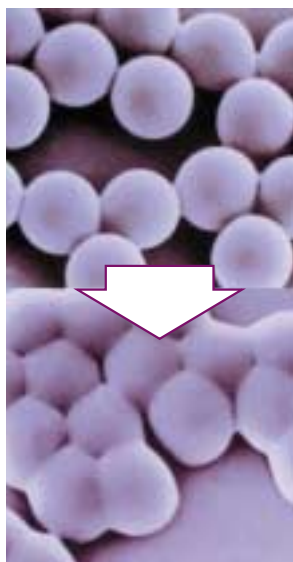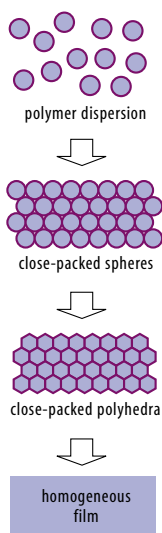
Polymer film structure revealed

The SANS scattering data revealed two pronounced peaks, which confirm that the film has an ordered structure as seen with an electron microscope. The scattering behaviour was independent of the actual water content of the films – as long as it was below about 10 per cent. This indicates that the peaks arise from the ordered polymer spheres rather than from the water seeping in around them.

We compared the scattering curve with that calculated for a simple packing arrangement – a face-centred cubic (fcc) lattice, and found that it matched exactly. The theoretical scattering patterns for alternative packing arrangements – a body-centred cubic lattice or an hexagonal close-packed lattice – are completely different.

We then carried out the same experiment on latex films that had first been heated to various temperatures for 120 minutes before being exposed to deuterated water. For temperatures below 150°C, we observe the familiar two-peak structure which indicates that the water can still diffuse preferentially into the gaps between the ordered array of polymer particles. Thus, the film remembers its initial state even after prolonged annealing. The picture changes drastically, however, once the film has been tempered for 2 hours at 180°C. Instead of the two peaks, which have almost completely disappeared, we see another increasing SANS signal, which we interpret as arising from domains of water molecules. We conclude that they can no longer squeeze into the spaces between the polymer spheres, so congregate elsewhere. Presumably this is because the polymer spheres have become glued together – by inter-diffusion of the particles' polymer chains – so block access. ■

Stages during the process of film formation from polymeric dispersions, as shown in the micrograph on the right

polymer dispersion

close-packed spheres

close-packed polyhedra

homogeneous film

Research team J. Rieger, G. Ley and E. Hädicke *(BASF Aktiengesellschaft, Germany),* and P. Lindner *(ILL)*

Reality chemistry in thin films

Neutron reflectivity digs beneath the surface of electrically active polymer films used in sensors

>> ANDREW GLIDLE AND ROBERT HILLMAN

Eric Lichtenscheidt

A typical biosensor system

In the past 50 years, plastics have come a long way. Today, chemists can make highly specialised polymers which have groups of atoms attached to them, rather like pendants along a necklace. These groups endow the material with valuable characteristics such as selective chemical reactivity, or electronic and photoelectric properties. If fabricated as a thin film, the active polymer can then be used in sensors and other electronic devices.

Although there are many techniques for studying the surface properties of these films, measuring inside them is much harder, particularly in 'working' environments. Fortunately, because neutrons pass easily through most polymers, the technique of neutron reflectivity can be used to probe their interiors.

The ILL's upgraded reflectometer

The ILL's upgraded D17 reflectometer (p.5) is particularly suited to such studies; it can accommodate a variety of auxiliary equipment and now delivers neutron beams intense enough to study physical and chemical processes inside films, as they happen.

We recently carried out two studies on D17 investigating reactions in polymer films. The first related to structural and compositional changes driven by electricity – as feature in materials in many everyday items such as batteries, mobile phone displays and biosensors. We were interested in the electrochemical response of poly(vinylferrocene), PVF, a thin-film electrode material that can be used in sensing and catalysis systems as well as fundamental studies of how electrochemical forces cause electrons and ions to move inside polymers. This polymer has pendant groups consisting of an iron atom sandwiched between two electron-rich carbon rings (ferrocene). These can be made to lose and then regain electrons by passing an electric current through the cell – in other words, go through a cycle of oxidation and reduction.

