Applications of Synchrotron Light to Noncrystalline diffraction in Materials and Life Sciences





Instituto de Estructura de la Materia, CSIC Madrid, Spain





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Thursday November 24 th ,2005	
9:00-9:30 Registration	
9:30-10:00 Opening Session	15:00-15:50 Plenary Lecture II
Welcoming by the Vice-President of CSIC,	O. Paris
the Director of IEM and	Structure and mechanical properties of
Organizers	hierarchical composite materials:
10 10 50 DI I / I	Synchrotron Radiation as a local probe
10-10:50 Plenary Lecture I	15:50-16:10 Z. Denchev
V. ADELZ Characterization of Black Conslymers by	Phase Transitions in Delversides as
Synchrotron Radiation	Phase I ransitions in Polyamides as Deveoled by Solid State C13 NMD and
Synchrotron Radiation	WAXS and SAXS from synchrotron
10:50-11:10 M A Gómez	16:10-16:30 S Roth
Synchrotron radiation studies of the	High resolution small-angle x-ray
crystallization behaviour of polyolefin	scattering as a tool to investigate
blends and composites	nanostructure colloidal and
*	nanocomposite surfaces
11:10-11:30 R. Davies	16:30-16:50 R. Pons
	Time resolved X-ray scattering
Probing polymer fibre structure using	experiments on emulsification processes
microfocus X-ray beams	
11:30-11:50 Coffee break	16:50-17:10 M. Pérez-Méndez
	Encapsulation of all-trans-lycopene
	molecule within helical cholesteric liquid-
	crystal biopolymer
11:50-12:10 M. Cócera	17:10-18:00 Round Table
Application of Synchrotron Radiation to	Perspectives of the Non-crystalline
linosome surfactant	uniraction beam-line in ALBA
12.10-12.30 A Nogales	21:00 Workshon Dinner
Structural evolution in polymers during	
drawing deformation by in situ SAXS and	
WAXS	
12:30-12:50 W. Pisula	
Investigation of the supramolecular	
arrangement of discotic hexa-peri-	
hexabenzocoronenes on surfaces	
12:50-13:10 A. Diaz	
SAXS studies of ordering phenomena in	
colloids confined by microcavity arrays	
15:10-15:50 E. Ferez-Taberhero Phase transition in liquid crystalline	
nolymers from WAXS/MAXS/SAXS	
synchrotron experiments	
LUNCH BREAK	

WORKSHOP PROGRAM

Friday November 25 th ,2005	
9·30-10·20 Plenary Lecture III	
C. Riekel	
Nanometer-sized X-ray beams for soft	
condensed matter SAXS/WAXS	
experiments	
10:20-10:40 A. Svensson	
Time-resolved Fibre Diffraction Studies of	
Live Contracting Muscle using	
Synchrotron Radiation	
10:40-11:00 A. Flores	
Synchrotron radiation studies of induced	
orientation in a liquid crystalline polyester	
under the influence of a magnetic field	
11:00-11:30 Coffee break	
11:30-11:50 A. Labrador	
Possibilities for SAXS experiments at the	
Spanish beamline BM16 in ESRF	
11:50-12:10 J.M. Lagarón	
Synchrotron radiation as a tool to identify	
structural modifications in polymers and	
nanocomposites related to packaged food	
quality and safety	
12:10-13:00 Plenary Lecture IV	
A.J. Ryan	
Structure and function in a synthetic	
muscle based on block-copolymers	
13-13:20 Closing session	
M.C. García-Gutiérrez, T.A. Ezquerra	

ABSTRACTS

Characterization of Block Copolymers by Synchrotron Radiation

Volker Abetz

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The presentation will address different topics, where X-ray scattering, especially synchrotron X-ray scattering, has proven to be an essential and powerful tool to get insight into the structural properties of microphase separated block copolymers. X-ray scattering techniques are complementary to electron microscopy microscopy and can help to identify morphologies in block copolymers, which often have complex structures. Morphological transitions as a function of temperature can be followed in temperature scans, which is impossible in electron microscopy.

The orientational behaviour of block copolymers in electric and mechanical fields will be discussed on some examples, which point out the advantages of high time resolution when using synchrotron radiation. In comparison to other methods like optical birefringence, scattering methods can give generally a more detailed picture of the orientational state in a sample.

