

### Effect of Shear on Block Copolymer Gels

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We have recently been investigating the effect of shear on lyotropic liquid crystalline phases formed by amphiphilic block copolymers. The particular focus has been on poly(oxyethylene)-poly(oxybutylene) diblock copolymers in aqueous solutions. We have constructed a facility for simultaneous SAXS and rheology, based on a modified commercial Rheometrics RSA II rheometer and this will be described. We have successfully demonstrated this instrument at the SRS, Daresbury Laboratory, UK [1]. A similar instrument has recently been installed at the SANS beamline at Risø National Laboratory, and we have also performed collaborative research there [2,3]. In addition, we have performed experiments using the Couette cell on BL4 at the ESRF where the effect of steady shear on ordered mesophases in block copolymer solutions was examined [3,4]. Shearing experiments at the SANS instrument at ISIS, U.K. have yielded additional information on the effect of high rates of steady shear [5]. Finally, we have recently constructed a highly flexible Couette cell for steady or oscillatory shear for use at the SRS (SAXS) and the ISIS (SANS) and this will be described. Selected results from all these experiments will be discussed. In particular (i) The effect of steady and oscillatory shear on generating macroscopically oriented cubic "crystals" of block copolymer gels, of bcc and fcc symmetry [1,3-5], (ii) The quantitative analysis of the extent of orientation of a hexagonal-packed cylindrical micellar phase and time-resolved studies of the orientation process [6], and (iii) The influence of shear on the orientation and domain spacing of a

lamellar phase formed by an amphiphilic block copolymer in solution [7]. This includes the intriguing observation of a shear-induced reduction in domain spacing.

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### Structural Transition in Hydrogel-Drug Systems

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This study aimed to investigate structural ordering/transition phenomena in a cross-linked poly(ethylene oxide) 4000 (PEO) matrix which is saturated with an active compound (paracetamol or caffeine) and used as a model drug delivery system. Time-resolved small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements were carried out using the synchrotron radiation source at Daresbury

Laboratory. The experiment consisted of, first, studies of PEO recrystallization at different degrees of hydration in the gel and, second, formation and dissolution of fine particulate drug materials within the hydrogel matrix. Other analytical techniques such as small angle neutron scattering, atomic force microscopy and drug dissolution complemented the experimental work. Unhydrated gels show a developed semi-crystalline structure which became more disordered as the hydrogel recrystallized. There is an indication of a kinetic ripening in the crystalline phase. The lamellar structure undergoes transition at 20-40% of water uptake in which the lamellar spacing decreases more than twice with increasing water content. This effect is attributed to the ordered hydrophobic/hydrophilic regions in the gel. Drug-loaded hydrogels exhibit a significant interaction between the polymer and drug molecules, for example, caffeine forms crystalline particles whereas paracetamol remains in an amorphous state likely forming molecular complexes with the polymer. This difference is explained on the basis of specific hydrogen bonding within the polymer matrix. Drug concentrations as small as 1 wt% have a pronounced effect on the mechanical and drug-release properties the hydrogel.

### Important Steps in the Analysis of X-ray Scattering and Fibre Diffraction Area Detector Data

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Area detectors are indispensable for efficient data collection for many types of experiment, but they are far from perfect and introduce various distortions into the data. For accurate analysis and interpretation of such data, characterisation of detector distortions and correction prior to further analysis is vital. For scattering data this particularly means that very careful attention must be paid to effects which distort intensities, as final intensities must be linear over a very wide dynamic range, and as a function of both detector position and angle of incidence. For fibre diffraction data, intensity accuracy is of lesser importance, but positional accuracy is of much greater importance. The effects which can lead to these distortions will be discussed as will the calibration techniques necessary to quantify and correct them. The manner in which the integration of

2-D regions from a variety of 1-D and multiple 1-D scans is performed is very important. In order to obtain accurate intensities a variety of geometrical effects, and the effect of polarisation on the intensities, must be accounted for during integration. Algorithms to perform integration and possible types of output will be discussed. Examples of data analysis and graphical display of results will also be presented.

