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Editorial

This newsletter represents two scientific articles written for a broader audience.

The first article – "Light-Responsive (Azobenzene-Containing) Polymers in Complex Fluids" – deals with stimuli-responsive 'smart' materials able to capable of manipulating the physical properties of systems using light as a clean trigger. Recent remote control advances achieved in soft systems are illustrated using examples, including the photo-switching of viscosity and gelation, setting droplets in motion or controlling their spreading on surfaces, and the photo-inversion and destabilization of emulsions.

The second article "Proteins Control Mineralization" focuses on an im-portant and widespread process in nature as occurs in the formation of bones in mammals, as well as of seashells and corals. The inhibition mechanism of pathological mineralization in mammals is discussed in some detail.

SoftComp would also like to take this opportunity to wish all of its readers a happy and successful New Year.

Friedrich Hugo Bohn
and Dieter Richter

In This Issue

Light-Responsive (Azobenzene-Containing) Polymers in Complex Fluids

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Figure 1

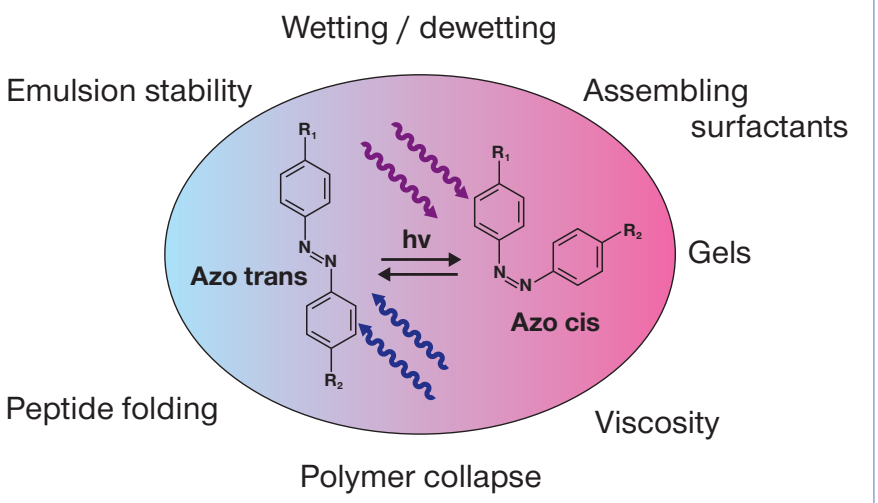


Figure 1: Azobenzene cis-trans photoconversion and possible application to control soft materials.

Stimuli-responsive 'smart' materials are based on the ability to reversibly manipulate physical and/or chemical properties of a system with an external trigger. The use of light as a stimulus is particularly attractive for the clean, rapid, and remote control of specific areas, and photo-responsive systems have been proposed as promising functional systems in all areas of material sciences. Since early work on photonic devices for optoelectronics [1], [2] (e.g. polymer matrices endowed with (re)writable colours, birefringence or dichroism using light-sensitive molecules, known as photochromes), researchers have expanded the range of applications to liquids and soft matter photo-systems.

This short review presents the state of the art of photo-actuation in soft materials. It outlines the variety of robust systems now available, such as light-responsive polymers and surfactants, which have been developed in the last decade, and which offer reliable systems for controlling of properties such as viscosity, elasticity, gelation, surface tension, wetting/dewetting, ionic conductivity, and triggered delivery (of drugs, pesticides, etc). It now seems feasible that photo-systems can be designed for applied purposes, in the agrochemical domain (e.g. night delivery vs encapsulation under sunshine), in microfluidic devices (remote actuation of flows), and in biology (a growing

Light-Responsive (Azobenzene-Containing) Polymers in Complex Fluids (continued)

domain, now called opto-genetics aiming to control cell fate or cell responses).

Recent achievements in the design of photo responsive systems proceeded by tailoring the interactions of photochromes with their environment to amplify their molecular responses. Azobenzenes are the most common isomerizable photochromes, partly because their chemical stability and versatility allow them to be integrated in many polymer chains or molecules. Their cis-trans photoisomerization (Figure 1) is robust to changes in environment (polarity, viscosity), allowing photo control of hydro-phobicity or ionization [3], and occurs even in solid matrices [2].

Azobenzene-based photochromic materials can now be used in applications that in the past seemed idealistic. They also offer an interesting platform for studying the dynamics of transitions in complex or biological fluids. We therefore focus on photo systems based on azobenzene as generic representative illustrations, though other photochromes exist for specific applications.

Solubility switches of polymers

Phase separation and the demixing of photochrome-containing polymers in solution has attracted much attention because of its high technological importance for coating and encapsulation. The variation in solubility upon light irradiation is driven by the gap of free energy of the solvation of photochromes between their different photostates. The solvation transition of a few photochrome monomers decreases the average excluded volume parameter of the whole chain and eventually causes a switch to poor solvent conditions (Figure 2).

For instance, polypeptide chains undergo solvation transition between their coil conformation in a good solvent and a phototriggered folded structure (helix formation), although no precipitation occurs [4], [5].

The precipitation of polymers from organic solvents by lowering the temperature was considered as early as the 1980s by Irie et al. with azobenzene-modified polystyrene in carbon disulfide [6]. The vast majority of systems aiming to control solubility are, however, based on demixing in aqueous solutions above the low critical solubility temperature (LCST).

Macromolecules with known LCST behaviour are made more hydrophobic by introducing azobenzene groups, which decreases LCST. In turn, LCSTs of modified chains become sensitive to the polarity of the azobenzene group. They increase under exposure to the UV-light because of the conversion to cis-polar isomers (Figure 2).

