

X-ray diffraction study of silicon oxycarbide glasses

H. Brequel, S. Enzo

Dipartimento di Chimica Via Vienna, 2 07100 Sassari (Italy)

Silicon oxycarbide compounds are promising materials with potentially improved properties compared to classical ceramics. They are amorphous and similar to silica, but with some oxygen atoms substituted by carbon. In order to better control the insertion of carbon atoms in the network, the Sol-Gel method was chosen as an alternative to the classical high temperature synthesis. Here, the mixture is made of two precursors with different content of Si-O and Si-C bonds: methyl-diethoxysilane $\text{HSi}(\text{OEt})_2\text{CH}_3$ (MDES) and triethoxysilane $\text{HSi}(\text{OEt})_3$ (TREOS). Each precursor leads to interconnected units with 2 (DH) and 3 (TH) silicon – oxygen bonds in the gel, respectively. During the hydrolysis and the condensation process there is no decomposition or loss of the carbon functional group, so that the final composition of the polysiloxane network is closely related to the initial atomic ratios (O/Si) and (C/Si). Subsequently, a pyrolysis under inert atmosphere is performed at various temperatures between 1000°C and 1500°C in order to remove the organic part of the material. This leads to a glass or partially amorphous ceramic. The structure of the materials obtained is investigated by X-ray diffraction techniques. When the materials are totally amorphous, the Radial Distribution Function approach is carried out from XRD patterns. On the other hand, the Rietveld method is used to fit the patterns when crystalline species are arising (high temperature of pyrolysis). This work is done under the European TMR contract # FMRX-CT98-0161, « Oxycarbide glasses » network.

Mesh Intermediate Phases in Surfactant-Water Mixtures

Marc Leaver*, Mike Holmes, Andrew Fogden(#) and Smita Puntambekar

Centre for Materials Science, Department of Physics, Astronomy and Mathematics, University of Central Lancashire, Preston, PR1 2HE, Lancashire, United Kingdom

(#)Physical Chemistry 1, Chemical Centre, Lund University, S-221 00 Lund, Sweden

Concentrated mixtures of amphiphiles and water can exhibit a number of liquid crystalline phases. The number, complexity and structure of the phases that are formed depend on the structure of the amphiphile in addition to the temperature and composition of the system. Whilst the structure of many of the liquid crystalline phases are delineated, a number remain a challenge. One such phase is the 'intermediate phase'. The structural units for such phases usually possess non-uniform interfacial curvature and are stable at amphiphile concentrations between that of the hexagonal and lamellar phases. In this presentation the structure of mesh intermediate phases formed in binary surfactant water systems will be discussed. Experimental results, from a number of techniques, will be presented to determine the stability range and structure of such phases formed in model non-ionic and ionic fluorocarbon surfactant systems. Having established the structure of the phase models for the structure of the phase are presented.

Daresbury Analytical Research & Technology Service

E.J. MacLean, J.M. Charnock, S.M. Slawson, R.W. Strange, E. Towns-Andrews

CLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD

Daresbury Analytical Research and Technology Service (DARTS) offers tailored data collection and analysis services for academic and industrial users of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The service provides a host of analytical techniques extending from hard X-ray to infrared for investigation of material science problems. The Service makes use of the myriad of techniques available using synchrotron radiation (SR) including: • protein crystallography • infrared microscopy • powder diffraction (including grazing incidence and reflectivity) • “micro-crystallography” • X-ray absorption spectroscopy • small and wide angle X-ray scattering • circular dichroism. By employing a range of techniques, it is possible to look at many different types of materials using the DARTS service such as polymers, inorganic samples, proteins, cells, glasses, mixed phases and formulated mixtures.

The formation of polymer-polymer interfaces

D.G.Bucknall*, S.Butler, J.S.Higgins

Dept Chemical Engineering, Imperial College, London *Dept of Materials, University of Oxford

The reinforcement of interfaces between polymeric materials, either by interdiffusion across the interface, or by the use of compatibilisers such as copolymers, raises interesting questions in fundamental polymer science, while being of considerable technological importance. Many artefacts made from polymers are moulded at elevated temperatures. The utility of the final article depends on the strength of the bond formed when two flowing and cooling fronts meet at a joint or seam. Understanding the interdiffusion of polymer molecules and hence the time dependent structure of the forming interface, is key to understanding its subsequent mechanical strength. Compatibilisers are

added to otherwise immiscible polymers during processing in order to strengthen the material at internal interfaces which would otherwise be weak. This is aimed at making useful new materials and exploiting synergies between the properties of the different species. One modern technique which has provided key information about polymer interfaces is neutron reflection. We report results from interfaces between miscible and immiscible polymer layers with and without the addition of copolymers. Recent data have been obtained in real time as the interfaces form without the need for quenching.

A Study of Structural Development and Morphology during Crystallization of Linear Hydrogenated Polybutadienes using Small & Wide-angle X-Ray Scattering (SAXS/WAXS) and DSC Techniques

E.L.Heeley, C.M.Fernyhough, A.Pryke, W.Bras*, R.J.Hanson & A.J.Ryan

Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

*ESRF, BP220, F-38043. Grenoble Cedex, France

Many semi-crystalline polymers are used in countless areas of everyday life. The overall structure of these polymers controls the aesthetic and mechanical properties of the material, which invariably affects its end use. The production of such polymeric materials requires much physical and chemical optimisation pertaining to its application. Thus, it is necessary to understand and develop further, a complete picture of the material's properties and relate this to its structural morphology. The structural morphology of a polymer can be described and controlled by its molecular crystallization. This is inherent from its chemical construction and mode of processing. The structural development in polymers during crystallization is generally well understood regarding the growth of crystals and several theories have been