We used neutron reflectivity to make measurements of the internal structure of the film in both the oxidised and reduced state in an aqueous electrolyte. We found that whereas the reduced film contained hardly any water, in the fully oxidised film the water content rose significantly to about 30 per cent, and the film swelled substantially. By coupling our electrochemical instrumentation to D17, we could probe these changes as they happened. This showed that although the water was taken up mainly at the beginning of the oxidation sweep, the swelling occurred at a more even rate. We are now attempting to use time-resolved neutron reflectivity to see whether neutral molecules such as glucose can be drawn into the polymer as the initial flux of water enters the film. This could be important in developing polymer sensors that detect small biomolecules.

The second study involved exploring how effectively sensor molecules might attach themselves to a chemically activated film of an electrically conducting polymer. We wanted to see whether a molecule's size affected how far it could penetrate into the film. Combining neutron reflectivity with reflectance infrared spectroscopy, we could follow the changing chemical composition of a film as it reacted with large or small molecules from solution. As might be expected, larger molecules are more likely to be immobilised near to the solution interface, and the neutron data provide the only way to quantify this amount.

Other neutron reflectivity measurements have shown us that the porosity of the polymer can be controlled by electrodeposition methods. Taken together with these new dynamic measurements of changing structure, solvation and chemical composition, neutron studies could have a significant impact on making sensors based on both large and small molecules. ■

Structure of a poly(vinylferrocene) unit

Fe
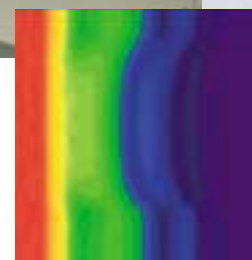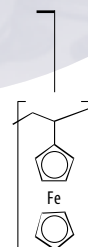
Neutron reflectivity profiles during the electrochemical cycling of the PVF film. The colour scale denotes the intensity of the reflectivity and changes in the pattern correspond to variations in the film thickness during cycling

The D17 reflectometer with the infrared spectrometer attached

Research team   A. Glidle, N. Gadegaard and J. M. Cooper *(University of Glasgow, UK)*, A. R. Hillman *(University of Leicester, UK)*, and K. S. Ryder and E. L. Smith *(University of Loughborough, UK)*

Light can be used to control
the properties of surfactants

>> JULIAN EASTOE

Photo-tuneable films

a. Before irradiation

b. After irradiation

Figure 1
The structure of a surfactant which is broken up into its water and oil-loving segments by light
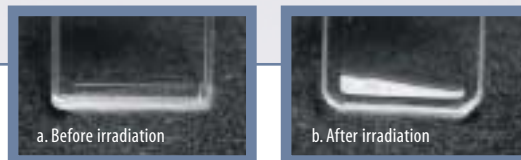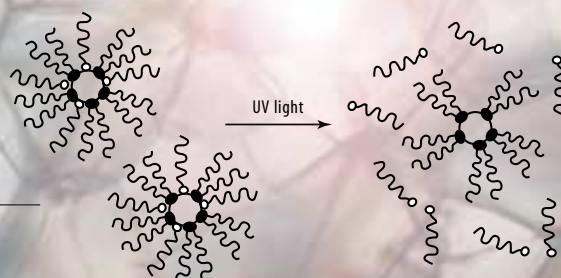

Figure 3
The effect of irradiation with UV light: initially the stable microemulsion sample is transparent (a) since dilute nanometre-sized aqueous droplets are present. After a burst of UV light (b), a milky emulsion containing micrometre-sized droplets begins to form, which eventually resolves into a clear upper microemulsion phase and a denser, opaque water-surfactant mixture seen at the bottom of the sample