Figure 2

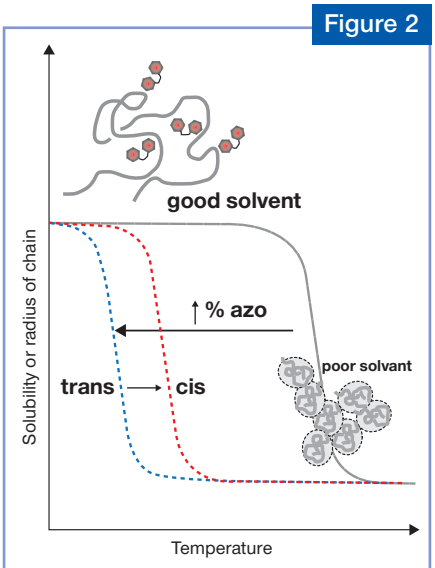


Figure 2: Principle of light-triggered collapse and/or aggregation of polymer chains. Increasing the density of (hydrophobic) photochrome in chains shifts LCST to low T; polarity recovery upon exposure to UV light increases LCST.

In practice, solutions of copolymers display photo-variations of a few °C in LCST, i.e. a functional window only compatible with conditions of highly controlled temperature. Host-guest inclusion complexes have been proposed in order to enhance the effect. For instance, association with cyclodextrin causes multiple new intra and interchain interactions that can be stronger than photochrome/solvent ones [7], [8].

Self-assemblies and photosurfactants

Early studies aiming to amplify the molecular response of photochromes in soft systems were based on cooperative self-assemblies, specifically with azobenzene-containing surfactants or photolysable surfactants [9]. The critical micellar concentration (CMC) of photochromic surfactants decreases with decreasing polarity of the photochrome when exposed to light.

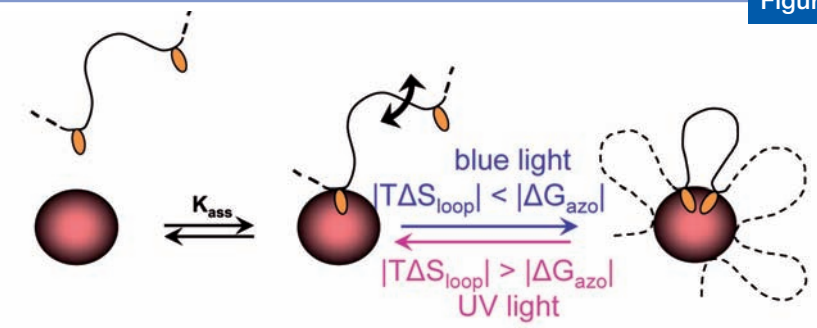
The optimal impact on self-assembly is reached when isomerization of the photochromic group markedly affects the aspect parameter of the entire molecule (in other terms, the spontaneous curvature). This is achieved in practice when the azobenzene group is flanked by two butyl groups on both ends [10]. Most systems based on solutions of photosurfactants must, however, be handled above the CMC, a concentration that is often above millimolar concentrations. High absorbance results from these high concentrations of photochromes, which hampers the propagation of photons through thick samples. It thus remains challenging to decrease the amount of surfactant, while maintaining marked photoresponses. Fortunately, surface properties do not suffer the same constraints (cf. ”interfacial dynamics“).

In solution, polymer complexes are good alternatives for preserving macroscopic effects with low densities of photochromes. In practice, associations of polymers with colloidal particles (e.g. micelles, proteins) form crosslinks that are responsive to light in a large window of composition (Figure 3).

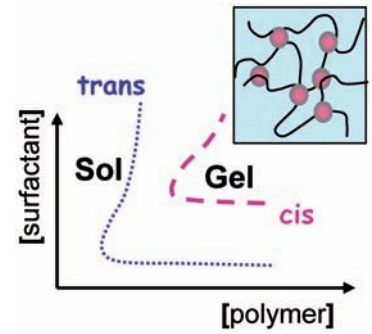
The number of azobenzenes integrated on the polymer chain defines the length of the shorter possible loops between two anchoring points, and in turn controls the regime of association (weak binding for low amount of photochromes per chain vs tight multipoint attachment above a critical density of photochromes per chain) [11].

Exposure to UV irradiation modifies the critical loop length (Fig. 3) and

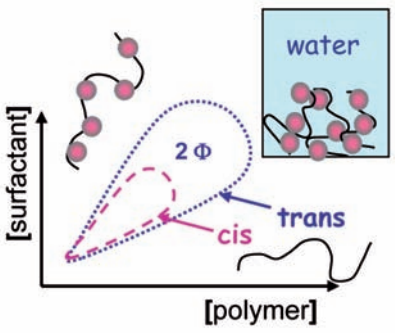
Figure 3



Transition between weak and tight binding controlled by a critical free energy of transfer from water to micelle.



Gelation of hydrophilic chains connected by micelles in a semi-dilute solution.



Associative phase separation of marginally soluble complexes of micelles and polymer chains.

Schematic drawing of light-responsive association between photochrome-modified polymers and micelles. Upper sketch: transition between weak and tight binding controlled by a critical free energy of tranfer from water into micelle. Left: gelation of hydrophilic chains connected by micelles in a semi-dilute solution. Right: associative phase separation of marginally soluble complexes of micelles and polymer chains.

allows abrupt detachment of most of the bound particles [12], [13]. In the dilute regime, this association with micelles may be used to modulate the solubility of polymers close to poor solvent conditions, caused by the detachment of micelles. Drops of 10°C-15°C in the theta-temperature have been reported [14].

In semi-dilute solutions, micelles, but more generally hydrophobic particles, may also act as transient "crosslinkers" thereby leading to viscosity and elasticity enhancements [12], [13], [15].