conceived to describe this over the last forty years(1). However, one area of crystallization kinetics which is vaguely understood, is that concerning the primary nucleation process prior to the growth period. Reasons for this lack of understanding lie in the difficulties of obtaining experimental data to support and expand pre-existing theories(2). Fortunately, polymer nucleation and crystallization takes place at a molecular level, which can be appropriately studied by X-ray scattering techniques. Here, experimental determination of nucleation in crystallizable linear hydrogenated polybutadienes has been studied with the aid of time-resolved X-ray scattering methods and Differential Scanning Calorimetry (DSC). Several linear polybutadienes (Mw 2-500k) were synthesized with controlled molecular architecture, using anionic methodology(3) and subsequently hydrogenated to give samples having a narrow molecular weight distribution. The crystallization and melting point information was then determined for each sample using classical laboratory DSC techniques. From this several isothermal crystallization temperatures were chosen in the sample melt for X-ray measurements. Time-resolved Small- and Wide- Angle X-ray Scattering (SAXS/WAXS) and DSC experiments were all performed at the European Synchrotron Radiation Facility (ESRF), France or the Daresbury Synchrotron Radiation Source (SRS), UK. Here, several polymer samples were crystallized in the melt at various temperatures whilst the SAXS/WAXS data were obtained. The SAXS/WAXS data collected provides an insight into the macro- and micro-molecular structure during the crystallization of the polymer sample. The SAXS details information on the long range structural ordering having associated density changes, whereas WAXS probes the ordering at an atomic level. Here, it has been possible to study the primary nucleation of crystallization, in terms of the spinodal decomposition theory described by Cahn-Hilliard(4) from the X-ray scattering data obtained. This has been seen with the hydrogenated polybutadienes studied during crystallization in the melt, when density fluctuations give rise to SAXS peaks during an induction period but, no WAXS Bragg peaks accompany these. The results indicate that crystallization in the melt consists of an induction period where large scale ordering persists prior to crystal growth. Evaluating such data will enable a complete picture of crystallization and associated kinetics to be determined. In turn this will provide valuable information in potentially controlling the

final morphology and physical properties of a polymer material in terms of its specific end use.

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Reaction Kinetics and Morphology Development in Flexible Polyurethane Foam

Wu Li, Ellen L Heeley, Anthony J Ryan

Department of Chemistry, University of Sheffield, Sheffield S3 7HF

Flexible polyurethane foams are formed from the simultaneous exothermic reaction between a diisocyanate with a polyether polyol and water. The morphology of these foams is determined by the competition between the polymerisation and the microphase separation of the 'hard' and 'soft' segments. The hard-segments are formed by the water and diisocyanate reaction producing a polyurea, whereas the soft-segments are formed by the polyether polyol chains. Adiabatic temperature rise measurement (ATR) and forced-adiabatic FT-IR spectroscopy (FT-IR) have been employed to simultaneously monitor polymerisation on a toluene diisocyanate (TDI) based flexible polyurethane foam system, varying the content of surfactant and catalyst. The decay of isocyanate is correlated to the

polymerisation kinetics. There is a good correlation between the conversion of isocyanate calculated from ATR and FT-IR data. As the catalyst concentration in the formulation is increased, it has been observed that the overall relative rate of reaction increases. However, the overall relative rates of reaction are the same among the foaming systems with different surfactant concentration. Forced-adiabatic, time-resolved synchrotron small angle X-rays scattering (SAXS) has been employed to investigate the dynamics of microphase separation during the fast bulk copolymerisation. Initially, there is little scattering (homogeneous liquid), and the peak that starts to grow at $q^*=0.06 \text{ \AA}^{-1}$ after 81 seconds is evidence for the structural development in the sample. The peak position does not change during the whole process. Microphase separation was observed to occur at a critical conversion of isocyanate functional groups and is shown to follow the kinetics associated with spinodal decomposition. The presence of covalent cross-links is observed to delay the microphase separation of the urea hard-segments. Dynamic rheological measurements have been conducted during the bulk copolymerisation via a vane rheometer. The increase of the modulus of the foaming mixture is resulted from the microphase separation of the hard-segment.

Fibre diffraction and diversity in filamentous plant virus structure

Gerald Stubbs, Greg Ferrell, Mitzi Reams, Nicholas Fletcher

Vanderbilt University

Fibre diffraction has a long history of successful structural analysis of tobamoviruses such as tobacco mosaic virus. Nevertheless, studies of other filamentous plant viruses have been fraught with difficulties. In general, these difficulties stem from

specimen preparation rather than the inherent complexity of the viral structures. In some cases it is difficult to obtain sufficient quantities of virions. The members of some virus groups are notoriously difficult to handle in solution. Even when these problems are solved or not present, virions are often difficult to orient. The flexibility of the virions in many groups has contributed to orientation problems. Structure determination at atomic resolution has been completed for four tobamoviruses and partially refined structures have been obtained for two others. Although no molecular details have yet been elucidated, fibre diffraction studies of tobamoviruses, hordeiviruses, and potexviruses have been described by various groups. Our current work is focussed on the potexviruses, and we are also attempting to obtain diffraction data from tobamoviruses and potyviruses.

A High-angle X-ray Diffraction Study of Collagen Fibre Structure in uniaxially Pre-stained Leather

C. Boote¹, M. Otunga², E.J. Sturrock², G. Attenburrow², K.M. Meek¹

[1] Dept. of Optometry and Vision Sciences, Cardiff University, Redwood Building, King Edward VII Avenue, PO Box 905, Cardiff CF10 3YJ, Wales UK.

[2] The Leather Sellers Centre, University College Northampton, Park Campus, Boughton Green Road, Northampton NN2 7AL, UK.

A structural investigation into the fibrous collagen assembly which constitutes leather is presented. High-angle X-ray fibre diffraction patterns from uniaxially pre-stained bovine leather samples have been recorded on beamline 7.2 at the Daresbury SRS. The orientation of collagen fibres has been estimated from the azimuthal intensity distribution of the annular reflection deriving from the regular spacing of molecules within collagen fibrils. The X-ray data is presented along with mechanical data

previously recorded in order to deduce the influence of industrial pre-straining on the strength, and hence quality, of the material during manufacture, and their relationship to the fibrous microstructure.

New approaches and programs for non-crystalline diffraction data analysis

Dmitri Svergun

European Molecular Biology Laboratory, Hamburg Outstation, EMBL c/o DESY, Notkestrasse 85, 22603 Hamburg, Germany, and

Institute of Crystallography, Leninsky pr., 59, 117333 Moscow, Russia

Advanced methods for the interpretation of scattering from different types of disperse systems are presented. For monodisperse systems, *ab initio* low resolution shape determination methods using envelope functions and dummy atoms are compared. The algorithms for computation of the scattering profiles from atomic models accounting for the hydration shell and for rigid body refinement are described. The methods to analyse the internal structure of particles by simultaneous fit of contrast variation data are presented. For polydisperse systems, the algorithms to interpret scattering from mixtures of particles of different types are described. In a linear case, they permit e.g. determination of the oligomer content in protein solutions. In a general case, a constrained non-linear optimisation is employed to find polydispersity and volume fractions and interactions between the components. The above methods are integrated into a program suite for advanced data analysis at the EMBL, Hamburg Outstation and are coupled with three dimensional graphic programs on IBM-PC and major UNIX platforms. Examples of their applications to the structure analysis of biological macromolecules, microemulsions, and nanoparticles in polymer matrices are given.