Figure 2
The concept behind photo-tuneable surfaces comprising a photo-destructible surfactant

Julian Eastoe's team

S urfactants are molecules that adsorb at interfaces between two liquids which don't normally mix, or between a liquid and vapour. They usually consist of two parts – a water-loving ionic component and an oil-loving carbon chain – and so can modify the structure and behaviour of the interface, perhaps creating tiny surfactant-coated droplets of one liquid dispersed in another (emulsion) or gas bubbles in a liquid (foam). It is this property that is responsible for the cleaning power of detergents, and the ability of living cells to take in materials, or lungs to absorb gases. Synthetic surfactant systems are being considered as a means of delivering drugs or even genes into cells.

In domestic cleaning products, the surfactant performance is controlled by adding an electrolyte like salt, or by changing the pH or increasing the temperature. We have been looking at another approach – using light to modify the behaviour of photo-sensitive surfactants. For example, UV light breaks up the molecule above (figure 1) into its separate water and oil-loving segments, thus 'switching off' the surfactant properties.

If mixed with an inert co-surfactant to give a water-in-oil nano-droplet dispersion, or microemulsion, we can then alter the behaviour of the system using UV light, which selectively destroys the photo-surfactant. This results in a dramatic drop in the stability of the microemulsion and also the size of the nano-droplets (figure 2), and some of the water separates out from the oily medium.

Shrinking water droplets

We were able to follow the shrinkage of the water nano-droplets using SANS (p.5), which can pick out the detailed structure of the droplets using the well-established contrast technique (p.5). First, deuterated water was used so that the SANS experiments revealed the dimensions of the water cores. Then both water and oil were deuterated to pick out the hollow surfactant shell. Detailed analysis reveals a shrinkage of the water cores from 6.3 to 4 nanometres after UV irradiation, corresponding to a decrease in nano-droplet volume of about 75 per cent. Therefore, using light to destroy the photo-surfactant is equivalent to reducing the effective surfactant concentration, thereby controlling the stability and size of the dispersed water droplets (figure 3).

Chemicals like the molecule in figure 1 represent a new generation of surfactants with additional chemical properties that can be tuned so as to control properties like surface tension, formation of droplets, stability of emulsions, and viscosity and gelation (p.13). These kinds of photosensitive systems could be used to transfer materials such as drugs, and pigments used in printing and paints. ■

Glossary

Bilayer
A term applied to double layers of lipid molecules as found in cell membranes.

Block copolymer
A material consisting of alternating segments of more than one type of polymer.

Carboxylate group
A negatively charged group of atoms in which carbon is bound to two oxygens.

Coil collapse
The shrinking of polyelectrolyte chains under specific conditions, leading finally to precipitation.

Colloid/colloidal suspension
A fine dispersion of one material in another. The colloidal particles are less than a micrometre in size. Colloidal suspensions can comprise various combinations of phases: for example, one liquid dispersed in another is an emulsion; a gas dispersed in a liquid or solid is a foam.

Conformation
Molecules, such as polymers, with directional bonds that can rotate freely, can form different shapes or conformations depending on their immediate environment.

Contrast variation
A technique in which certain atoms in a sample are substituted by another isotope with a different scattering strength in a way that preferentially enhances the scattering pattern of particular components of interest.

Dendrimer
A polymer with a highly branched structure.

Deuteration
The (chemical) replacement of a hydrogen atom in a molecule with its isotope deuterium.

Deuterium
A heavier isotope of hydrogen having a neutron as well as a proton in the nucleus.

Emulsion
A colloidal dispersion of one liquid in another liquid (usually water and oil).

Gel
A semi-solid solution in which large amounts of liquid solvent are confined within a flexible network of polymer or other colloidal particles.

Glass transition
The temperature at which a solid polymer melts into a liquid.

Head-group
The component of a surfactant molecule that is hydrophilic.

Hydrophilic
Water-loving.