Photo-variation by several decades of elastic modulus and viscosity can be achieved in a few seconds upon irradiation. In summary, all phenomena discussed above, (gelation, precipitation or syneresis) can occur at low photochrome concentrations provided that the stoechiometry of attachment is limited to a few photochromes per polymer-bound particle. This condition is generally fulfilled with amphiphilic macromolecules forming complexes with nanoparticles and micelles.

Complex interfacial dynamics

Finally, the control of interfaces is a promising area of application for clean triggers, such as light. On solid surfaces, light controls the orientation and/or polarity of grafted photochromes. Exposure to spatially modulated light with varying wavelengths thus produces gradients of wettability. The resulting modulation of contact angles bring into motion a sessile drop (~30 ms^{-1}, [16]). Applied to superhydrophobic surfaces, similar principles significantly enhance the photo-variation of contact angles [17]. However, the more rapid motion is generated at liquid interfaces by Marangoni effects: light can be used to control the density of photo-surfactants on oil-water or on air-water interfaces nearby solid particles or a droplet floating on the water [18],[19] (Figure 4).

Interestingly, the detachment of pendant water droplets at apparently constant surface tension (variation below 2 mN/m) was reported by [20]. The latter result brings hints of an important contribution of dynamics on film rupture and/or dewetting. Non-equilibrium states also play an essential role in emulsion properties. Various emulsifiers are now proved to be efficiently phototriggered at oil/water interfaces:amphiphilic polymers/photo-polymer pairs provide irreversible orientation of emulsion type, while surfactant/photo-polymers or photo-surfactants provide renversable stability and reversible photo-inversion of emulsions [21], [22].

Figure 4

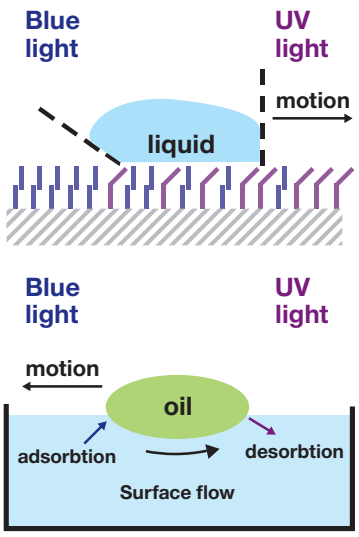


Figure 4: Light-driven motion under exposure to a gradient of wavelengths of liquid droplets on (top) solid surfaces coated with photochromes, or (bottom) water surface in presence of amphiphilic photochromes.

On most of the interfaces described above, the equilibrium may not be reached. Part of the response to stimulus could rely upon changes in the dynamics of the photochrome

Light-Responsive (Azobenzene-Containing) Polymers in Complex Fluids (continued)

assembly or diffusion on surfaces [19] The time scales and length scales involved in the intermediate steps of molecular motions on surfaces are not yet understood.

How rapid are photo switches?

Ultrafast laser spectroscopy measurements proved that the photochromic reaction of an isolated azobenzene molecule is completed on a picosecond time scale. At the level of the whole population of photochromes, the transition is therefore only limited by the absorption of photons and the quantum yield of cis-trans photoconver-sion (vs thermal or fluorescence relaxations). Conventional azobenzenes have quantum yields (approx. 20%) that are compatible with applications. A relatively low efficiency of capturing photons (extinction coefficient of about 10^4-10^5 $L.mol^{-1}.cm^{-1}$) can be compensated by increasing the photon flux. Hg lamps and photodiodes deliver irradiances ranging between 1 mW/cm^2 and 100 mW/cm^2 to spots with radii in the of millimetre to centimetre range. Under the latter intensities of light, the time of photoconversion of a (dilute) solution of azobenzenes is typically shorter thana few seconds, and can be as low as millisecond. Rate-limiting steps may thus lie in dynamics that are specific to the inner structure of materials: rate of molecular assemblies, exploration of conformational space of polymers, or ordering in liquid crystal phases, etc.

Finally, photochrome-based responsive materials are promising tools for applications, and in addition offer opportunities to investigate complex dynamics in soft systems with short response times. In both cases, it is of prime importance to have access to systems that are doped by a minimal amount of photochromes. Among the soft systems described above, those based on (co)polymers can be designed with a low content of photochromes to fulfil this criterion. Very interesting ongoing studies are also being conducted on rapid switches of surface propertiesto investigate complex reorganization and motion on interfaces that would otherwise be extremely difficult to control.