Synchrotron radiation studies of the crystallization behaviour of polyolefin blends and composites

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Composites and polymer blends occupy a prime position as high performance polyolefin materials and represent an area of major commercial importance in which research is very active. The properties of these type of materials, specially the mechanical properties, are determined by the crystalline nature of the matrix and the influence of the different components on the structure, morphology and crystallization behaviour of it.

Our present research is related to the development of binary and ternary blends and composites of polyolefins, mainly isotactic polypropylene, with elastomers, selective nucleating agents, liquid crystalline polymers and different fillers or fibers as reinforcements. The aims of these types of blends are directed towards the improvement of some specific mechanical properties in order to obtain advanced materials based on polyolefins. One of the fundamental objectives of this work is the investigation of the influence of the nature and concentration of the different components in the crystallization, polymorphic and morphological behavior of the matrix as a function of the blending and processing conditions and the thermal history of the materials and its correlation with their thermal and mechanical properties. In this research the performance of time resolved SAXS and WAXS experiments using synchrotron radiation as well as microdiffraction experiments using also a synchrotron source has been a valuable tool in order to correlate structural parameters with the mechanical performance of the blends.

Changes in the polymorphic structure of isotactic polypropylene have been observed in their blends with a thermotropic liquid crystal depending on composition. When the liquid crystal polymer was introduced as fibers in quiescent and sheared iPP melts very different crystalline interfaces were generated which have been investigated by microdiffraction. Some of the elastomers exert a nucleating effect on the crystallization behaviour of the polypropylene matrix in their blends depending on their nature and concentration. In the presence of nucleating agents there is a competition between the nucleation efficiency of the additive and the elastomer. Results related with the experiments performed on these polyolefin blends and composites will be discussed during the talk [1-3].

[1] F.J.Torre, M.M. Cortazar., M.A.Gómez, G.Ellis, C. Marco, J. .*Polym. Sci. Polym. Phys.*, **42**, 1949 (2004).

[2] N.Fanegas, M.A.Gómez, G.Ellis, I.Jiménez, C.Marco. Hasylab Annual Report 2004.

[3] F.J.Torre, M.M. Cortazar, M.A.Gómez, G.Ellis, C. Marco, C. Riekel, P.Dumas, *in preparation* (2005).

Probing polymer fibre structure using microfocus X-ray beams

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Polymer fibres can be found almost everywhere, from high-performance composite materials to technical apparel. However, despite their abundant use, many of the fundamental relationships between their structure and properties still elude researchers. One reason for this is their small sample volume, prohibiting the use of many experimental techniques. Additionally, there are relatively few experimental methods capable of monitoring deformation processes in-situ. Consequently, the microfocus X-ray beams available at synchrotron facilities have become one of the most important tools for studying the structure of single polymer fibres. Modern microfocus beamline optics can offer high-brilliance beams of sub-micron dimensions as a matter of routine¹⁻³. As such beam dimensions are generally smaller than individual fibre diameters, it is therefore possible to probe heterogeneities within single fibres. The investigation of skin-core variations in high-performance fibres is a recent example that demonstrates the application of such techniques^{2,3}. In this case, microfocus X-ray diffraction data enabled a model to be developed, highlighting some previously unknown aspects of skin-core morphology³. As well as probing morphological variations across single fibres, microfocus X-ray beams can also be used to investigate stress variations along single fibre lengths. Such studies benefit from the use of small beam diameters as it minimises the variation in stress within the material volume illuminated by the X-ray beam. This technique has recently been used to successfully probe local fibre stresses within composite materials during deformation4. The results provide valuable information which is not accessible using other experimental techniques4.

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2. S. Roth, M. Burghammer, A. Janotta and C. Riekel, Macromolecules, (36) 2003, 1585-1593

3. R. J. Davies, M. Burghammer and C. Riekel, Macromolecules, (38) 2005, 3364-3370

4. R. J. Young, S. J. Eichhorn, Y. T. Shyng, C. Riekel and R. J. Young, Macromolecules, (37) 2004,

9503-9509

Application of synchrotron radiation to the structural and the kinetic study of liposome-surfactant systems: Improving time resolution

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The liposome-surfactant systems have been widely studied attending their feature as models of interaction between small amphiphilic molecules and membranes. These interactions (solubilization/reconstitution) involve different structural transitions of the membranes, being analogous phenomena to those existing in the biologic systems (virus adsorption, endo-/exocytosis, delivery and interaction of neurotransmitters with cells, etc.). Our work in this field have consisted in the characterization of the processes and the structures implicated to understand better their physicochemical bases¹, however some technical limits in time resolution (10-30 sec) were found. The application of the SAXS and Synchrotron radiation using a stopped-flow cell with time resolution <1 sec has allowed us to follow the steps at short contact times liposome-surfactant².