### SANS/WANS Anyone?

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Simultaneous SAXS/WAXS has become a highly-regarded technique for the study of soft condensed matter, particularly polymers. The complementary technique with neutron radiation has however been slower to develop. Late 1997 saw the culmination of an SERC funded upgrade to the "white-beam", "fixed-geometry", time-of-flight SANS instrument (called "LOQ") at ISIS. The upgrade has more than quadrupled the available Q-range, now  $0.008-1.4\text{\AA}^{-1}$ , all of which is accessible - with full azimuthal coverage - in a single measurement without the need for any reconfiguration of the instrument. This talk will describe the nature of the upgrade, some early results, and the opportunities that exist for Non-Crystalline Diffraction at ISIS.

### Thin film studies of diblock copolymers on 16.2

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Thin films of block copolymers can be cast onto surfaces by various means. Spin casting forms a thin coating, which is dependent on the concentration, and spin speed. On application, the copolymer

molecules are trapped in non-equilibrium structures. These structures can be annealed into equilibrium structures over a period of a few hours. The surface of the substrate may be selective for one block. If this is the case then the blocks tend to segregate and stack in alternating layers on the surface. We have used reflectivity and Grazing Incidence Diffraction to study the self-assembly of these layers in a range of materials. We have shown that the stems of short crystalline block copolymers selective for the substrate surface align perpendicular to the surface, without tilting as was previously assumed.

### X-PLOR for Polycrystalline Fibre Diffraction

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The X-PLOR system [1] for NMR and protein crystallography is a flexible software package which allows molecular structures to be investigated. Among other things, the package allows a chosen target function to be used as an empirical X-ray energy term which can be added to the potential energy of a molecule. Techniques such as energy minimization and simulated annealing can then be applied to ensure reasonable stereochemistry and an optimal fit to the X-ray data.

Wang & Stubbs [2] have addressed the problem of applying X-PLOR to filamentous viruses which give rise to unsampled layer-lines of intensity and are constrained by a high degree of non-crystallographic symmetry. Further modification to some X-PLOR routines has been necessary to allow covalent bonding between symmetry related portions of molecular structure and to treat the systematically overlapping but not symmetrically related reflections common in diffraction patterns of polycrystalline fibres.

These modifications and some trial applications of the modified program will be discussed.

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### End Functionalised Polymers Grafted To An Interface

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At sufficiently high number of polymer molecules per unit area (grafting density), polymers attached by their ends to a planar surface form a 'brush' like layer where the molecules stretch in a direction normal to the interface. In addition to the grafting density, the characteristics of the brush like layer, i.e. the surface volume fraction, the surface excess and the brush height (or layer thickness) are also controlled by the nature of the surrounding matrix. The two extremes are a stretched 'wet' brush when the matrix is a low molecular weight thermodynamically favourable solvent and a 'dry' brush when the matrix has a molecular weight greater than or equal to the grafted polymer. A 'phase diagram' of relationships for the brush height has been proposed. Moreover such grafted polymer layers are also susceptible to analysis by mean field methods enabling the 'sticking' energy of the attaching species to be evaluated.

Reflectometry is an aspect of small angle scattering using neutron beams that has been developed in the last 8-10 years. The scattering vector is normal to the surface on which the beam is incident and thus the characteristics of grafted layers can be obtained if use is made of selective deuteration. An outline of the principles will be presented and the importance of using confirmatory data, where obtainable, will be stressed. Attention will be focussed on mixtures of deuteropolystyrene functionalised at both ends (molecular weight  $\sim 100,000$ ) mixed with hydrogenous polystyrene matrices with a range of molecular weights (52,000 to  $1 \times 10^6$ ). We show that the near surface depth profiles are narrower than those for the same polymer functionalised at one end only as predicted by theory. However, contrary to expectations based on the grafting density and the molecular weights of the matrices, the brush height (and other parameters) exhibits stretched wet brush behaviour. Sticking energies evaluated from a mean field theory will also be presented.