Acknowledgements

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1. Shibaev, V., A. Bobrovsky, and N. Boiko, Progress in Polymer Science, 2003. 28(5): 729-836.
2. Zhao, Y. and T. Ikeda, Smart light-responsive materials: azobenzene-containing polymers and liquid crystals. 2009: Wiley.
3. Emond, M., J. Sun, J. Gregoire, S. Maurin, C. Tribet and L. Jullien, Physical Chemistry Chemical Physics 2011. 13(14): 6493-6499.
4. Willner, I. and S. Rubin, Angewandte Chemie International Edition in English, 1996. 35(4): 367-385.
5. Pieroni, O., et al., Accounts of Chemical Research, 2001. 34(1): 9-17.
6. Irie, M. and R. Iga, Macromolecules, 1986. 19(10): 2480-2484.
7. Inoue, Y., et al., Journal of the American Chemical Society, 2007. 129(20): 6396.
8. Pouliquen, G., C. Amiel, and C. Tribet, Journal of Physical Chemistry B, 2007. 111(20): 5587-5595.
9. Eastoe, J. and A. Vesperinas, Soft Matter, 2005.1(5): 338-347.
10. Shang, T.G., K.A. Smith, and T.A. Hatton, Langmuir, 2006. 22(4): 1436-1442.
11. Ruchmann, J.; Sebai, S. C.; Tribet, C., Macromolecules, 2011. 44 : 604-611.
12. Pouliquen, G., et al., in ACS Advances in Chem. Series 833 "Polymer gels: Fundamentals and Applications", H. Bohidar, P. Dubin, and Y. Osada, Editors. 2002: chap 18, 262-289.
13. Pouliquen, G. and C. Tribet, Macromolecules, 2006. 39(1): 373-383.
14. Howley, C., D.G. Marangoni, and J.C.T. Kwak, Colloid and Polymer Science, 1997. 275(8): 760-768.
15. Lee, C.T., K.A. Smith, and T.A. Hatton, Macromolecules, 2004. 37(14): 5397-5405.
16. Ichimura, K., S.K. Oh, and M. Nakagawa, Science, 2000. 288: 1624-1626.
17. Lim, H.S., et al., J. Am. Chem. Soc., 2006. 128(45): 14458-14459.
18. Diguet, A., et al., Angewandte Chemie International Edition, 2009. 48(49): 9281-9284.
19. Chevallier, E. et al., Soft Matter 2011.
20. Shin, J.Y. and N.L. Abbott, Langmuir, 1999. 15(13): 4404-4410.
21. Khoukh, S., et al., Chemphyschem, 2005. 6(10): 2009-2012.
22. Eastoe, J., et al., Langmuir, 2003. 19(17): 6579-6581.

About SoftComp

SoftComp is a Network of Excellence – a tool developed under the 6th Framework Programme of the European Commission dealing with the integration of European research, with the intention of strengthening scientific and technological excellence. In particular, SoftComp aims to establish a knowledge base for an intelligent design of functional and nanoscale soft matter composites. It will do so by overcoming the present fragmentation of this important field for the development of new materials at the interface of non-living and living matter, where the delicate principles of self-assembly in polymeric, surfactant and colloidal matter prevail. This Network of Excellence has created an integrated team that is able to activate the European potential in soft matter composite materials and thus disseminate excellence through extensive training and knowledge transfer chemes. Since December 2009, when EU funding came to an end, Softcomp has been a self-supporting consortium consisting of 38 research groups belonging to 33 different institutions.

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Proteins Control Mineralization

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Biomineralization - Introduction

Mineralization under the control of organic molecules is an important and widespread process in nature. The formation of bones and teeth in mammals, as well as seashells and corals, is subsumed and explored under the concept of "Biomineralization". Two examples are shown in Figure 1. Figure 1a displays a SEM image of an *Emiliania huxleyi* coccosphere. The individual plates are specified as coccoliths which are composed of calcite crystals, representing the stable polymorph of calcium carbonate ($CaCO_3$) [2,3]. These entities represent a wonderful aesthetic structure which could distract attention from their environmental relevance. *Emiliania huxleyi* coccospheres are one of the most abundant unicellular marine algae, swimming at the surface of the ocean and forming a mineral shell. In this way, large amounts of carbonates, such as the White Cliffs of Dover, were deposited over geological ages [4].

Spicules from sponges represent another class of biominerals. They are made from calcium carbonate of calcite or aragonite. Sponges are a class of marine animals typically found in shallow tropical water. A selection of these sponges are depicted in Figure 1b as drawn and published about 140 years ago by the German natural scientist Ernst Haeckel (*1834 in Potsdam; †1919 in Jena) (Table 5 in ref. [5]). His book "Biologie der Kalkschwämme" [6] was one of the first detailed presentations of this topic and was also understood by the author as an "analytical proof of a common descent of all species from a homogeneous group". For a modern overview of sponges, see ref. [7].

Nature and Art

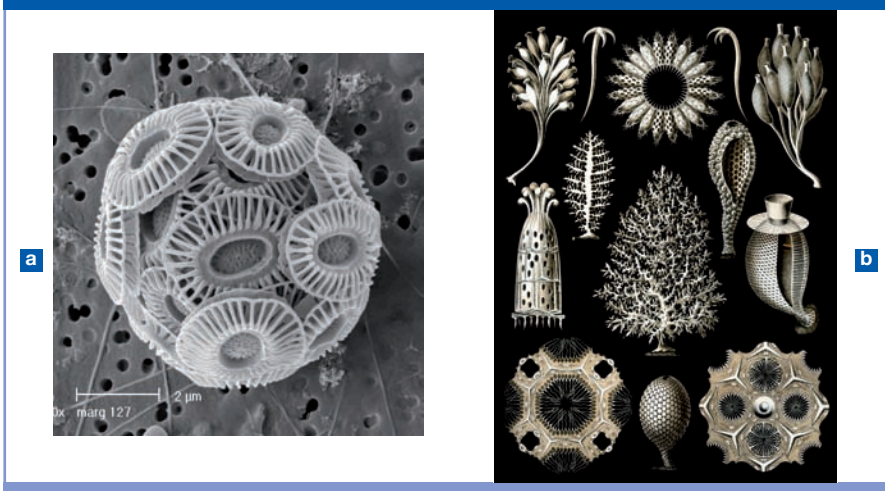

Figure 1: (a) Scanning electron microscopy (SEM)image of an ***Emiliania huxleyi*** coccosphere [1].The individual plates are coccoliths which are composed of calcite ($CaCO_3$) crystals and attached on an oval-shaped organic base plate. The scale bar represents 1 µm length. (b) A series of sponges: "Nature as art. Ascandra. Calcispongiae - Kalkschwämme"

