crystalline state towards smaller concentrations as compared to the MA case. At some concentration of SA/MA a partial aggregation (regions with liquid crystals of acid molecules in the solution) is observed as a deviation of the scattering curves from the Guinier law at the smallest q-values. As the concentration increases, the SANS signal from these aggregates becomes rather distinguishable, and the corresponding characteristic size can be roughly estimated from an additional Guinier-type term as ~10 nm. The further increase in SA/MA concentration leads to the alignment of these aggregates (transition to a smectic phase), which is reflected in the appearance of the diffraction peak at $q \sim 2$ nm^{-1} (corresponding correlation length ~3.2 nm). The position of the peak shifts to higher q-values (smaller distance between aggregates) with an increase in the acid concentration. The possibilities of the wide-angle diffraction for the study of the observed liquid crystalline phase in solutions of linear molecules with comparatively short alkane chains are considered.

The formation of the found LC-phase in bulk solutions of mono-carboxylic acids is an important factor, which influences the stabilization efficiency of the studied acids in colloidal solutions of magnetic nanoparticles.

[1] M.V. Avdeev, D. Bica, L. Vekas, V.L. Aksenov, A.V. Feoktystov, O. Marinica, L. Rosta, V.M. Garamus, R. Willumeit *J. Coll. Inter. Sci.* **2009**, *334*, 37-41. [2] V.I. Petrenko, M.V. Avdeev, L. Almasy, L.A. Bulavin, V.L. Aksenov, L. Rosta, V.M. Garamus *J. Col. Surf. A* **2009**, *337*, 91-95. [3] T. Shimada, M. Doi, K. Okano *J. Chem. Phys.* **1988**, *88*, 2815-2821.

MS26.P02

Nanostructures in a supramolecular side-chain liquid crystalline block copolymer

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Hydrogen-bonding amphiphilic nonmesogen 4'-(3,4,5-triocty loxybenzoyloxy)benzoic acid (TOB), of a wedge shape, is bound to P4VP block for suparmolecular side-chain liquid crystalline blocks in polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP). We have demonstrated that rich phase transitions of hierarchical structures can be manipulated by adjusting the mesomorphic ordering of P4VP(TOB)$_x$ block via the TOB grafting fraction ratio, *x*, in the PS-*b*-P4VP(TOB)$_x$ thin films under solvent-casting and stretch-annealing treatments. Using synchrotron-based small- and wide- angle X-ray scattering and transmission electron microscopy (SAXS, WAXS and TEM), we observed global phase transitions of the PS-*b*-P4VP(TOB)$_x$ compound from lamellar (LAM), hexagonal-packed cylinder (HC), undulating hexagonal-packed cylinder (UHC), face-centered cubic sphere (FCC), to tetragonally perforated layer (TPL) structures, upon increasing the TOB content for an increasingly ordered mesomorphic phase of the hydrogen-bonded complex of P4VP(TOB)$_x$, from nematic (N), smectic A (SmA), hexagonal columnar disordered (Col$_{hd}$), to hexagonal columnar ordered (Col$_{ho}$) phases. The mechanism of stretch-induced phase transition form FCC to TPL in the PS-b-P4VP(TOB)$_{0.7}$ thin film was also investigated by simultaneous SAXS and in-situ stretching mechanical measurement. When the SAXS patterns from the stretching film of PS-b-P4VP(TOB)$_{0.7}$ were examined, we found that the FCC spheres become oblate ellispoids by the initial deformation and than merging of each oblate ellispoids along ⟨110⟩ direction of FCC form TPL mesophase by thermal annealing. The TPL, a kinetic trapped phase, is directed by strong local ordering columns of TOB with π-π interactions at a sufficient grafting density. The FCC-to-TPL phase

transition^b is described for the first time in block copolymers.

[1] W.T. Chuang, H.S. Sheu, U.S. Jeng, H.H. Wu, P.D. Hong, J.J. Lee *Chem. Mater.* **2009**, *21*, 975-978.