## Interplay of solution scattering, crystallography and 3D modelling of proteins

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X-ray scattering is a very effective technique for obtaining low-resolution structural details of proteins and their complexes in solution. Recently, there has been significant progress with the development of an ab initio method for shape restoration in terms of spherical harmonics from scattering data [Svergun & Stuhrmann (1991) *Acta Cryst.* **A47**, 736-744]. Crystallographic data clearly contain more information and provide much higher resolution. However, solving the phase problem is the crucial and quite often the most difficult and time consuming step in crystallographic structure determination. The traditional methods of isomorphous replacement or molecular replacement require the availability of isomorphous heavy atom derivatives or the structure of a homologous protein, respectively. Here we demonstrate that the low-resolution molecular shape determined from solution X-ray scattering data can be located in the crystallographic unit cell using experimental diffraction data. It is anticipated that the low-resolution molecular envelope can be used as a starting model for phase extension by maximum entropy and density modification methods. Protein crystals are a prerequisite for high-resolution structure determination. Let us assume the specific case where suitable crystals are lacking, no noticeable sequence homology to any other structurally characterized protein is available, but a molecular shape has been determined from solution scattering data. This scenario has been investigated in order to evaluate the possibility of using solution scattering in conjunction with biochemical information and structure prediction techniques for protein modelling. Results will be presented and discussed.

## Developments to Sample Environments within NCD

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Developments in the Sample Environment portfolio of NCD will be discussed, including designs for a new automatic sample changer and a pressure cell together with the possibilities for magnetic studies on the NCD Stations. This is also an opportunity to discuss the direction that we want to take where sample environment is concerned. Station 16.2 has been incorporated into the NCD group as of April 1st 1998. The station will also be described and its modes of operation investigated. Station 16.2 has been designed and constructed to study the structure of surfaces and interfaces. It is configured as a 6-circle, horizontal diffractometer and vertical reflectometer. The diffractometer is equipped with an analyser stage and therefore has triple axis capabilities.

## The DUBBLE SAXS/WAXS Beamline

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A new ESRF beamline, built by a Dutch/Belgian consortium and dedicated to combined time resolved SAXS/WAXS and fibre diffraction experiments, will be described. The expected performance, the problems encountered and the ones to be expected will be discussed.

A major problem will be in detectors that can handle the extremely high count rates that can be generated by beamlines on third generation sources. Therefore we have developed a new type of detector with a relatively high count rate capability. This detector is based on well known technology already widely used in high energy physics experiments but in order to use this technology a new electronic system had to be designed.

Some other experimental problems that can be encountered will be mentioned as well.

## The Crystal Structure of Poly(ethylene terephthalate) Revisited

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In 1954, Daubeny, Bunn and Brown, reported the first determination of the structure of poly(ethylene terephthalate) [1]. With the wealth of new technology, we have decided to revisit this polymer. A data set from a PET monofilament has been collected using an image plate (APS, 0.100nm radiation) and a powder diffractometer (symmetrical transmission, 0.154nm radiation). The diffraction data has been processed using XDPP and a data set consisting of the positions and intensities of ~80 reflections were determined. The structure has been determined by direct methods and by LALS refinement. The methodology and results will be discussed.

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## First Beamline Results from the RAPID system

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Multiwire proportional counters have been used for many years to capture X-ray images from synchrotron sources. They are particularly well suited to dynamic experiments and have time resolutions of the order of microseconds. They are almost noise free, have high dynamic range and large active areas. However, they do have limitations in the global and local count rate performance. RAPID, the Refined ADC per Input Detector, is a two dimensional detector system which delivers a more than twenty fold increase in throughput over present systems on the SRS. It comprises a wire micro-gap detector and a sophisticated multi channel data

acquisition system. RAPID has a global count rate limit of greater than 30 million photons per second and a maximum local rate limit of greater than 1 million photons per square millimeter. The system has shown spatial resolutions of 250 microns (FWHM) and has a 200 mm by 200 mm active area. The performance of the detector and readout system during its first 'user' tests will be presented.

## Neutron Fibre Diffraction Studies on Instrument D19 at the Institut Laue-Langevin

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Neutron high-angle fibre diffraction techniques offer unique opportunities in structural studies, and can provide information that is difficult or impossible to obtain using X-ray methods. Such techniques can be applied to a wide variety of natural and synthetic polymer systems and are particularly powerful in the study of biological systems in which ordered water plays a central role or where the location of individual hydrogen atoms is important. These methods were used very successfully to study the location of ordered water around different conformations of the DNA double helix, and have subsequently been used by a number of groups in the study of other biological fibrous systems, including cellulose, filamentous viruses, and hyaluronic acid. The main features of neutron diffraction that are exploited in these studies are (i) the fact that the coherent scattering length of hydrogen is greater (in comparison to other atoms) for neutrons than is the case for X-rays and (ii) the fact that deuterium has a strikingly different scattering length from its lighter isotope. Isotopic replacement methods can therefore be used to image particular atoms or molecules within a structure.