Inhibition mechanism of calcium phosphate by the protein fetuin-A

The purpose of mineralization in the two examples in Figure 1 is the forma-

Neutron small-angle scattering as a tool in biomineralization

Neutron small-angle scattering (SANS) experiments do not produce such beautiful pictures as shown in Figure 1. It "only" delivers scattering curves in an abstract reciprocal Q-space. The scattering vector Q represents the momentum transfer neutrons undergo from interaction with the atomic nuclei and is determined according to $Q=(4\pi/\lambda)\sin 2\delta$ from the neutron wavelength λ and the scattering angle 2δ. SANS is a widespread technique used in many fields of materials science such as metals, soft matter, and biology with the aim of exploring magnetic and non-magnetic structures on length scales between 1 nm and 10^3 nm. The use of SANS in the field of biomineralization is rather new and promising as it delivers the right length scales, particularly during the early stages of mineralization and it offers an easy use of contrast variation by light and heavy water, (H_2O and D_2O). Furthermore, neutrons in SANS do not damage the sample material and in situ experiments are standard. Contrast variation allows the organic and inorganic compounds of biomaterials to be explored. This is an important issue as will be demonstrated by the experimental examples below, and it becomes apparent from the partial scattering functions according to:

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_M - \rho_W)^2 S_{MM}(Q) + (\rho_P - \rho_W)^2 S_{PP}(Q) + 2(\rho_M - \rho_W)(\rho_P - \rho_W) S_{MP}(Q)$$

In the case of a three-component system such as mineral (M), protein (P) and water (W), the result of a scattering experiment, the macroscopic scattering cross-section $d\Sigma/d\Omega(Q)$, can be separated into three partial scattering functions $S_{ij}(Q)$. The structure functions $S_{MM}(Q)$ and $S_{PP}(Q)$ characterize the mineral and organic (protein) phase, whereas the cross-term $S_{MP}(Q)$ shows correlations between the two components.

The coefficients in front of $S_{ij}(Q)$ represent the difference of the corresponding coherent scattering length density ρ_i of the mineral, protein and water. These numbers describe the strength of interaction between neutron and sample. Relevant ρ_i's are depicted in Figure 2 in relation to the D_2O content of water. The blue line represents water. It is the large difference of scattering from H_2O and D_2O (ρ_{H_2O}=-0.561x 10^{10} cm^{-2} and ρ_{D_2O}=6.39x10^{10} cm^{-2}) which is a relevant basis of neutron scattering. The other values are given for the three proteins, fetuin-A, albumin (BSA) and the egg-white ovalbumin, as well as calciumphosphate (polymorph: hydroxapatite) and calcium carbonate (the metastable polymorph aragonite). The proteins depicted by the red symbols show very similar values, with a slight increase with D_2O content. The scattering of proteins in water is matched at about Φ_{D_2O}= 0.44 as the coefficient (ρ_p-ρ_w) becomes zero and the protein invisible for neutrons (eq 1). The other two green lines represent a calcium phosphate and calcium carbonate polymorph. Both minerals are matched at around 73 % and 81 % of D_2O content. This means that the matching conditions for minerals and proteins are well separated, thereby allowing the organic and inorganic components to be distinguished with neutron scattering. This property of easy contrast variation in neutron scattering is a unique and important gift from nature extending the usefulness of SANS tremendously. Matching the first two terms in eq 1 allows us to determine the partial structure factor $S_{MM}(Q)$ and $S_{PP}(Q)$ from which the structure of the mineral and protein can be

Proteins control Mineralization (continued)

Scattering Contrast

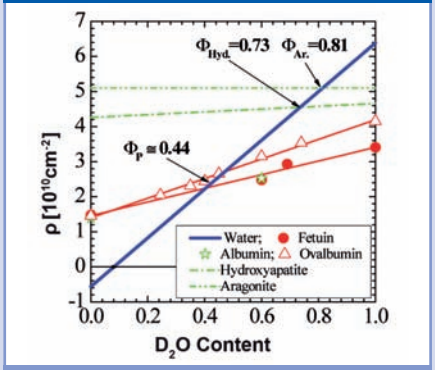

Figure 2: Coherent scattering length density of water, minerals, proteins, and calcium phosphate.

derived. The cross-term $S_{MP}(Q)$, describing the correlation between mineral and protein, can only be derived by the so-called method of singular value decomposition [9].

The two pin-hole SANS instruments KWS 1 and 2 from JCNS at FRM II in Garching (Germany) are shown in Figure 3. Both instruments are 40 m long, i.e. 20 m collimator for adjusting the divergence of the neutron beam and 20 m detector tank. With the standard settings of detector and collimation, both instruments cover a Q range of 10^{-2} nm^{-1} $\leq Q \leq$ 5 nm^{-1}. The installation of aspherical neutron lenses in front of the samples [8] in combination with a high-resolution detector with a pixel size of less than 1 mm extends the Q range to less than 10^{-3} nm^{-1}, thereby allowing a complete analysis of particles with a size between nm and µm.

Neutron Small-Angle Diffractometer

Figure 3: Photo of the JCNS SANS instruments KWS1 and 2 at FRM II in Garching (Germany).

tion of protective and load-bearing material for soft tissue. In this respect mineralization is a desired process. However, there are also several forms of "unwanted" mineralization in living creatures and in technical systems. As an example, biofouling and scaling as a result of mineralization pose a large problem for technical equipment in water treatment technologies, such as water transport and recycling, and they cause substantial economic harm [9]. Unwanted mineralization is also present in our body, from kidney stones to the blocking of our blood vessels. Such "unwanted" minerals are shown in Figure 4a and b, as observed in the peritoneal fluid of a dialysis patient [10]. From the TEM micrographs as well as from SANS, large anisotropic particles were detected with long and short axes measuring about 230 nm and 60 nm, respectively. Contrast variation SANS in Figure 4c determines the matching point of these particles at a concentration of 61 % D_2O which is in between the expected matching conditions of proteins and minerals (Figure 2), and thereby indicates that these particles represent a composite of mineral and protein, so-called CPP (calci-protein) particles. Such pathological mineralization is possible because of strong supersaturation of our blood with respect to calcium and phosphate. Both entities are needed for bone and teeth formation. Hence, there is an inhibition mechanism preventing such pathological mineralization, efficiency of which declines in for dialysis patients.