From a structural point of view, we have detected the surfactant pure micelles, and different bilayer thickness as a function of the composition. From a kinetic point of view, we have found that electrostatic charge modifies both, the adsorption of surfactant, and the release of mixed micelles. Our results using SAXS and Synchrotron radiation indicate that if surfactant and lipids have the same type of electrostatic charge, the adsorption of surfactant on the liposome is slower and the release of mixed micelles from the liposome surface is faster than when the species are oppositely charged³. Consequently, electrostatic charge slows down or enhances the kinetic of the intermediated steps of the global process of solubilization. Although these differences in kinetics are small, the rate of interaction of some molecules with biologic membranes could be determinant for the above-mentioned phenomena took place. Finally, we want to highlight the huge amount of data obtained from kinetics of these experiments. This makes it necessary to design specific strategies to treat the data. In this case, we have proposed a method to deconvolute the contribution of the different structures to follow the kinetics of the process⁴.

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- O. López, M. Cócera, R. Pons, H. Amenitsch, J. Caelles, J.L. Parra, L. Coderch, and A. de la Maza, Spectroscopy, 16, 343-350, 2002
- 3. M. Cócera, O. López, R. Pons, H. Amenitsch, and A. de la Maza, *Langmuir*, 20(8), 3074-3079, 2004
- 4. O. López, M. Cócera, J. Pereira, R. Pons, H. Amenitsch, L. Coderch, J.L. Parra, and A. de la Maza, *Biophys. J.*, 86(1), 76a, **2004**

Oral Contribution

Structural evolution in polymers during drawing deformation by in situ SAXS and WAXS

A. Nogales

The structural variation during heating for a set of polymers containing in main chain dibenzo-18-crown-6 ether unit linked to a variable aliphatic spacer (C10 or C14) is presented. X ray diffraction measurements reveal the existence of a smectic phase. Simultaneous medium (MAXS) and wide (WAXS) x-ray diffractograms during heating of melt-quenched films have been recorded. The real time x-ray results have revealed that the start of destruction of the smectic phase is accompanied by an incipient lateral crystallization of chain segments. Comparison with differential scanning calorimetry corroborates this finding. By simultaneous study of the mechanical behaviour upon uniaxial deformation and structural transformation by simultaneous 2D MAXS and WAXS, we observe the changes in the structure associated to an orientation of the smectic phase (Fig.1)



Figure 1: Stress-strain curve for a crown-ether polymer at 65C. The panels show, for specific values of strain and stress, the simultaneously collected WAXS and MAXS reflections

Investigation of the Supramolecular Arrangement of Discotic Hexa-*peri*-hexabenzocoronenes on Surfaces

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Electronic devices based on organic semiconductors have gained increased attention in nanotechnology, especially applicable to the field of field-effect transistors and photovoltaics. A promising class of materials in this research field are discotic liquid crystals. The disc-like molecules arrange into one-dimensional columnar superstructures due to strong π - π interaction between the aromatic cores. Hexa-*peri*-hexabenzocoronenes (HBC) exhibit some of the highest values for the intrinsic charge carrier mobility for mesogens, which makes them promising candidates for electronic devices.



Figure 1. a) Chemical structure of hexa-*peri*hexabenzocoronene, b) "edge-on" arrangement of the discotic molecules arranged in uniaxially oriented columnar structures parallel to the substrate, c) "face-on" organization of the molecules leading to the homeotropic phase, the columnar axes are perpendicular to the substrate.

Two different supramolecular organizations are characteristic for the disk-shaped molecules. In general, "edgeon" organization of discotics arranged in uniaxially oriented columns with the normal parallel to the substrate is essential for field-effect transistors (FETs) (Figure 1b) in which charge carriers drift through the columns from the source electrode to the drain electrode under controlled gate voltage. In contrast, the large monodomain "face-on" arrangement of the discs where the axis of the self-assembled column is perpendicular to the substrate leads to a homeotropic phase, allowing faster charge transport between the top and down electrodes and favoring the photovoltaic performance (Figure 1c). Thus, detailed studies on the control of the

supramolecular order and alignment on the surface leading to device applications have been carried out.