The D19 diffractometer at the Institut Laue-Langevin is unquestionably the best instrument in the world for neutron high-angle fibre diffraction experiments. The methods used in sample preparation, data

collection, and data analysis will be discussed, and illustrative examples taken from recent work on DNA.

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## Peptide Self-Assembly: A Route to Novel Biopolymers

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In 1994, a research student, Amalia Aggeli, working in the SOMS Centre, made the unexpected observation that a peptide she was making as a model for a transmembrane ion channel, formed a gel in solution. Driven by curiosity, we proceeded to establish that these gels consisted of a network of entangled polymeric beta-sheet tapes, each a single molecule in thickness. What in effect we had stumbled on was a new kind of polymer. These polymers are of especial interest because, firstly, they are produced by biological-like molecular self-assembly, which can be switched on or off by chemical triggers. And, secondly, they are tape-like rather than string-like in structure. This discovery was reported in *Nature* in 1997 (vol 386, pp 259-262). We have gone on to establish a set of rational design principles for the production of tape-forming peptides and to study their properties in solution and their interaction with surfaces. Under certain conditions the tapes supercoil to form fibrils similar to those encountered in Alzheimers or Parkinsons disease. An overview of this work will be presented.

## X-Ray Rheology of Unstructured and Structured Polymer Melts

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Time-resolving X-ray scattering measurements performed on samples subjected to shear flow provide both a powerful insight to the structural re-organisation which accompanies flow and an approach to interpret mechanical rheological data. Novel equipment which facilitates such measurements is described and the procedures developed to analyze the scattering patterns are outlined. With this X-ray rheology system we explore the flow behaviour of both structured and unstructured polymer melts. In particular, we show how such procedures may be used to understand the complex flow behaviour of liquid crystal polymer systems. We contrast the development of macroscopic orientation during flow in thermotropic systems with that observed for equivalent lyotropic materials and study the relaxation behaviour following cessation of flow. We compare such behaviour with the much more delicate balance in thermotropic side-chain liquid crystal polymers between the liquid crystal component and the transient polymer network.

## In-situ X-ray diffraction study of the effect of flow upon surfactant liquid crystalline phases

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The equilibrium structures of aqueous surfactant liquid crystalline mesophases are mostly well established, as is their dependence on surfactant type. Simple concepts of molecular and micellar size and shape, involving 'packing constraints', have been fundamental to this understanding. Both shear

and extensional flow have a profound effect on the structure and orientation of these complex fluids. Time-resolved X-ray diffraction has been utilised to probe the dynamic response of these mesophases, so that the macroscopic rheological behaviour can be related to the flow-induced structural changes observed. In-situ X-ray diffraction studies will be presented examining the effect of flow upon hexagonal and lamellar surfactant liquid crystalline phases. For each system, significant flow deformation occurred. The interpretation of the rheological behaviour in terms of molecular structure will be discussed and compared to the molecular theories for liquid crystalline flow.

### High-temperature BCC lattice formation /disappearance in triblock copolymer gels: morphological transition or order frustration?

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Triblock ABA copolymer gels, based on a three-dimensional physical network of polystyrene-rubber-polystyrene copolymers in a relatively low molar mass ( $M_w \sim 400-500$ ) solvent selective for the midblock (B), are soft solid materials [1-2]. They have high elasticity and deformability (100 - 1000%), depending on molar mass and block ratio of the copolymer [3-4]. At ambient temperature a short-range ordered arrangement of the network nodes (spherical domains of the endblocks) results in a morphology intermediate between liquid-like and a highly distorted crystalline one [2,5]. For some gels a real polycrystalline (BCC) structure has been observed developing within a certain temperature range [6,7]. However, it tends to disappear beyond these temperature limits. While the existence of the high-temperature limit sounds reasonable, the reason of the low-temperature one is disputable. It is worth mentioning that BCC structure is also reported for micellar solutions of the same triblock copolymer in a different solvent (for instance, in hexane at room temperatures) although they do not have elastic rubber properties.