Application of SANS in the study of a surfactant layer adsorbed on anisotropic clay particles

I. Grillo*, P. Levitz** and Th. Zemb***

*ILL, DS/LSS, Av. des Martyrs, 38042 Grenoble Cedex 9

** CNRS, CRMD, 1 bis rue de la Férellerie, 45071 Orléans Cedex 2

*** CEA Saclay, DRECAM/SCM, 91191 Gif/Yvette Cedex

D11 and D22 are the two Small-Angle Neutron Scattering facilities at the ILL with the highest flux at the sample position, in a wavelength range of 4 to 40 Å. They are mainly used for soft condensed matter and biologic studies to determine the size, shape and long-range order of small colloidal particles, proteins, polymers, fibers,... Firstly, the technical features of D11 and D22 will be described (flux, sample environments,...). Secondly, an application of SANS, for the structural characterization of a surfactant layer adsorbed on anisotropic clay particles will be presented.

Polyisocyanurates as Functional Damping Coatings

A.L. Abbott, A.J. Ryan, M.L. Turner

Department of Chemistry, University of Sheffield Dainton Building, Brook Hill Sheffield, S3 7HF

Poly(ether-isocyanurate) elastomers formed from polyethers and diisocyanates can be made with variable stiffness, or glass transition temperature, by combining rigid, three dimensional cross linked molecular structures with flexible chains. Cross linking arises from the catalysed trimerisation of isocyanate end groups to form an isocyanurate ring. The reaction between the polyether diols and excess

diisocyanate to form a diisocyanate functional copolymer is used and the unreacted diisocyanate distilled off. In a thin film separation of oligomers of various lengths occurs, due to the requirement of free volume for the chain ends. Trimerisation of the end groups in the resulting mixture will lead to a graded cross link density, and thus graded stiffness properties. Materials of this type are of interest for use as vibrational dampers, since they act as constrained layer damping coatings. The coatings are characterised by rheology, reflectivity, SAXS, and FTIR microscopy.

Synchrotron X-ray diffraction studies of the mechanism of contraction in intact single fibres from skeletal muscle

Malcolm Irving

School of Biomedical Sciences, New Hunt's House, King's College London, Guy's Campus, London SE1 1UL, UK

Improvements in the brightness and collimation of available synchrotron X-ray beams over the last few years have driven three types of development in X-ray studies of the mechanism of muscle contraction. First, the brightest X-ray reflections can now be recorded from a short segment of a single muscle cell (a fibre) which is structurally homogeneous and under precise physiological control. Second, kinetic studies of changes in these reflections can be made with sub-millisecond time resolution, which is fast enough to isolate the structural transitions that drive force generation in muscle. Third, fine structure of the X-ray reflections arising from interference between the two arrays of myosin molecules in each muscle sarcomere can be resolved; this interference effect allows Ångstrom-scale motions of the myosin molecules to be measured. Crystallographic studies have produced atomic models for the contractile proteins actin and myosin, and for the conformational change in myosin that is thought to drive force generation. These atomic models have been used to interpret fibre diffraction data, and have led to a detailed model for the mechanism of the

myosin motor in muscle. Examples of these developments will be presented using X-ray data collected at beamline 16.1 at CLRC Daresbury, and ID2-SAXS at ESRF Grenoble, as part of a long-term collaboration with the group of V. Lombardi and G. Piazzesi (Università di Firenze) and of M.A. Ferenczi (National Institute for Medical Research, London).

Influence of flow and deformation on block copolymer melts

Frank S. Bates

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis MN 55455

The macroscopic state of order in block copolymers can be influenced by flow and deformation. A plethora of experimental studies have documented the effects of flow geometry, strain amplitude, strain rate, proximity to the order-disorder transition, and molecular architecture on the state of alignment of lamellae, cylindrical and other block copolymer morphologies when subjected to steady and oscillatory deformation. This lecture will focus on model linear block copolymers near the order-disorder transition (ODT) temperature. Diblock, triblock and pentablock copolymer melts have been investigated using in-situ large amplitude shear with simultaneous small-angle neutron scattering. The results of these studies clarify the role of mechanical contrast in controlling the orientation of lamellae and cylinders in the ordered state, and the shear-rate dependence of the ODT. Resulting anisotropic mechanical properties, particularly failure, of the solidified specimens confirms the importance of molecular architecture and processing conditions in this class of nanocomposites.

Crystallisation of cordiriete glass studied with SAXS and WAXS

W. Bras, M. Oversluizen, G.N. Greaves, S.M. Clark

DUBBLE CRG / ESRF Netherlands Organisation for Scientific Research

Aberystwyth University

Daresbury Laboratory

The crystallisation of glass after at high temperatures can be rather complicated depending on the composition and phase diagram of the glass. Several different crystalline structures can evolve in which it is not always clear what the order of the different events is. Moreover, the overall shape, size and growth mode of the crystallites themselves poses an interesting problem for both applied as well as fundamental physics. We have addressed these issues by using high temperature SAXS and WAXS.

Collagen Organisation in the Corneas of Developing Chicks

Veronique Siegler, Keith Meek, and Andrew Quantock

Cardiff University

One important aspect of the cornea's ultrastructure that is thought to influence transparency is the mode of packing of its constituent collagen fibrils. X-ray diffraction studies of developing chick corneas show a general trend for more mature corneas to have more closely packed collagen; the mean centre-to-centre collagen fibril spacing a week before hatching (when the cornea is hazy) being approximately 20% higher than a day or two before hatching (when the cornea is transparent). The level of corneal hydration also

drops during development, and our measurements show that the bulk of this tends to take place 3 to 5 days before hatching. X-ray diffraction studies of developing chick corneas should provide us with a better appreciation of the spatial arrangement of collagen during tissue maturation, compaction and transparency acquisition.

The Synthesis of Model Hydrogenated Polybutadienes and their Crystallisation Behaviour

C.M. Fernyhough, E.L. Heeley, A. Pryke, A.J. Ryan, R.N. Young

Department of Chemistry, University of Sheffield, Brookhill, Sheffield. S3 7HF

By synthesising polymers using "living" techniques, control can be exerted over various parameters such as molecular mass, polydispersity, architecture and microstructure. Butadiene can be polymerised anionically then hydrogenated to give a semi-crystalline polymer, analogous to poly(ethylene-co-butene). Initially, linear hydrogenated polybutadienes (hPBd) have been synthesised. They have polydispersities of <1.05 and predetermined molecular weights ranging from 2,200g/mol to 500,000g/mol. hPBds with "comb" structure have also been produced in order to investigate the effects of long-chain branching i.e. by varying the length and number of branches, the crystallisation behaviour may be altered. Preliminary experiments have been performed using Differential Scanning Calorimetry (DSC) and the results of isothermal crystallisation have been used to devise experiments using simultaneous SAXS/WAXS/DSC to probe long-range structural changes prior to nucleation.