References: [1] a) A. Tracz, J. K. Jeszka, M. D. Watson, W. Pisula, K. Müllen, T. Pakula, J. Am. Chem. Soc., 125, 1682 (2003); b) D. W. Breiby, O. Bunk, W. Pisula, T. I. Sølling, A. Tracz, T. Pakula, K. Müllen, M. M. Nielsen, J. Am. Chem. Soc., accepted; W. Pisula, Ž. Tomović, M. Stepputat, U. Kolb, T. Pakula, K. Müllen, M. M. Sirringhaus, T. Pakula, K. Müllen, Adv. Mater. 17, 684 (2005); b) J. Piris, M. G. Deije, N. Stutzmann, B. W. Laursen, W. Pisula, M. D. Watson, T. Bjørnholm, K. Müllen, Adv. Funct. Mater. 14, 1053 (2004); c) J. Piris, W. Pisula, A. Tracz, T. Pakula, K. Müllen, J. Warman, Liq. Cryst, 31, 993 (2004). [3] a) W. Pisula, M. Kastler, D. Wasserfallen, T. Pakula, K. Müllen, J. Am. Chem. Soc. 126, 8074 (2004); b) M. Kastler, W. Pisula, D. Watson, T. Pakula, K. Müllen, J. Am. Chem. Soc. 127, 4286 (2005). [4] W. Pisula, Ž. Tomović, B. El Hamaoui, M. D. Watson, T. Pakula, K. Müllen, Adv. Funct. Mater. 15, 893 (2005).

SAXS studies of ordering phenomena in colloids confined by microcavity arrays

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Theoretical studies predict ordering of molecules in a fluid confined between two opposing surfaces when the distance between the surfaces is of the order of few times the size of the molecules. Indirect evidence for this phenomenon has been provided in experiments using a surface force apparatus [1]. Previous x-ray waveguiding studies on colloidal solutions within a single confining cavity confirmed the existence of a strong layering effect in planes parallel to the confining walls [2]. Colloids serve here as a model of a hard-sphere molecular liquid.

We recently developed a new method for the study of confinement-induced phenomena in a colloid [3]. For the confinement of a colloid we employ 1-D periodic arrays of microcavities with gap sizes down to 250 nm. Using SAXS (small angle x-ray scattering) we measure the structure factor of the colloid with a 2D detector. The advantage with respect to previous methods is that a large number of well defined, identical microcavities give rise to a large diffraction signal.

We have measured a strong confinement effect on the structure factor on both hard-sphere and charged solutions (measurements performed at beamline X04SA at the Swiss Light Source and beamline ID2 at the ESRF). A beam of 12.4 keV photons was scattered from a confined colloid solution of 112 nm-diameter SiO₂ spheres in an alcohol mixture (figure 1). In figure 2 a typical measurement of the structure factor of the confined colloid is shown. A beam-stopper in the form of a stripe blocks the diffracted intensity from the microcavity array in the (0, q_y)-direction, as well as the primary beam intensity. The structure factor is approximately circular, as expected for a liquid, and clearly stronger along the confinement direction. The position of this peak corresponds that of the 1st Bragg peak of an fcc packing of colloid spheres. The results indicate an ordering of the colloidal particles along the confinement direction, probably related to the formation of small colloid clusters near the confining walls.



Figure 1: experimental setup with SEM picture of a 1 µm period microcavity array.

Figure 2: measured 2D structure factor of a 112 nm-diameter colloid confined in a microcavity array with gap size 670 nm.

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- [2] M.J. Zwanenburg et al, Phys. Rev. Lett. 85 (2000) 5154.
- [3] A. Diaz et al, Physica B 357 (2005) 199.

Oral Contribution

Phase transitions in liquid crystalline polymers from WAXS/MAXS/SAXS synchrotron experiments

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Liquid crystalline polymers combine the characteristics of the liquid crystalline state with the specific properties of high molecular weight systems. They exhibit anisotropy like conventional 3D crystals, and an extensive polymorphism, which may include both threedimensional crystalline phases and mesophases with different degrees of order.

The more significant characteristic of liquid crystals is the presence of rigid mesogenic groups, which give rise to the inherent anisotropy of these systems, and, in the case of smectic mesophases, are responsible for the organization in layers with sizes typically in the range of 1.5 to 5 nm, i.e. in the so called MAXS region of the diffractogram. Moreover, the analysis of the WAXS and SAXS regions are also of interest in liquid crystalline polymers, as in regular polymers.