Hydrophobic
Water-hating.

Incoherent elastic scattering
Scattering, without any energy transfer, in which an incident neutron wave interacts independently with each nucleus in the sample to give randomly scattered waves.

Inelastic scattering
A neutron technique in which there is an exchange of energy between the neutrons and the molecules being studied, thus giving information about their motion and flexibility. (When a neutron is scattered elastically, there is no energy transfer.)

Ion
An atom or molecule that has gained or lost electrons so that it has become electrically charged. A multivalent ion has gained or lost several electrons.

Latex
A colloidal dispersion of a polymer in a liquid (usually water).

Lipid
A molecule consisting of a long hydrocarbon chain with an electrically charged group of atoms at one end. Lipids arrange themselves in layers and are the basis of biological membranes.

Liposome
A microscopic sac-like structure consisting of a lipid or detergent membrane in which molecules or even genes can be inserted.

Lysosome
An intracellular membrane-bound body containing enzymes in an acidic environment, which breaks down large molecules.

Endosome
An intracellular compartment surrounded by a permeable membrane.

Micelles
Clusters of small molecules such as surfactants that assemble together in a solution, often with distinctive arrangements depending on chemical composition.

Microemulsion
An emulsion stabilised by surfactants in which the dispersed droplets are just a few nanometres in size.

Nanometre
One-billionth of a metre (10^{-9} metres).

Nanoparticle
Particles of matter at the scale of a nanometre. They often have specific properties connected with their size.

Nano-composite
A material composed of more than one compound organised at the nano level.

Neutron
One of the two particles found in the atomic nucleus. They have a characteristic wavelength depending on energy.

Neutron backscattering
A technique in which neutrons hit the monochromator and analyser crystals head-on and are reflected back along the same path. The energy of the backscattered neutrons is precise enough to allow measurement of small changes associated with very slow motions in a material.

Neutron reflectivity
A technique in which neutrons are reflected off a surface or interface. It is used to characterise the structure of surfaces and thin layers.

Neutron spin echo
A neutron technique which measures the changes in the spins of neutrons passing through a material, caused by small transfers in energy associated with molecular movements over relatively long timescales.

Phospholipid
A class of lipid containing a phosphate group.

Plastic
A colloquial synonym for a bulk polymer.

Polyelectrolyte
An electrically charged polymer, usually water-soluble. An example is sodium polyacrylate.

Polymer
A molecule comprising repeating molecular units (monomers), usually in long chains.

Polyphenol
Polymers derived from phenols – ring-shaped molecules with hydroxyl groups attached.

Quasielastic scattering
Inelastic scattering but with much smaller energy transfer (close to zero) between the neutron and the atomic nucleus.

Redox reaction
A chemical reaction in which a molecule reversibly gains or loses electrons.

Reptation
The mechanism by which a single polymer chain moves through the entangled environment of other chains in melts or concentrated solutions. It is thought of as moving through a virtual tube defined by the surrounding chains.

Rheometer
A device for measuring the rheological properties of fluids, such as the viscosity.

Self-assembly
Molecules, such as surfactants, can spontaneously assemble themselves into complex structures at the nano-scale.

Shear thinning
The reduction of viscosity with increasing shear rate.

Small angle neutron scattering (SANS)
Measurement of neutron scattering at small angles used to investigate structures with large interatomic distances such as polymers or biological structures.

Soft condensed matter
Materials such as polymers, gels and colloidal dispersions that are soft at room temperature – in other words, can deform or change shape under mechanical pressure. Such materials often have complex structures at the nano or meso-scale.

Specular reflection
Reflection of waves in which the angle of reflection equals the angle of incidence.

Surfactant
A class of molecule that adsorbs at surfaces or interfaces. Surfactants are usually molecules with a hydrophilic head-group and a hydrophobic tail. They dissolve in both water and oil, forming organised structures such as micelles. They stabilise emulsions and act as cleaning agents (soaps and detergents) by binding to oily materials and dispersing them in water.