Crystal structure studies on cellulose polymorphs

Yoshiharu NISHIYAMA, Paul LANGAN*, Masahisa WASA, Henri CHANZY**

The University of Tokyo (Japan)

* Los Alamos National Laboratory (U.S.A)

** CERMAV / CNRS (France)

We are involved in a long-term project to determine precisely the molecular and crystal and structure of the main cellulose polymorphs. For native cellulose or cellulose I, we have selected specimens having large crystalline domains and developed a method to extract the cellulose crystals and re-orient them uniaxially for X-ray fibre diffraction recording. We used cellulose from (i) the tests of *Halocynthia roretzi* (a sea animal) corresponding to 1b allomorph (ii) the cell wall of *Cladophora wrightiana* (a sea weed) corresponding to Ia+Ib allomorphs and the cell wall of *Glaucozystis nostochinearum* (a micro alga) corresponding to the pure Ia allomorph. As these samples presented some uniplanar axial orientation, a method was developed to derive the orientation function of the crystals with the goal of obtaining a reliable diffracted intensity data set for structure refinement. Cellulose II resulted either from the alkali treatment of cellulose I (mercerization) or the regeneration of cellulose solutions. Other highly oriented specimens included the preparation of cellulose III-I and cellulose III-II resulting from a high-pressure ammonia treatment of respectively *Cladophora* and cellulose II. The samples of cellulose II had conventional fibre symmetry and from their fibre diagrams we could extract the diffraction intensities using the CCP13 software suite. Combining the phases resulting from the X-ray refinement with the amplitudes from neutron diffraction data followed by Fourier analysis resulted in the positioning of the hydrogen atoms involved in the H-bondings.

Low-angle X-Ray Diffraction Studies of the Corneas of Transgenic, Lumican-Deficient Mice

Andrew J. Quantock, Keith M. Meek, Jennifer Paul,* Shukti Chakravarti*

Cardiff University

* Case Western Reserve University, Cleveland, Ohio.

An electron microscopic study of the hazy corneas of mice homozygous for a null mutation in lumican, an important corneal proteoglycan, has reported that the lateral fusion of collagen fibrils may locally increase the interfibrillar space (Chakravarti et al. *J Biol Chem* 1998;141:1277-86). To examine the extent of this, we studied the corneas of lumican knockout mice by X-ray diffraction. Low-angle X-ray patterns from 6-month-old, wild-type corneas contained well-defined interfibrillar reflections. X-ray patterns from 6-month-old mutants, on the other hand, contained no appreciable interfibrillar reflection. The absence of well-defined interfibrillar reflections in the corneas of lumican-deficient mice thus implies widespread loss of order.

Investigation of the morphology of thin films prepared from solutions of block copolymers and their blends

C.L.O. Salou, A.J. Ryan and J.P.A. Fairclough

University of Sheffield, Chemistry Department

Diblock copolymers upon cooling (from the melt) or upon solvent evaporation (from solution) exhibit different microphase-separated morphologies including spheres, hexagonally packed cylinders and lamellar structures. The relative volume fraction of each block along with the Flory-Huggins interaction parameter (χ) and the degree of polymerisation dictates the phase separation.

For this project, the lamellar morphology is of interest. It requires using materials with the volume fraction of one block being $0.4 < \phi < 0.6$, to obtain alternating layers. If asymmetric starting materials are used, it is possible to obtain a lamellar morphology by preparing blends with

homopolymer(s). In these blends, the free energy is reduced when the homopolymers segregate to the appropriate domains of the ordered structure reducing the number of unfavorable segmental A/B contact. The microdomains swell in order to accommodate the homopolymers resulting in transitions from one type of microstructure to another in the process¹.

Solutions of commercially available diblock copolymers, polystyrene-polybutadiene (PS-b-PB) or polystyrene-polyisoprene (PS-b-PI), with homopolymer(s) were prepared in toluene. Four polymers are used in this study; an asymmetric PS-b-PB ($\sim 83,000 \text{ g.mol}^{-1}$, $\phi_{\text{PS}}=0.36$), a symmetric PS-b-PB ($\sim 300,000 \text{ g.mol}^{-1}$, $\phi_{\text{H}} \text{ PS} = 0.46$), and two PS-b-PI ($600,000 \text{ g.mol}^{-1}$, $\phi_{\text{H}} \sim 0.4$ and 0.5). The homopolymer(s) was added to the diblock copolymers in order to obtain series of samples with different volume fractions of homopolymer but with symmetrical morphology (i.e., $0.4 < \phi_{\text{PS}} < 0.6$). The solutions were spin-cast onto polished silicon wafers, covered with a native oxide layer. The uniformed thin films were investigated by X-ray reflectivity to determine their total film thickness and by Neutron reflectivity to determine the lamellar spacing. The same solutions were also used to cast films using a draw bar. These films were embedded into epoxy and once polished, the samples were used for AFM and ESEM works. Such techniques are used to image the ordering of the microdomains within the films. From the evaporated solutions, bulk samples were prepared and used to determine the d-spacing by Small Angle X-ray Scattering, and by Transmission Electron Microscopy.

From this work, it was shown that the d-spacing increased upon increase in volume fraction of homopolymer in the blends. Nevertheless, from our neutron reflectivity results it was suggested that the addition of homopolymer to the diblock copolymer was limited. Above a certain value the once flat interfaces were distorted. This problem could be overcome by using a block copolymer with higher molecular weight, giving a repulsion criterion α close to zero².

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Templated crystallisation: soft phases controlling hard materials

J.P.A. Fairclough, S. Turner, S-M. Mai, C. Booth, W. Bras, I.W. Hamley, M.W. Matsen & A.J. Ryan

Department of Chemistry, University of Sheffield, Sheffield, S3 7HF.

Throughout nature, the structure of hard materials eg bone, is controlled by a soft template. We have examined crystallisation in shear oriented block copolymers, where a soft phase of microphase separated melt controls the preferred direction of crystallisation. In lamella phases, the comparison is simple and direct over a range of molecular weight and domain sizes. For hexagonal arranged cylindrical systems and for cubic gyroid structures, the choice of preferred directions is limited. We have used real time SAXS & WAXS to monitor the structure formation upon crystallisation paying particular attention to the orientation of the crystal stems with respect to the lamellar interfaces. Recent experiments at the ESRF will also be reported. The microfocus beamline was used with an X-ray spot of 10 microns. Diffraction was recorded from 500 to 1 Å on one detector from single grains of block copolymer during crystallisation.