The protein fetuin-A plays a significant role in the inhibition mechanism of calcium phosphate mineralization. This is reflected by the fact that dialysis patients suffer from a deficiency of this protein, and is made clearer from the pathological mineralization of the knock-out mouse displayed in Figure 4d [11]. The fetuin-deficient nine-month-old mouse shows strong calcification of its soft tissue compared to the wild-type mouse. This observation inspired more systematic in vitro explorations, including contrast variation SANS. For a recent review of this topic, see ref. [12]. Figure 5a displays a series of scattering patterns from a sample measured in situ over 14 hours starting from the mixing of 10 mM $CaCl_2$, 6 mM Na_2HPO_4, and 2.5 mg/mL fetuin in D_2O. Scattering from large particles was observed at low Q following a two stage process in time. Particles with radii of gyration of about 30 nm were stable during the first 5 hours, after which they then increased over several hours to 50 nm large particles and became stable for at least 24 hours. Small particles of the size of the order of the fetuin monomer were found at larger Q. An analysis of contrast variation experiments revealed that the large particles in the second stage were stabilized by a compact fetuin monolayer, as shown by the illustration in Figure 5b. The experimental as well as the analytical procedure, which led to this conclusion, are given in ref. [10]. TEM investigations showed that the CPP particles were of ellipsoidal shape, similar to the particles in the peritoneal fluid (Figure 4a).

A further quantitative analysis of the SANS scattering data showed that only 5 % of the proteins were involved in stabilizing the CPP particles, which comprises only half of the mineral. This means that a second inhibition mechanism of mineralization must exist, as the concentration of the other half of minerals still represents a supersaturated solution and sedimentation was not observed. It was natural to assume that the other 95 % of the fetuin remaining as monomers in solution must play a relevant role. We therefore performed contrast variation experiments at the large Q regime where the fetuin monomers dominate the scattering.

The results of this experiment are shown in Figure 5c and d. We performed experiments with constant salt concentration as given above and two fetuin concentrations of 2.5 mg/mL and 0.5 mg/mL. The average scattering from the latter sample measured for various D_2O contents is plotted in Figure 5c. For both samples, we found a parabolic shape according to the scattering contrast $\Delta\rho^2$ as discussed for eq 1. The minima of scattering were

Pathological Mineralization

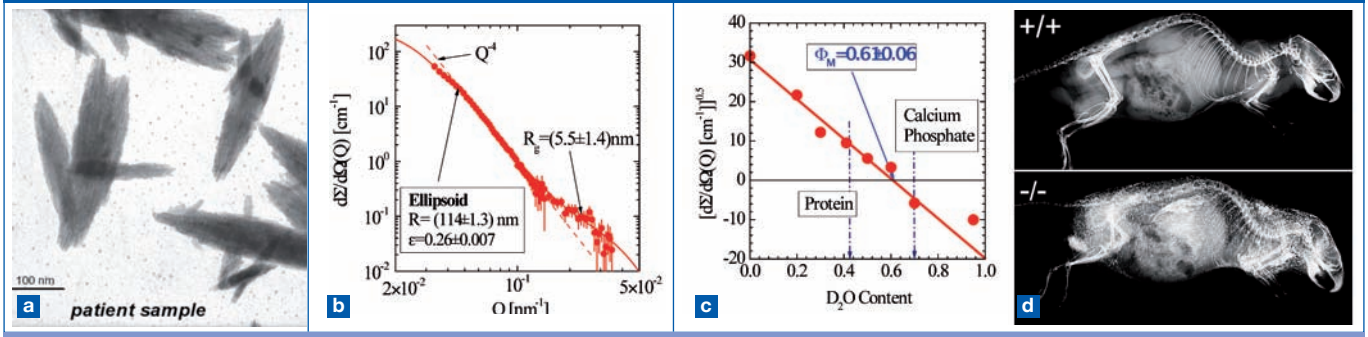

Figure 4: (a) and (b) results from a peritoneal fluid of a dialysis patient containing protein – calcium phosphate particles. These composite particles are of ellipsoidal shape with a longer and shorter axis measuring about 230 nm and 60 nm, respectively [10].
c) The content of protein is obtained from SANS, measuring the particles in varying D_2O/H_2O concentrations, thereby changing the scattering contrast. The matching condition of the particles is in between the protein (Φ_{D_2O}=0.42) and mineral (Φ_{D_2O}=0.70) value.
d) (top) Wild-type mouse (nine months old); (bottom) Fetuin-A deficient mouse of same age. In contrast to the "wild-type" mouse, the "fetuin-A" deficient mouse shows strong calcification in the soft tissue [11].

found at Φ_{D_2O} of 0.505 and 0.68 (red arrow) in comparison with the expected Φ_{D_2O}=0.44 for fetuin (green arrow). The displacement of the scattering minimum to a larger D_2O concentration was caused by a larger scattering contrast of the particles, and is considered as clear evidence that mineral is attached to the protein monomer. A quantitative analysis showed that the other half of the mineral was indeed attached at the fetuin monomers [13].

A further surprising result was the identification of these minerals as Posner clusters [$Ca_9(PO_4)_6$], which are widely discussed in the literature as pre-nucleation clusters forming amorphous calcium phosphate before transforming to the stable crystalline polymorph [14]. Therefore, pre-nucleation clusters appear to be the initial step in a general scheme of mineralization in contrast to classical nucleation theory.