The short acquisition times required for the synchrotron experiments make this technique particularly useful for the characterization of liquid crystal systems where more than one mesophase are formed, or where the mesophases present a short interval of existence.

The main applications of synchrotron radiation for the characterization of liquid crystalline polymers are reviewed in this presentation. The applications in the characterization of these systems include, among others, the study of thermal transitions under real time conditions, by using scattering techniques both at wide, middle and small angle (WAXS, MAXS and SAXS, respectively).

Structure and mechanical properties of hierarchical composite materials: Synchrotron radiation as a local probe

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Advanced materials with directional mechanical properties are mostly fiber composites. They are frequently hierarchical structured, covering several length scales from the molecular or unit cell level to up to millimeter length scales. The most prominent examples of outstanding hierarchical complexity are biological tissues such as bone and wood, for instance. But also modern man-made composites - in particular those which benefit from the imitation of natural materials by biomimetic principles - show always a certain degree of hierarchy.

Recent developments of microbeam instrumentation at third generation synchrotron radiation sources allow to use scanning techniques in combination with Small- and Wide-angle X-ray scattering (SAXS/WAXS) to image the nanostructure of such materials with a real-space resolution corresponding roughly to the beam size. SAXS/WAXS techniques cover length scales from atomic distances up to around 100 nm in reciprocal space, and X-ray microbeams of sub-micron sizes are frequently available for scanning. Therefore the whole range of hierarchies from about 0.1 nm up to several hundreds of microns (almost 7 orders of magnitude) is in principle covered by one single technique. Moreover, apart of nanostructure mapping, *in-situ* experiments combined with microbeam SAXS/WAXS allows to address structural changes locally. For instance, in-situ mechanical testing within a microbeam can help to detect local deformation mechanisms in composites at a specific hierarchical level.

The present contribution reviews some recent microbeam SAXS/WAXS studies on several different hierarchical fiber composites. Results from the imaging of nanostructural parameters such as shape, size and orientation of fibers or particles in biological tissues are presented. Moreover, recent in-situ mechanical testing experiments of single carbon fibers are discussed and in particular a unique combination of *in-situ* bending with X-ray nanobeam scanning is demonstrated. Finally, a short status report about instrumentation and experimental possibilities at the new µ-SAXS/WAXS/Fluorescence beamline at BESSY II in Berlin will be given. Future challenges such as the development of high-throughput on-line data reduction, -analysis and –visualization are also addressed, limiting currently scanning microbeam SAXS/WAXS from being widely recognized as a real imaging technique.

Phase Transitions in Polyamides and Their Relation to Mechanical Properties

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Polyamides belong to the semi-crystalline polymers most frequently used in engineering applications. Their processing involves heating/cooling cycles with or without melting, as well as mechanical treatment below or above the melting temperature. The resulting changes in the fine crystalline structure have a direct impact on the mechanical properties of these materials.

The changes in the crystalline structure caused by temperature in isotropic and oriented polyamide 6 (PA6) and polyamide 12 (PA12) samples were investigated by a combination of solid state ¹³C Nuclear Magnetic Resonance (NMR) and synchrotron wideand small-angle X-ray scattering (WAXS and SAXS). The NMR spectra obtained at 20°C showed that in all PA6 samples there is a co-existence of α - and γ -PA6 crystalline forms. In the PA12 samples resonance lines corresponding to γ - and γ - PA12 phase were only detected. Deconvolution of the WAXS patterns of both PA6 and PA12 was performed to follow the temperature dependence of the α - and γ -form unit cell parameters and of the degree of crystallinity. It was concluded that when PA6 is heated in the 120 - 200 °C range, phase transitions between α - and γ -PA6 crystalline forms take place in both isotropic and oriented samples, whereby the content of the initial major crystalline phase decreases and that of the initial minor one increases, reaching a point of almost equal concentrations of the two forms. Close to 200 °C, a γ - to α -transition occurs in all samples, irrespective of their thermal prehistory. Quenching to room temperature after melting leads to PA6 crystallites predominantly in α -form, the small amounts of remaining γ -phase being with hexagonal lattice. In PA12 samples, the γ -crystalline form is the most characteristic. Transition from γ to α -phase was only observed close to the melting point in the 160-175°C range. After cooling to room temperature, the γ -modification is restored in both isotropic and oriented PA12 samples. Annealing of oriented PA12 samples does not result in polymorphic changes but rather in a growth of crystallinity index, crystallite size and perfection.