The relationships between morphology, irradiation and the ductile-brittle transition of isotactic polypropylene

X.C. Zhang, M.F. Butler and R.E. Cameron

University of Cambridge, Department of Materials Science and Metallurgy, New Museums Site, Pembroke Street, Cambridge, CB2 3QZ

The effect of initial morphology, irradiation, and temperature on the micromechanical response of polypropylene is explored using simultaneous SAXS and tensile deformation. Several deformation mechanisms were identified including lamellar separation and shear, stable and unstable fibrillated deformation and cavitation. The ductile-brittle transition rises dramatically with irradiation, while the glass transition shows only a small increase. Changing the initial morphology moderates the effect of irradiation.

The Phase Behaviour of BEB block copolymer solutions

A. Norman*, J.P.A. Fairclough, S.C. Turner, S. Mai, C. Booth

University of Sheffield, Dept. of Chemistry University of Manchester.

*Manchester Polymer Centre

The phase behavior of a series of BnEmBn block copolymers (where B represents polyoxybutylene and E represents polyoxyethylene) in aqueous solution were studied using Tube inversion, SAXS, Optical microscopy, Light Scattering and Rheology. The B block is known to provide a unit of enhanced hydrophobicity. The solubility of the block copolymers decreases with increasing B block length, and with decreasing E block length. The phase diagrams of such systems were constructed. The various phases were recognised by their typical appearance under polarised light microscopy and by their peak ratios in the SAXS patterns. Clouding complicated the phase diagrams, which can be attributed to micellar bridging which causes an attractive interaction between micelles.

A software system for rigid body modelling of solution scattering data (software demonstration)

M.B. Kozine, D.I. Svergun *

EMBL Hamburg Outstation, Notkestrasse 85, D-22603 Hamburg, Germany.

*Institute of Crystallography, Leninsky prospekt 59, 117333 Moscow, Russia.

A computer system for rigid body modelling against solution scattering data is presented. Fast algorithms to compute scattering from a complex of two arbitrary positioned subunits are implemented and integrated into 3D graphics program. Mutual positions and orientations of subunits (represented by low-resolution envelopes or/and by atomic models) can be determined automatically or interactively fitting the experimental scattering curve from the complex. Applications to the quaternary structure studies of some proteins are demonstrated.

X-ray fibre diffraction from F-actin at Spring-8

Toshiro Oda^{1,2}, Kouji Makino², Kazuya Hasegawa³, Keiichi Namba^{3,4} & Yuichiro Maéda²

[1].Max Planck Institute for medical research Jahnstrasse 29, D-69120 Heidelberg, Germany

[2].RIKEN Harima Institute at Spring-8 1-1-1 Kouto, Mikazuki, Sayo, Hyogo, 679-5198, Japan

[3].Protonic Nano-machine project, ERATO, JST 3-4, Hikaridai, Seika, Kyoto, 619-0237, Japan

[4].International Institute for advanced research, Matsushita Electric Industrial Co LTD. 3-4, Hikaridai, Seika, Kyoto, 619-0237, Japan

Actin, one of the most conserved and abundant proteins in living cells, is helically assembled into filaments (F-actin) that play the most crucial roles in events such as cell division and cell motility. F-actin has been pointed out to be a flexible filament and to have an ability of propagating structural changes along its axis. However the biophysical and biochemical meanings of these structural properties

have not yet been made clear. The aims of our study are to make clear the architecture of the flexible filament with multiple conformations sensitive to the environments, and finally to find the biological significance of these properties. We have used X-ray fibre diffraction to solve the high-resolution structure of the F-actin filament. As the specimen for the method, preparation of well-oriented F-actin filament sols is essential, because the filament orientation strongly influences the validity and quality of the results. First, factors governing the filament orientation in sols were studied. The sensitive factors were found to be the filament length and the ionic strength of sols. As the practical procedures, concentration of the filaments using low speed centrifugation and application of a strong magnetic field (13.5 Tesla) worked well. Taking these factors into account, well-oriented F-actin sols were prepared, and diffraction patterns were recorded with angular distributions of filaments less than 2° . The resolution limit to which the layer-line amplitudes can be extracted from diffraction patterns is dependent on the angle of disorientation as well as the property of the diffraction camera, such as the size of the X-ray beam, its divergence, its monochromatism, and spatial resolution of the detector. Synchrotron radiation generated by undulator produces an ideal beam in all of these aspects. We collected fibre diffraction patterns using a SPring-8 beam line, BL41XU. Since this beam line is designed specifically for protein crystallography, we made a slight modification: we attached a four way guard slit to the collimator and installed a small beam stop with a helium chamber. The size of the beam was 0.1 mm x 0.1 mm and its wavelength was 1 Å. We used an image plate detector (Rigaku RAXIS-IV). Diffraction patterns of high quality, comparable to those obtained with an exposure time of 10 hours by using the Yale mirror optics on a generator, FR-C (50 kV, 70 mA), were obtained with an exposure time of 5 second. The obtained diffraction patterns showed sharp layer-lines and a very low background intensity as expected. Short exposure of strong X-ray may be advantageous in obtaining high quality diffraction patterns from oriented filament sols. We might be able to extract layer-line intensities from the diffraction patterns from F-actin out to 10 Å resolution.

The Origin of Specific Changes of Small-Angle X-ray Diffraction Pattern of hair and their Correlation with the Element Content

A.A. Vazina¹, P.M. Sergienko¹, V.S. Gerasimov¹, N.F. Lanina¹, A.M. Aksirov¹, V.N. Korneev², G.N. Kulipanov³, N.A. Mezentsev³, V.I. Kondratyev³, V.A. Trunova⁴, B.P. Tolochko⁵, V.P. Letyagin⁶

(1) Institute of Theoretical and Experimental Biophysics RAS, Pushchino, Moscow Region, Russia