Outlook

The observation of Posner clusters stabilized by the protein fetuin-A is interesting for several reasons. First of all, it confirms the idea of Posner clusters as pre-nucleation centers of calcium phosphate mineralization. Second, the complexation of Posner clusters and fetuin monomers could be relevant for bone formation in our body. In the literature (see figure 8 in ref. [15]) a scenario considers apatite and fetuin monomer complexes, which approach the collagen fibrils and release the apatite mineral. The mineral particles have to be sufficiently small to enter the collagen structure. Our SANS experiments suggest that Posner clusters are the units entering the collagen fibrils. This suggestion appears reasonable as Posner clusters have a diameter of about 0.8 nm and are the more unstable polymorph providing a stronger driving force for the formation of the bone material.

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References

1. This picture was taken from: "Emiliana huxleyi" www.soes.soton.ac.uk/staff/tt/.
2. Stephen Mann. *Biomineralization: Principles and Concepts in Bioorganic Materials Chemistry,* Oxford University Press, Oxford 2001.
3. Mary E. Marsh. *Regulation of Coccolith Calcification in Pleurochrysis carterae,* Chapter 12 in Handbook of Biomineralization, Vol. 1 (E. Bäuerlein, P. Behrens, M. Epple, eds.), Wiley-VCH, Weinheim, 2007.
4. Kurt Kronhauser. *Introduction to Geomicrobiology,* Blackwell Publishing, Oxford 2009.
5. Ernst Haeckel. Kunstformen der Natur, Prestel München, New York 1998.
6. Ernst Haeckel. *Biologie der Kalkschwämme,* Vol 1. Georg Reimer, Berlin 1872. (Reprint of Bibliolife; www.bibliolife.com).
7. Werner E.G. Müller, Xiaohong Wang, Heinz C. Schröder. *Formation of Siliceous Spicules in Demosponges: Example Suberites domuncula,* Chapter 4 in Handbook of Biomineralization, Vol. 1 (E. Bäuerlein, P. Behrens, M. Epple, eds.), Wiley-VCH, Weinheim 2007.
8. H. Frielinghaus, V. Pipich, ...D. Schwahn. J. Appl. Cryt. 42, 681-690 (2009).
9. Sustainable Science and Engineering Vol. 2, *Sustainable Water for the Future: Water Recycling Versus Desalination,* (Isabel Escobar and Andreas Schäfer eds.), Elsevier Amsterdam 2010.
10. A. Heiss, W. Jahnen-Dechent, H. Endo, D. Schwahn. Biointerphases 2, 16-20 (2007).
12. W. Jahnen-Dechent, A. Heiss, C. Schäfer, M. Ketteler, Journal of the American Heart Association, Circ. Res. 108, 1494-1509 (2011). www.circres.ahajournals.org/cgi/content/full/108/12/1494).
13. A. Heiss, V. Pipich, W. Jahnen-Dechent, D. Schwahn. Biophysical Journal 99, 3986-3995 (2010).
14. A.S. Posner and F. Betts. Acc. Chem. Res. 8, 273-281 (1975).
15. P.A. Price, D. Toroian, J.E. Lim. J. Biol. Chem. 284, 17092-17101 (2009).

Inhibition Mechanism of Calcium Phosphate Formation

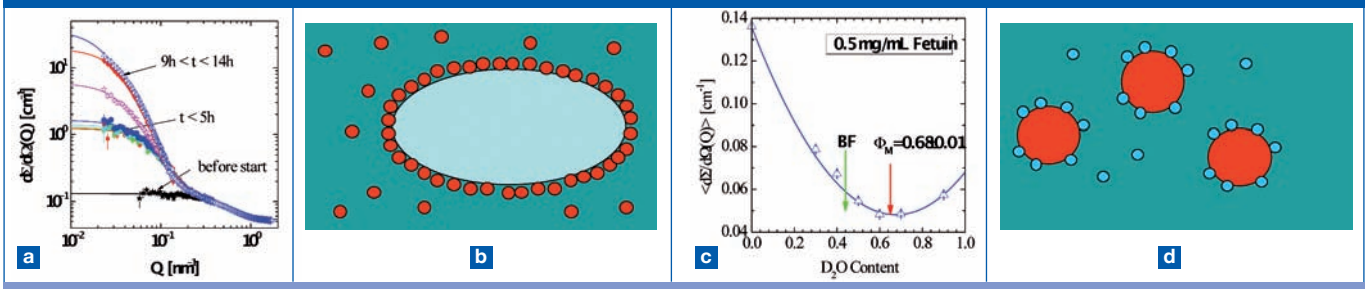

Figure 5: (a) In-situ time evolution of scattering from calci-protein particles. A two-stage process of mineralization is observed. (b) Illustration of a mineral particle in the second stage. The red dots represent the protein forming a compact monolayer, thereby stabilizing the particle from further growth. (c) Average intensity at large Q in different D_2O content water. The minimum scattering at Φ_{D_2O}=0.68 shows a larger scattering contrast because of mineral attachment. (d) Illustration of the mineral-attached monomers.

SoftComp
SOFT MATTER COMPOSITES

newsletter

SoftComp Annual Meeting 2011

The SoftComp Annual Meeting 2011 took place from 15 to 19 May at Hotel Knossos Beach in Heraklion, Crete, Greece. The 2011 meeting was a great success, with 118 participants from 33 of the 38 SoftComp groups and with four invited speakers.

Three parallel sessions were held for the SoftComp Network Areas, comprising a total number of 72 presentations. A full afternoon was devoted to interaction with the European Soft Matter Infrastructure (ESMI).