At ambient temperature, the structure of the network in our gels can be described in terms of a highly distorted crystalline lattice of close-packed spheres (CPS, either HCP or FCC) or in terms of liquid with effective hard-sphere interaction. Therefore two possible mechanisms exist for the low-temperature transformation: frustration of the BCC morphology or a change to a different one. We are going to discuss this matter on the basis of real-time SAXS scans during cooling-heating or isothermal annealing and equilibrium SANS measurements.

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### Better Access for Regular use of Networked Software: B.A.R.N.S

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Although the ILL is in France, more than 70% of the 2000 visits per year are from people outside France, and because their visits are necessarily short, serious

data treatment and analysis usually begins when they return to their home institute. Traditionally, much analysis has been made using remote-access to the ILL, but a number of recent developments have made remote-user access almost useless:

1. Firewalls complicate remote-terminal use.
2. Many programs use X which performs badly over remote connections.
3. Most ILL programs are platform dependent.

The solution is obvious: Create a server at the ILL (we call it BARNS) which allows programs to execute on ILL computers but with input/output via the internet to "standardised" frames and applets within the clients web-browser. This is not simply an exercise in creating an HTML form for each program. BARNS must:

1. Appear multi-user, multi-threaded, and access multiple nodes.
2. Handle all aspects of user login, accounts, processes, zombies etc.
3. Create standardised frames which can handle almost any program requirements with minimum effort.
4. Automatically direct output to the correct frame: program, graphics or tools.

We will show how little modification is necessary in order that programs can run under BARNS and how interactivity is achieved.

### **Real Time X-Ray Diffraction Studies on the Formation of Intermediates in Phospholipids Induced by Laser T-Jump**

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Supramolecular phospholipid aggregates - bilayers - form the matrix of all membranes. Their structural variability confers the characteristics of dynamics to cell membranes which is of utmost functional importance. So far there were no methods existing which would allow the study in real time of these structural dynamics, because they are characterized

by relaxation times in the subsecond time domain. Synchrotron radiation with its extremely high X-ray flux has now made this possible. At the Austrian SAXS-Station of the synchrotron radiation light source ELETTRA in Triest, a dedicated experimental facility for such X-ray kinematographic jump relaxation studies has been installed by the IBR. Here is a first report on the detection of short-lived non-equilibrium intermediate structures.

### **Mammographic imaging using the SRS**

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It has been reported that the use of synchrotron radiation for mammography results in images of higher quality, at lower dose, than those obtained using conventional hospital equipment. A direct comparison of the image quality obtained by conventional and synchrotron based mammographic imaging systems has been performed. The work was carried out at the SRS station 8.4, and the Nightingale Breast Screening Centre, a major regional screening centre in Manchester.

The results of these tests are presented along with some preliminary data on the simultaneous imaging, and diffraction measurements of breast tissue, which can be used to obtain tissue specific images.

### **Fibre diffraction using the BioCAT undulator beamline at the Advanced Photon Source**

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The BioCAT undulator-based beamline at the Advanced Photon Source, Argonne IL, USA, is

designed to be a superb instrument for biological non-crystalline diffraction and X-ray absorption spectroscopy. The optics consist of a vertically focussing mirror and a sagittally focussing second monochromator crystal allowing independent focussing of the beam in the vertical and horizontal direction virtually anywhere in the 12 m experimental enclosure. We have documented a focal spot with a 2 m fibre diffraction camera of less than 40 x 200 microns (FWHM) containing essentially all of the  $1.5 - 2.0 \times 10^{13}$  ph/s delivered by the water cooled Si(111) double crystal monochromator. At the minimum focal distance, a less than 25 micron (FWHM) vertical focal spot has been achieved. Here we present results of fibre diffraction experiments performed during our commissioning activities since first light was achieved in September of 1997. This combination of optics and the very low divergence of the very small source have yielded very high quality patterns from various muscle specimens and collagens from human tissues. Most of these patterns were taken on BAS-V image plates scanned with a FujiBAS2500 image plate scanner. This combination is a significant improvement over earlier models for fibre diffraction work. We have also just taken delivery of a 1k x 1k CCD detector that has been optimized for SAS applications and will be capable of various streak camera modes that can be used for time framing applications. Future developments will include commissioning of a cryogenically cooled monochromator, in vacuum beam monitoring, longer camera lengths (6-8 m), and optimizations to improve first order resolution.