All oriented and isotropic PA6 and PA12 were subjected to mechanical tests and their mechanical performance was correlated with the corresponding crystalline microstructure.

High resolution small-angle x-ray scattering as a tool to investigate nanostructure colloidal and nanocomposite surfaces

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Small angle x-ray scattering (SAXS) is a powerful tool in materials science to investigate nano- and microscale structures and morphologies in bulk matter to surfaces and interfaces. The beamline BW4 at the DORIS-III Bypass of HASYLAB is designed as an ultra smallangle scattering (USAX) beamline allowing to resolve in transmission structures of one micron. We present the capabilities of BW4 dedicated to materials science in the field of high resolution small-angle x-ray scattering. High-resolution covers the range from lowest qvectors corresponding to real-space structures in the 1micron range to small beams of 30micron in their smallest dimension. Due to BW4's high incoming flux several SAXS and USAX options can installed. In combination with the low background of BW4, this offers especially the possibility to perform grazing incidence ultra small-angle x-ray scattering (GIUSAX) experiments [1,2]. This USAX setup in reflection mode covers lengths scales from 30nm up to several microns at a very large sample-to-detector distance $L_{SD}=13m$ [2]. We use this method for investigating large scale surface arrays and noble metal nanostructured surfaces produced by high-temperature annealing. We compare our results with measurements in the visible regime. In the other extreme we established a microfocus option as part of the newly installed SAXS setup. This at BW4 novel option uses compound refractive lenses and allows for beamsizes on the order of 10micron. We prove the enhanced resolution and background by applying it to grazing incidence small-angle x-ray scattering (GISAXS). With this order-of-10micron beamsize combinatorial mappings of single dimensional gradients can be performed. We present first results on model gradient samples.

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Time resolved X-ray scattering experiments on emulsification processes

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We have followed the process of spontaneous emulsification by temperature jump from isotropic solutions in the ternary system water/tetra ethylene glycol dodecyl ether/decane. During the temperature increase, the system suffers several structural transitions. Those structural changes can be observed by monitoring the corresponding xrays diffraction patterns. The temperature jump is produced by the insertion of the sample that was at the initial temperature, to the interior of a capillary that is heated to the final temperature. By following the evolution of the scattering patterns, we detect the transformation from O/W microemulsion droplets to scattering profiles compatible with an L3 phase via a mixture of both patterns. At higher temperatures some indication of a lamellar phase (long range ordering) is present in the spectra mixed still with the scattering pattern of the L3 phase and finally the appearance of the signals of formation of a water-in-(water-in-oil microemulsion) emulsion. Those phase transitions occur at temperatures higher than the observed equilibrium phase transition temperatures, with differences as big as 6°C. The experimental velocity of heating seems to be fast enough to prevent the complete structuring of the liquid crystalline lamellar phase, even for the slowest rate of heating, or the complete disappearance of the signal of this phase at higher heating rates. From our results, the formation of the final emulsion is produced directly from the L3 phase structure. The structure of the emulsion continuous phase (W/O microemulsion droplet size) and emulsion droplet sizes slightly depends on the initial and final temperatures. In order to better understand the process the oil-to-surfactant ratio and total amount of water have been systematically investigated reaching compositions at which the emulsification procedure fails.

Encapsulation of all-trans-lycopene molecule within helical cholesteric liquid-crystal biopolymers

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Cholesteric liquid-crystal polymers have probed to behave both as thermotropic and lyotropic when dispersed in acqueous media and also in organic solvents. The amphiphilic character of the monomeric unit would explain their tendency to self-associate in helical macromolecular chains whose conformation is highly dependent in the solvent nature, concentration and temperature. These helical cavities observed by steady state fluorescence and Raman spectroscopy make the cholesteric polymers potential vehicles to encapsulate smaller molecules such as drugs or active principles. This is one of our main scientific interest.

Encapsulation is used to protect compounds from oxidation, evaporation, off-flavour and can be based on extrusion, coacervation and molecular inclusion by complexation.