(2) Institute of Cell Biophysics RAS, Pushchino, Moscow Region, Russia

(3) Budker Institute of Nuclear Physics SD RAS, Novosibirsk, Russia

(4) Institute of Inorganic Chemistry, SD RAS, Novosibirsk, Russia

(5) Institute of Solid State Chemistry SD RAS, Novosibirsk, Russia

(6) Blokhin Science Center of Oncology Department of Breast Timor, Moscow

The recent correspondence from V. James *et al.*, "Using hair to screen for breast cancer" (*Nature*, 1999, 398, 33-34) shows the presence of a diffuse ring in keratin fibres that corresponds to a molecular spacing of 4.44 nm. At least five teams were involved in the attempt to replicate her results. But none of all studies had been able to find the correlation between the diagnostic features mentioned in the "Nature" article and clinical knowledge of the state of patients. X-ray diffraction and fluorescent investigations of human hair with using SR (VEPP-3 Novosibirsk) have shown that the origin of the diffuse ring (4.5 nm) is not "lipid" but most likely glycoprotein. The X-ray patterns were classified into two groups according to the appearance or non-appearance of the diffuse 4.5 nm ring. X-ray patterns with the weak equatorial arc at spacing 4.5 nm were called as "no ring" and those with rings were called as "ring" one. We have shown that X-ray patterns obtained from the near-root segment of hair belong to "no ring" type of patterns always. "No ring" patterns for most donors can be transformed to "ring" patterns via intermediate ones by scanning along the sample point by point from the root region to the tip. In this case the law of conservation of integral intensity for this set of diffraction patterns wasn't realized. There is a class

of donors whose hairs always give X-ray patterns without ring throughout the hair length. We call those diffraction patterns “ring free” patterns. In this case the law of conservation of integral intensity is realized. The X-ray fluorescent element analysis study has shown: there are no changes of element contents along hair for “ring free” type donors; but there are some changes of element contents along the hair from the root region to the tip for donors with “ring” type of hair. For “ring” type of hair the distribution of element content along the hair has bimodal character: the first pool with low element content has a narrow distribution of element concentration, and the distribution for the second pool with higher element content is wider. The correlation between the character of X-ray patterns and the element contents for Ca, Sr and Br was shown: for “no ring” type - low Ca and Sr concentration and high Br concentration; for “ring” type – high Ca and Sr concentration and low Br concentration. We were lucky to show that a prolonged soaking of hairs in 1M CaCl₂ at pH 10-11 could transform the hair sample which initially gave a typical “ring free” X-ray pattern in such way that it was able to produce the “ring” X-ray pattern. We propose a two-component structural model of hair tissue, which consists of a flexible component of extracellular matrix (ECM) in series with an inflexible component of keratin intermediate filaments (IF). We have interpreted the weak diffuse arc at spacing 4,5 nm as arising from interference between assemblies of flexible ECM units consisted of glycoproteins that can be either fibrillar and ribbon-like or random-coil in morphology and which have low electron density. Positively charged metals can transform the configuration of glycoprotein chains due to electrostatic interaction with multiple anion groups of polysaccharide chains and this results in the increasing of electron density. So, the interaction between ECM and metals can result in the appearance of intensive diffuse ring on X-ray pattern of hair.

Microphase Separation of Triblock copolymers: Comparison with diblocks

S.C. Turner, A. J. Ryan, S. Mai, J.P.A. Fairclough, C. Booth

University of Sheffield, University of Manchester

Polymer architecture has an important role to play in understanding the microphase separation of these block copolymers. A linear diblock can pass through one interface, whereas triblock copolymers (e.g. AnBmAn or BmAnBm) have to pass through two interfaces or loop twice through the same interface, while cyclic diblock copolymers (c-AnBm) must pass twice through the same interface. Microphase separation of a linear diblock carries a much lower entropy penalty than is the case for the other three architectures. Oxyethylene/oxybutylene triblock copolymers [$B_{n/2}E_mB_{n/2}$ and $E_{m/2}B_nE_{m/2}$, E = oxyethylene, OCH₂CH₂; B = oxybutylene, OCH₂CH(CH₂CH₃)] were prepared and characterised in the range $f_B = 0.3-0.7$ at the University of Manchester. Seven of these systems were seen to exhibit microphase separation in the melt. These microphase separated states were investigated using small-angle X-ray scattering under temperature ramps, in order to determine order-disorder transitions (ODT), disorder-order transitions (DOT) and domain spacings (d-spacings) in the ordered phases.

Programs for Non-linear Modelling of the Small-Angle Scattering Data

Konarev P.V., Volkov V.V., Petoukhov M.V., Svergun D.I.*.

Institute of Crystallography, Russian Academy of Science, 117333, Leninsky prospect 59, Moscow, Russia

*European Molecular Biology Laboratory, EMBL c/o DESY, Notkestraße 85, D-22603 Hamburg, Germany

Newly developed programs for non-linear fitting of small-angle scattering data from monodisperse and polydisperse systems are presented. To characterize ordering in partially ordered systems a one-

dimensional peak fitting program "PEAK" with graphic interface was written. This program allows one to interactively fit peaks in the scattering curves and yields the Bragg spacing, long-range order dimension, interaction radius, degree of disorder as well as the peak area. The peak is parametrized by a Gaussian function with a constant and linear background and can be fitted both in logarithmic and absolute scale. The analysis of polydisperse multi-component systems (e.g. microemulsions) requires both size and shape fluctuations to be taken into account. The scattering intensity is decomposed into a sum of non-interacting contributions from the particles with different shape (spheres, cylinders, etc.) while the polydispersity and interference effects are considered inside each of these components. This approximation is reasonable at low and medium concentrations of particles in the system. We have developed a program "MIXT", to fit experimental data by scattering from such models and were able to quantitatively describe the composition and parameters of water-in-oil AOT microemulsions in a wide range of temperature, water and salt concentration. Relative volume fractions, average radius and its polydispersity as well as the magnitude of interaction potential for each component were obtained. The program can use spherical, cylindrical and dumb-bell particles and can be applied to various multi-component systems. A 3D display program "COMPLEX" was written to manipulate atomic and low resolution models and coupled with the programs to compute scattering intensity from complex particles and refine their relative positions by fitting the experimental scattering data, either interactively or automatically. The program runs under Windows NT, Windows95, Windows 98.

as a function of immersion time. The effective nanometre resolution of the technique, allied with the contrast variation method, has revealed the presence of two layers containing water. The first layer occurs at the glass surface and has a thickness that remains constant at 30 Å under conditions of 100% relative humidity. The second layer penetrates ever deeper into the glass as the time of immersion lengthens, and is accompanied by a loss of material from the glass itself. X-ray reflectivity measurements can also yield useful complementary information about the interfacial regions of many materials and is commonly used as an investigative tool. It is not always possible to make a unique determination of the surface structure from X-ray reflectivity because of the "phase problem" but we have shown that the wide range of reflectivity can enhance the resolution obtained from neutron reflection from gel coated glass. A very useful application of X-rays is to use X-ray induced fluorescence from glass samples to determine the distribution of specific atoms at low concentrations in the surface region. This has been used to investigate the penetration of ions that are believed to enhance durability into the glass surface. In an experiment to determine the sensitivity of this method, a number of Langmuir Blodgett multilayer structures were deposited onto perspex® substrates as a means of constructing a well characterised model system. The structures consisted of 2 layers of behenic acid deposited from pure water subphase followed by a single bilayer of behenic acid deposited from a 0.002M aqueous solution of Manganese Chloride. This single bilayer containing ions that fluoresce on exposure to 1.355 Å X-rays was then progressively buried by subsequent bilayers of behenic acid deposited from a pure water subphase. 3 samples were produced with 2,3 and 4 additional layers on top of the fluorescing layer. The measured fluorescent intensity showed the predicted variation as the manganese layer was progressively buried under more material. The results from ion penetration into glass could then be interpreted.