### Improved Structural Data on Native Cellulose from Neutron and Synchrotron Fibre Diffraction Diagrams

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The current sets of coordinates that are commonly used for the definition of the molecular and crystal

structure of native cellulose were established in 1974 independently by Gardner - Blackwell and Sarko - Muggli, who used X-ray data recorded on fibres pulled out from Valonia cell wall [1,2]. Since that time, it has been recognized that such cellulose consisted of the superposition of two phases, namely a triclinic one-chain (Ia) and a monoclinic two-chain (Ib) phase [3,4]. There is therefore a necessity to establish a revised molecular and crystal structure corresponding to the two phases of cellulose, using improved experimental diffraction data on highly crystalline samples, but if possible containing pure Ia and pure Ib.

To tackle this problem, we took advantage of a recent method [5] to prepare reconstituted oriented films of cellulose microcrystals resulting from the acid hydrolysis of (i) purified tunicin (*Halocynthia roretzi*), consisting essentially of Ib cellulose, and (ii) *Cladophora* sp. consisting of a mixture of Ia and Ib phases. Some of these films were subjected to intra-crystalline deuteration by an hydrothermal treatment in D<sub>2</sub>O in the presence of dilute NaOD. This treatment converted all the intra-crystalline OH groups of cellulose into ODs, without affecting the crystallinity and the orientation of the samples. X-ray fibre diffraction diagrams were recorded at room temperature with a wavelength of 0.782Å, using the microfocussing beam line ID13 from ESRF. Neutron fibre diffraction diagrams were obtained at room temperature with both the hydrogenated and deuterated samples, using the 4-circle diffractometer D19 at the Institut Laue Langevin operated with a wavelength of 1.3Å. Both neutron and X-ray fibre patterns contained more than one hundred independent reflections up to a resolution of around 1Å. The intensities of the X-ray patterns were substantially different from those obtained with neutrons. In addition with neutrons, the diagrams of the hydrogenated samples differed also markedly from the deuterated ones. Data sets resulting from the analysis of these fibre diagrams were extracted with the use of CCP13 software. The X-ray data were analyzed with linked atom least squares (LALS) methods together with the X-PLOR program. A Fourier difference analysis was also achieved in the neutron data to locate the H/D atoms of the OH/OD. The best resulting models of cellulose Ia and Ib will be presented.

### Acknowledgments

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removing  $\text{Ca}^{2+}$  from the system alters the position and relative intensity of the diffraction series. This is interpreted as the strengthening of the diffraction from the entire population of the microfibrillar bundle. In vitro experiments have indicated that the microfibrillar spacing becomes less variable in the absence of  $\text{Ca}^{2+}$ . X-ray diffraction of extended tissue samples indicates a change in the fundamental periodicity of the structure. This information has provided a molecular basis for the elasticity of such tissues.

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### Fibrillin X-ray diffraction: studies of an elastic protein

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Fibrillin is a long fibrous protein found in the extracellular matrix. It is thought to provide elasticity and also acts as a site for the deposition of elastin in mature tissues. Some anatomical locations however consist entirely of a fibrillin network. Zonular filaments from the mammalian eye contain fibrillin rich microfibrils and no detectable collagen or elastin. These provide an ideal system for the study of the molecular packing of fibrillin microfibrils. X-ray diffraction studies of zonular filaments on beamline 2.1 and 16.1 at the CLRC Daresbury reveal the structure to contain a fundamental axial periodicity of 56nm. This is comparable to the measurements made on isolated microfibrils studied by electron microscopy. X-ray diffraction allows the structure of the microfibrils to be conducted in the fully hydrated state and also under extension. The X-ray diffraction pattern indicates a number of features.