Lycopene has a strong antioxidant capacity, because of its ability to trap peroxyl radicals and represents more than 85% of total carotenoids in tomatoes with a concentration which varies from 30 to 200 mg/kg in the fresh fruit and from 430 to 2950 ppm on a dry basis. The physiological effects of lycopene are partly determined by its bioavailability. Actually, it has been observed that in nature all-trans-configuration exist predominantly and it is more stable thermodynamically. The objective of this work was to stabilise all-trans-lycopene obtained from skin tomato fruit obtained by supercritical fluid extraction in order to avoid its isomerization.

For that purpose we have studied the capability as encapsulating agents of helical cholesteric liquid-crystal biopolymer PTOBDME [C34H36O8]n [1] to entrap lycopene by complexation.

Structural data of the interaction are presented on the base of simultaneous SAXS/WAXS of PTOBDME, performed at 16.1.1 beamline of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, Warrington, U. K. with a monochromatized beam (λ = 1.4 Å). In the interaction the polymeric helical molecules enlarge wheir d-spacing when lycopene is added while their cross section decrease. At the same time lycopene molecules lose planarity and twist along the main chain, addopting the polymer helicity.

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Plenary Lecture III

Nanometer-sized X-ray beams for soft condensed matter SAXS/WAXS experiments

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Time-resolved Fibre Diffraction Studies of Live Contracting Muscle using Synchrotron Radiation

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Synchrotron radiation studies of induced orientation in a liquid crystalline polyester under the influence of a magnetic field

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The physical properties of thermotropic liquid crystalline polymers (LCP) are strongly dependent on the final molecular orientation achieved by means of external fields. The use of strong magnetic fields has been shown to induce orientation even in polymers which do not present typical mesophases (PET, PEN, iPS, iPP) [1, 2]. For thermotropic main-chain LCP, studies of the magnetic orientation (or relaxation) have been carried out after quenching to room temperature from the mesophase [3,4].

The motivation of this work is to clarify the mechanisms of induced orientation in LCP under the influence of a magnetic field, by means of *in-situ* Wide Angle X-ray Scattering studies using synchrotron radiation. Variations in the initial molecular orientation during heating, and upon thermal treatment at temperatures where a nematic phase develops will be presented. Analysis of the WAXS patterns reveals that orientation kinetics depends not only on temperature but also on whether molecular orientation is developed after cooling from the molten state or upon heating from the solid state. Finally, we have found evidence that the maximum orientation achieved at a given temperature in the mesophase can significantly change during rapid cooling to room temperature.

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Possibilities for the SAXS station at BM16

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BM16 is a Spanish hard x-ray beamline at the ESRF, the energy range goes from 6 keV (2 Å) to 17 keV (0.73 Å) being optimized at the Se-edge (12.6 keV, 0.98 Å). The Multi wavelength Anomalous Diffraction (MAD) experimental station was opened to the protein crystallographic users in September 2003. BM16 is now becoming available also to the Spanish non-crystallographic community. The first simultaneous Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS) images were taken in May 2005 within the frame of a collaboration with T. Ezquerra's group. Part of the newly SAXS/WAXS sample environment setup includes a Linkam oven that was integrated in the data acquisition control. This was one step forward in the commissioning of the experimental station for Non Crystalline Diffraction (NCD). The next scheduled action is to characterise and install the multiwire gas filled detector for time resolved measurements.

During this talk the current developments for the future station will be explained and, maybe, new possibilities will be discovered.





Oral Contribution

Synchrotron radiation as a tool to identify structural modifications in polymers and nanocomposites related to packaged food quality and safety

J.M. Lagarón

Institute of Agrochemistry and Food Technology, CSIC . P.O. Box. 73, 46100 Burjassot. Valencia. Spain **Plenary Lecture IV**

Making muscles from block copolymers

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If you take a reductionist attitude a muscle is a device that converts chemical energy into mechanical energy. Muscles are self-assembled from molecules that are both responsive to their environment and contain information to form a specific morphology. They have a response on the nanoscale and macroscopic motion is achieved by serial addition of many such responses. This lecture will describe a device made from block copolymers that generates force from the nanoscale response to an oscillating chemical reaction. The molecular scale response has been measured by synchrotron x-ray scattering and when compared to the macroscopic response shows that the device is affine over 5 orders of magnitude in length scale. Along the way we will dispel many of the myths surrounding grey goo and nanobots.

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Workshop venue

 The workshop will take place at: Institutode Estructurade la Materia,CSIC Serrano 119, Madrid, Spain

•The talks are public



Workshop Organization

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