X-ray and neutron reflection studies of glass surfaces

A.C. Barnes , T Brennen, R.M. Dalgliesh, M. R. Lovell, R. M. Richardson

H H Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL

Specular neutron reflection has been used to depth profile water incorporation into float glass surfaces

Recent Fibre Diffraction Studies of Complex Biological Materials using the BioCAT Undulator Beamline at the Advanced Photon Source

Tom Irving

BioCAT, CSRRI & Dept. BCPS Illinois Institute of Technology Chicago IL USA

The combination of high flux and low angular divergence of undulator radiation from third generation synchrotron sources make them nearly ideal for studies of complex biological materials which typically involve small, weakly diffracting specimens and for dynamic studies of such systems. The BioCAT facility at the Advanced Photon Source (which has just finished its commissioning period and is now accepting outside users) uses highly demagnifying focussing optics with this kind of source to achieve very high flux densities ($> 5 \times 10^{15}$ ph s^{-1} mm^{-2}) and very small focal spot sizes ($< 0.04mm \times 0.2$ mm) which allow collection of very high quality diffraction patterns in very short times. I will give various examples of experiments that have been done which demonstrate how this new beamline has enabled new and interesting science to be done.

Highly constrained scattering modelling fits using crystal structures

Stephen J. Perkins

Department of Biochemistry and Molecular Biology, Royal Free and University College Medical School, University College London, Rowland Hill Street, London NW3 2PF, U.K.

If solution scattering data can be used to derive molecular structures, this would represent a major enhancement of the utility of this structural technique for biologists. Accordingly procedures for the extraction of molecular structures from X-ray and neutron solution scattering curves and from sedimentation coefficients by analytical ultracentrifugation will be discussed. If atomic structures are known for fragments or subunits of the large macromolecule to be investigated, these provide powerful constraints for determining what turns out to be a limited number of arrangements of these fragments or subunits within the

macromolecule that are compatible with the scattering data. A good example of the possibilities offered by these modelling analyses is given by the structural analysis of IgA1 antibody. Human immunoglobulin A (IgA) is an abundant antibody that mediates immune protection at mucosal surfaces as well as in plasma. The IgA1 isotype contains two four-domain Fab fragments and a four-domain Fc fragment linked by a glycosylated hinge region made up of 23 amino acids from each of the heavy chains. Automated X-ray and neutron curve fit searches were based on homology models for the Fab and Fc fragments and hinge peptide models created by molecular dynamics. A three-dimensional search based on these identified a limited family of only about 100 IgA1 structures from 12,000 trial structures that gave good curve fits to the experimental data. These structures contained extended hinges of length about 7 nm that positioned the Fab-to-Fab centre-to-centre separation 17 nm apart while keeping the corresponding Fab-to-Fc separation at 9 nm. This shows that IgA1 has an extended T-shaped structure that is distinct from IgG antibody structures previously determined by scattering and crystallography. Other examples will be discussed, where in particular scattering modelling is able to extend the understanding of newly-determined crystal structures.

SAXS Study on Agglomeration of Nano-MgAl₂O₄ Spinel from Micro-Emulsion and CVD Techniques

Rudolf Winter, Michael Quinten, Andrea Dierstein, Rolf Hempelmann, Andreas Altherr, Michael Veith

Physikalische Chemie, Universität des Saarlandes, Saarbrücken, Germany

Anorganische Chemie, Universität des Saarlandes, Saarbrücken, Germany

Department of Physics, University of Wales Aberystwyth, Aberystwyth, Wales, UK

Nanocrystalline MgAl₂O₄ spinel has been prepared via a micro-emulsion synthesis route and via chemical vapour deposition. For both materials, the size and size distribution of primary particles and

agglomerates and their dependence on several synthesis parameters have been determined by small-angle X-ray scattering. In both cases, the primary crystalline particles show a median diameter of well below 10nm. Contrary to XRD, in SAXS agglomerates also contribute to the scattered intensity. Therefore, we obtain scattering patterns which are consistent with a bimodal mixture of primary and agglomerate particles. The microemulsion route particles show a smaller particle size with slightly narrower distribution than those prepared by CVD; the agglomerates behave in the opposite manner.

X-ray Scattering from Ion Containing Polymers

T.A.Waigh¹, C.E.Williams², G.Grubel³, A.Roberts³

[1] Polymers and Complex Fluids, University of Leeds, Leeds, LS2 9JT, UK.

[2] College de France, 11 Place Marcelin Berthelot, Paris 75005, France.

[3] ESRF, BP220, F-38043 Grenoble, France

We consider the application of X-ray scattering to two separate ion containing systems: polyelectrolytes in poor solvents and ionomeric micelles. The static incoherent X-ray scattering provides evidence for the Rayleigh charge instability in semi-dilute solutions of highly charged flexible polyelectrolytes in poor solvents. Preliminary data will be presented for the use of X-ray photon correlation spectroscopy with ionomer micelles to study their structural arrest transition at high volume fractions.

Combined X-Ray Small-Angle and Wide-Angle Scattering on Fibres with a Microbeam

Martin Mueller, Manfred Burghammer and Christian Riekkel

European Synchrotron Radiation Facility, B. P. 220, F-38043 Grenoble Cedex, France

Fast scanning microdiffraction using a synchrotron radiation X-ray beam is a novel technique, which provides information about the nanostructure of a material with microscopic position resolution [1]. At the ESRF Microfocus Beamline (ID13) the undulator x-ray beam is focussed by an ellipsoidal mirror to a size of about 40 microns in diameter. With collimators, spot sizes of 5 or 10 microns at sample position are obtained. Alternatively, further focussing with a tapered glass capillary produces a 2 micron beam. A high-precision DC motor x/y translation stage allows one to perform two-dimensional scans of areas on the sample, which have been selected in advance using a calibrated optical microscope. With this set-up, experiments providing simultaneously information on two length scales are possible: (1) The sample can be scanned on the micron scale, corresponding to optical microscopy. (2) Each recorded diffraction diagram contains information on crystallographic parameters such as cell parameters, crystal size, or orientation. Introducing an additional pinhole for background reduction, simultaneous recording of small-angle and wide-angle scattering patterns on a single high-resolution CCD detector becomes possible [2]. Thus, a third intermediate length scale is accessible: (3) Mesoscopic particle and/or pore sizes as well as their shape and orientation are obtained in the same experiment [3]. Furthermore, the scattering experiments can be easily combined with X-ray fluorescence measurements. The scanning technique described is very suitable for investigations of hierarchically structured materials like polymers. Applications ranging from polymer science through high-tech carbon fibres to native cellulose fibres will be presented. The perspectives of further reducing the beam size into the sub-micrometer region are currently under investigation. In the instrumental set-up, stepping motors have to be replaced by piezo devices. Results of first experiments in the 100 nm range will be shown.