Fibrillin microfibrils give strong first, third and sixth orders of a meridional series. This is interpreted as the presence of a specific axial alignment of fibrillin microfibrils within the fibrillar bundles. In this the adjacent molecules are staggered by one third of the fundamental axial periodicity. The effect of

### A high-angle neutron fibre diffraction study of the hydration of B-DNA

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A high-angle neutron fibre diffraction study of the hydration of the B conformation of DNA has been performed on instrument D19 at the Institut Laue-Langevin, Grenoble, using a wet-spun sheet sample of DNA. In common with our previous neutron fibre diffraction studies of DNA, this work exploited the ability to isotopically replace  $\text{H}_2\text{O}$  around the DNA by  $\text{D}_2\text{O}$ . However, in contrast to previous studies, the sample exhibited 'double orientation' so that it was possible to record a three dimensional diffraction data set. Fourier synthesis techniques were used in order to image ordered water surrounding the DNA. Two chains of ordered water have been identified in the minor groove of the molecule in positions that are consistent with water bridging of sugar O4 and purine N3 or pyrimidine O2 atoms.

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### SAXS/WAXS & GIXD as a Tool to Investigate Thin Films

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A block copolymer is formed from two or more incompatible polymer segments. High molecular weight copolymers will generally form a microdomain structure on cooling. The relative volume fraction of each block dictates the morphology of this microdomain.

Commercially available block copolymers such as Polystyrene-Polybutadiene (PS-PB), Polystyrene-Polyisoprene (PS-PI) or Poly(ethylene-propylene)-Polydimethylsiloxane (PEP-PDMS) mainly have classical morphologies, for example lamellar, BCC spheres or hexagonally packed cylinders. Lamellar structures are obtained if the relative volume ratio of the blocks, determined by NMR, is in the order of 0.5.

X-ray scattering and Reflectivity are methods that can be used to investigate the microdomain morphology of block-copolymer thin films that are spun cast on substrates (e.g. silicon wafers). Reflectivity measurements are also useful for the determination of film thickness, and in the case of lamellar morphologies, in layer thickness determination.

### 1-D High Resolution Structure of Type I Collagen

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Although the tri-peptide repeat and periodic features of type I collagen are thought to be well understood, it has not yet been possible to produce a calculated structure with meridional intensities that closely match that of the observed data. The conformation of the n and c terminal telopeptides are still to be established, along with several aspects of the lateral organisation of microfibrils. For the purposes of this project, meridional orders have been observed and recorded for native, and heavy atom stained collagen from rat tail tendon beyond 120 orders (previously, the highest published set of intensities included the 52nd order). This data has been used to produce a model independent set of phases (currently using 92 orders) and hence calculated 1-D axial structure of the molecule at approximately 0.73 nm resolution, the highest resolution previously achieved being approximately 1.29 nm. Also, a large number of models have been constructed where the d-stagger repeat of each of the five chains has been altered, and various different contracted and folded telopeptide conformations used to generate calculated intensity sets that were compared to that of the observed data systematically.

### Ordered water around deuterated A-DNA by neutron fibre diffraction

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A neutron fibre diffraction study of A-DNA hydration has been carried out using instrument D19 at the Institut Laue-Langevin, Grenoble. Deuterated DNA was used in order to minimise incoherent

scattering and sample absorption effects. Fourier analysis of data collected from the sample in a D<sub>2</sub>O environment has revealed four distinct major groove ordered water sites. A network of ordered water involved in the bridging of successive O1 phosphate oxygen atoms along the double helix backbone has been identified. Extensive hydration of the major groove base edges has been observed as a continuous core of density running down the helix axis. The other two hydration features are located in the centre of the major groove, one at the opening of the groove and the other located deep in the groove.

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### An Investigation into the Properties of Polyurethane Hot-Melt Adhesives

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Reactive hot-melt adhesives (RHM's) are thermoplastic polymers which are applied to the substrate in the molten state. Upon cooling, the adhesive solidifies and subsequently cross-links on reaction with ambient moisture to form a thermosetting polymer with desirable mechanical properties. Manufacturing processes which use RHMs, such as bookbinding, require the rapid build up of adhesive strength so that bonded parts may be set aside in the minimum time. Important in determining the effectiveness of such adhesives is the strength before curing and the mechanism of solidification leading to this "green strength". Mechanisms may include vitrification, crystallisation and microphase separation. In this study, techniques including rheometry, X-ray scattering and optical microscopy have been used to investigate the solidification mechanisms and viscoelastic properties of polyurethane reactive hot-melt adhesives.