Thixotropy
The property of some fluids to thicken into a gel when left standing but convert into a more fluid state when agitated.

Contacts

Scientific Coordination Office (SCO)
Email: cicognani@ill.fr *or* kjenkins@ill.fr

Dr Peter Lindner
Email: lindner@ill.fr

Dr Ralf Schweins
Email: schweins@ill.fr

Institut Laue Langevin
6 rue Jules Horowitz
BP 156
F-38042 Grenoble Cedex 9
France

Page 6
Professor Matthias Ballauff
Department of Physical Chemistry
University of Bayreuth
Universitätsstrasse 30
D-95440 Bayreuth
Germany
Email: matthias.ballauff@uni-bayreuth.de

Page 12
Dr Jean-François Berret
Department of Complex Materials & Systems
University of Paris 7
140 rue de Lourmel
F-75015 Paris
France
Email: jean-francois.berret@ccr.jussieu.fr

Page 19
Dr François Boué
Laboratory Léon Brillouin
CNCE Saclay
F-91191 Gif-sur-Yvette
France
Email: boue@llb.saclay.cea.fr

Page 9
Professor Juan Colmenero
University of the Basque Country
Department of the Physics of Materials
Apartado 1072
20080 San Sebastián
Spain
Email: wapcolej@sc.ehu.es

Page 22
Professor Julian Eastoe
The School of Chemistry
University of Bristol
Bristol BS8 1TS, UK
Email: julian.eastoe@bristol.ac.uk

Page 11
Professor Stephan Förster
Institute for Physical Chemistry
University of Hamburg
Grindelallee 117
D-20146 Hamburg
Germany
Email: forster@chemie.uni-hamburg.de

Page 21
Dr Andrew Glidle
Department of Electronics and
Electrical Engineering
University of Glasgow
Glasgow G12 8LT, UK
Email: a.glidle@elec.gla.ac.uk

Page 15
Dr Pete Griffiths
School of Chemistry
Cardiff University
Cardiff CF10 3AT, UK
Email: griffithspc@cardiff.ac.uk

Page 13
Professor Ian Hamley
School of Chemistry
University of Leeds
Leeds LS2 9JT, UK
Email: i.w.hamley@chem.leeds.ac.uk

Page 16
Professor Klaus Huber
Department of Physical Chemistry
University of Paderborn
Warburger Strasse 100
D-33098 Paderborn
Germany
Email: huber@chemie.upb.de

Page 18
Dr Valeria Lauter-Pasyuk
Department of Physics
Technical University of Munich
James Franck Strasse 1
D-85748 Garching
Germany
Email: vlauter@ill.fr

Page 14
Professor E. Lopez Cabarcos
Department of Pharmaceutical
Physical Chemistry
University Complutense
Plaza Ramon y Cajal s/n
28040 Madrid
Spain
Email: cabarcos@farm.ucm.es

Page 10
Professor Walter Richtering
Institute for Physical Chemistry
RWTH Aachen University
Landoltweg 2
D-52056 Aachen
Germany
Email: richtering@rwth-aachen.de

Page 20
Dr Jens Rieger
BASF Aktiengesellschaft
Polymer Physics
D-67056 Ludwigshafen
Germany
Email: jens.rieger@basf-ag.de

Page 17
Professor Johan van der Maarel
Department of Physics
National University of Singapore
2 Science Drive 3
Singapore 117542
Email: phyjrcvd@nus.edu.sg

Page 8
Dr Andreas Wischnewski
Institute of Solid State Research
Jülich Research Centre
D-52425 Jülich
Germany
Email: a.wischnewski@fz-juelich.de

Page 7
Dr Drazen Zanchi
Laboratory of Theoretical and
High Energy Physics
Universities of Paris 6 and Paris 7
4 Place Jussieu
F-75252 Paris
France
Email: drazen@lpthe.jussieu.fr