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Modeling and analysis of disorder in fibrous systems

R.P. Millane, A. Goyal and J.L. Eads

Whistler Center for Carbohydrate Research and Computational Science and Engineering Program Purdue University West Lafayette, IN 47907-1160 USA

Natural and synthetic fibrous materials are by their very nature disordered. The disorder is often related to the functional properties of the material, and always affects its X-ray diffraction patterns. Modeling of disorder and calculation of diffraction from such models is therefore useful in studying these materials and in analysis of their diffraction data for structure determination. Specimens that are either fully crystalline or fully non-crystalline are the easiest to deal with, since diffraction from model structures is easily calculated. For cases of intermediate order, where the molecules pack in disordered crystallites, the relationship between the structure and the diffraction data is more complicated and depends on the type and degree of disorder present. These effects are not usually accounted for in structure determination. Models of disordered polycrystalline fibers, methods for calculating their diffraction, and applications to some biopolymers will be described. Results of analysis of images of myosin filament thin sections from frog sartorius muscle (from Luther and Squire) used to study superlattice structure will also be described.

The three dimensional molecular packing structure of native type I collagen

Joseph P.R.O. Orgel*, Andrew Miller*, Tom Irving[^], Robert Fischetti[^], Andrew P. Hammersley**, and Tim J.Wess*.

* Department of Biological Science, University of Stirling, UK.

[^] Advanced Photon Source, Argonne National Laboratory, USA.

** European Synchrotron Radiation Facility, Grenoble, France.

Collagen is the most abundant protein in mammals where it functions as the main component of the connective tissues which maintain the structural integrity of the organism. Until now, our understanding of the three dimensional molecular packing of collagen within the collagen fibril has come from modelling, based on the X-ray diffraction and electron microscopy evidence. From a recent structural solution to the phase problem of the meridional section of the fibre diagram, the conformation of the non-helical telopeptides, and the length of the telopeptide containing segment have been determined using 124 of the 140 meridional orders observed (Orgel *et al* 2000). This one dimensional study has formed the basis upon which to attempt a much more ambitious project; the separation of the overlapping Bragg reflections of the equatorial diffraction pattern of collagen, so that the phase component of the structure factors could be determined using isomorphous addition. Each collagen molecule consists of 4 segments of length D (~67nm) and a fifth of length 0.46D. Segments 1 and 5 contain the non-triple helical telopeptides which are sites of intermolecular crosslinking and which provide the structural integrity and strength of the fibrils. In the X-ray fibre diffraction pattern, the strong near-equatorial reflection at a spacing close to that expected from near neighbor molecules, was shown to be split into three strong components and this suggested a quasi-hexagonal packing of collagen molecules (Hulmes and Miller 1979). In the work presented here, we have measured the intensities of the equatorial and meridional diffraction pattern, which were then corrected for the cylindrical disorientation in reciprocal space and scaling of the native and derivative amplitude sets. These values were used to calculate the phases corresponding to each of the amplitudes and, by Fourier

transformation, to calculate the electron density map. This electron density map, and the difference Fourier maps have enabled us to identify the crosslink forming molecular segments. Therefore, in addition to demonstrating the quasi-hexagonal nature of the molecular packing and orientation of the molecules relative to the unit cell axis, we have also been able to identify the key role of the telopeptide containing molecular segments in maintaining the integrity of the molecular packing structure.

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have observed an elastic behaviour of the coiled coil structure at low strain (beyond 3%), followed by a progressive unravelling of the coiled coil domains at higher strains. We have also observed a common behaviour of the coiled coil content, the mean distance between protein chains and the microfibril radius. The three parameters decrease with strain. Finally we show that the direct alpha-helix to beta-sheet transition postulated by previous workers [4] is not valid for our experiments which were done at low humidity conditions. Hence we propose another molecular model of keratin fibre deformation which is based on an alpha-helix to coil transition.

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Mechanical behaviour of hard alpha-keratin fibre, an X-ray diffraction study

L. Kreplak, F. Briki, J. Doucet

LURE Centre universitaire Bât. 209D, B.P. 34, 91898 Orsay Cedex, France.

Hard alpha-keratin is a protein from the intermediate filament family. The main function of these filaments is to ensure the mechanical support of the cell or of biological tissues such as skin and hair [1]. Moreover, they share a common molecular and supramolecular structure. Our aim is to correlate these structural levels with the outstanding mechanical properties of the keratin filaments. In hard alpha-keratin fibres such as hair or wool, the keratin filaments, called microfibrils, are cylindrical shaped (7.5 nm in diameter), close packed assemblies of long heterodimeric keratin molecules characterised by a double stranded α -helical coiled coil central domain [2]. Laterally the microfibrils are embedded in a sulphur-rich protein matrix forming an hexagonal paracrystal [3]. In this study, we have performed mechanical experiments combined with WAXS and SAXS. We present the mechanical stretching effects on the microfibril structure. We

Forthcoming Meetings

10th Annual Fibre Diffraction and Non-Crystalline Diffraction Workshop

June 13-15, 2001, University of Stirling

(Organised by Matthew Rodman and Trevor Forsyth)

[For further information and registration, see the web pages at

<http://www.srs.dl.ac.uk/CCP13>

or contact m.j.rodman@dl.ac.uk]

3rd Alpbach Workshop on Fibrous Proteins: "Coiled-Coils, Collagen and Co-Proteins"

September 16-21, 2001, Boglerhof Hotel, Alpbach, Austria

(Organised by David Parry, John Squire and Bob Goldman)

[Details from Prof. John Squire j.squire@ic.ac.uk, 0207 594 3185]

DARTS Bursaries

DARTS at Daresbury Laboratory has funded several bursaries for PhD students to attend the 10th Annual Fibre Diffraction and Non-Crystalline Diffraction Workshop at the University of Stirling (see above and inside back cover). These bursaries will cover the cost of accommodation and registration and may include a contribution to travelling expenses. An application for a bursary can be made through the web pages at

<http://www.srs.dl.ac.uk/CCP13>

All bursary applications must be accompanied by the submission of a poster abstract to the Workshop.