The very dense scientific programme also facilitated informal sessions, which took place during the long lunch breaks and in the late afternoon. This informal side to the SoftComp Annual Meeting is considered very important and is highly appreciated by the scientists and the students who attend.

The high level of science at SoftComp is reflected in the large demand for new accessions, despite the end of EU funding.

During the SoftComp Annual Meeting 2011, the Network Governing Board accepted the request of accession proposed by the Institut Laue Langevin, Grenoble, France, which is now the 39th SoftComp group.

Due to the great success, of the 2011 meeting, it has been decided to hold the 2012 meeting at Hotel Knossos Beach once again (28 May - 1 June 2012).

Please,make a note of these dates in your diary!

F. Carsughi

Scientific highlights

The scientific achievments of SoftComp during 2011 are highlighted on the SoftComp website:

http://www.eu-softcomp.net/news/highlights

Vacancies

PhD positions

The polymer theory group in Halle has two openings for PhD students working on polymer crystallization: one position for analytical work, one for Monte Carlo simulations. Both will work within the local collaborative research program SFB TR 102.

Contact: Wolfgang.Paul@physik.uni-halle.de

PhD positions

There is an opening for a postdoc position for a biochemist with interest in soft condensed matter and biophysics research at the Division of Physical Chemistry, University of Lund, Sweden. The project focuses on the structure and dynamics of concentrated protein mixtures.

For more information please contact: anna.stradner@fkem1.lu.se

Coming Up...

SoftComp Conferences & Workshops

9 Jan. - 10 Feb. 2012
Molecular Biology of the Cell 2012 Laboratory and Lecture Course
Jointly organized by Institut Pasteur and Institut Curie.
Paris, France
R. Bruzzone, P. Chavrier, C. Zurzolo
http://www.pasteur.fr/ip/easysite/pasteur/en/teaching/mechanisms-of-living-organisms/molecular-biology-of-the-cell

Jan. 2012
IRC Courses in Polymer Science and Technology
The University of Sheffield
http://www.polymercentre.org.uk/training/

5-16 March 2012
43rd IFF Spring School 2012: Scattering Methods for Condensed Matter Research: Towards Novel Applications at Future Sources
Juelich, Germany · D. Richter
http://www.fz-juelich.de/SharedDocs/Termine/

20-23 March 2012
Colloidal Dispersions in External Fields
Bonn, Germany · H. Loewen

7-11 May 2012
NaNaX5. Nanoscience with Nanocrystals
Fuengirola, Spain · L. Liz-Marzan

28 May - 2 June 2012
Laboratory Course on Dielectric Spectroscopy
San Sebastian, Spain · A. Alegria

28 May - 01 Jun 2012
SoftComp Annual Meeting 2012
Heraklion, Crete, Greece · F. Carsughi

7-14 June 2012
11th European Summer school on Scattering Methods Applied to Soft Condensed Matter
Bombannes, France · J. Oberdisse

20-30 July 2012
AMPERE NMR SCHOOL ZAKOPANE 2012
Poznan, Poland · S. Jurga
http://www.staff.amu.edu.pl/~school/

3-13 July 2012
The Enrico Fermi Summer School on "Physics of Complex Colloids"
Villa Monastero, Varenna, Italy
Organized by the ITN-COMPLOIDS
F. Sciortno, C. Bechinger, P. Ziherl
http://www.itn-comploids.eu/

3-14 Sept. 2012
16th JCNS Laboratory Course Neutron Scattering
Jülich and Garching, Germany · R. Zorn
e-mail: reiner.zorn@gmail.com

Coming Up (continued) ...

SoftComp Conferences & Workshops

11-13 Sept. 2012
Faraday Discussion 161: Lipids and Membrane Biophysics
London, United Kingdom · J. M. Seddon
12-19 Sept. 2012
Polymeric Materials
Halle (Saale), Germany · W. Paul

24-26 Sept. 2012
German Neutron Scattering Conference
Gustav-Stresemann-Institut, Bonn, Germany
T. Brückel
http://www.fzjuelich.de/SharedDocs/Termine/

8-11 Oct. 2012
Trends and Perspectives in Neutron Scattering for Soft Matter and Biophysics
Tutzing, Munich, Germany
R. Bruchhaus, J. Colmenero, D. Richter (DIPC, JCNS)
http://www.fz-juelich.de/SharedDocs/Termine/

13-16 Nov. 2012
Juelich Soft Matter Days
Bad Honnef, Germany
J. Dhont, G. Gompper, D. Richter

12-15 Dec. 2012
Cell Shape Changes: Cell Motility and Morphogenesis
Paris, France · J. Plastino

16-19 Sept. 2013
International Soft Matter Conference
Rome, Italy · F. Sciortino

Personalia

Christos Likos
(University of Vienna) is, as of September 1, 2011, Associate Editor of "Soft Matter".

F. Carsughi
has accepted the position of the head of the JCNS User Office Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Munich, Germany. His Task as project manager of the SoftComp Network of Excellence will continue.

Rideal Lecture by GC Mailand
The Rideal lecture is an annual award given by SCI's Colloid and Surface Chemistry Group and the RSC's Colloid and Interface Science Group.
The 2012 Rideal Lecturer is Geoff Maitland of Imperial College, London. Geoff has been a key contributor to SoftComp for many years.
Geoff has had a distinguished career in both industry and academia, so he is ideally placed to describe understanding and application of soft materials.
Geoff is particularly well noted for his excellence as a rheologist and for encouraging collaboration between industry and academia.
http://www.soci.org/General-Pages/Display-Event?EventCode=COLL348

For more frequently updated information, please see also the SoftComp web pages...
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SoftComp Events: **www.eu-softcomp.net/news/cal**

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