MS26.P03

Virus matrix protein M1: SAXS data analysis and modeling

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Structural analysis of the influenza A virus full-length matrix M1 protein was performed using small-angle X-ray scattering (SAXS). The structure of the M1 protein macromolecules in solution was for the first time reconstructed using advanced methods of SAXS data analysis and interpretation [1-6]. The detailed analysis of the scattering data and modeling revealed a structurally polarized molecule with a compact NM-fragment and weakly ordered C-terminal domain. These structural peculiarities explain the ability of the matrix M1 protein to mediate the multistep process of cell infection due to flexibility of the C-terminal regions.
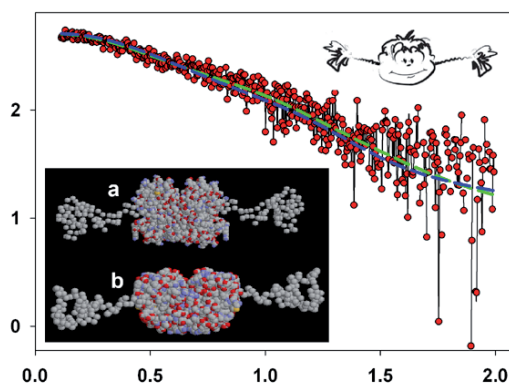
[1] L.A. Feigin, D.I. Svergun, *Plenum Press*, New York, **1987**. [2] P.V. Konarev, V.V. Volkov, A.V. Sokolova, M.H.J. Koch, D.I. Svergun, *J. Appl. Crystallogr.* **2003**, *36*, 1277-1282. [3] D.I. Svergun, *J. Appl. Crystallogr.* **1992**, *25*, 495. [4] D.I. Svergun, *Biophys. J.* **1999**, *76*, 2879-2886. [5] M.V. Petoukhov, D.I. Svergun, *Biophys. J.* **2005**, *89* 1237-1250. [6] D.I. Svergun, C. Barberato, M.H.J. Koch, *J. Appl. Cryst.* **1995**, *28*, 768-773.

MS26.P04

SAXS study of phase separation process in the SiO$_2$-SnO$_2$ nanostructured materials

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Tin oxide is a well-known wide band gap semiconductor that is used in particular in optoelectronic devices as SnO_2 nanocrystals dispersed in silica matrix [1]. The optical properties are directly related to the mean size of the nanocrystals [2]. We have elaborated such nanostructured materials using sol-gel process starting from alkoxide precursors [3]. After the synthesis at room temperature the amorphous bi-cationic material is homogeneous at the molecular level [4].

The aim of this communication is to present a detailed analysis of the phase separation process involving in such material synthesized far from the equilibrium state. This study has been realized through Small Angle X-ray Scattering (SAXS) in-situ measurements performed at the BM02 beamline at ESRF. Bulk samples were studied in transmission mode at 16 keV using a 2D detector. Isothermal and isochrones records of the SAXS curves were realized in a dedicated furnace between room temperature and 600°C.

A temperature increase of the thermal treatment induces decrease of the scattered intensity at low q values and simultaneously a clear increase of the signal in the high q range. A "cross over" is observed and its position shifts to low q value when the amount of tin oxide increases (see figure 1). This invariant point is due to the formation of a composition fluctuation related to the formation of tin-rich zones and the increases of the intensity in the high q range indicate an increase of the number of short Sn-Sn distances which means a tin enrichment of these zones.

Thermal treatment at temperature higher than 350°C induces a rapid modification of this self-organized microstructure (see figure 2). Indeed, the tin-rich zones grow rapidly and tin oxide particles appearing probably through a coalescence process.
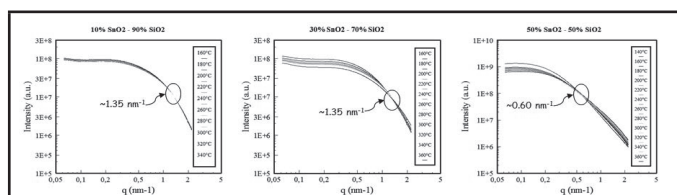

Figure 1. Direct in-situ SAXS observation of the phase séparation process.
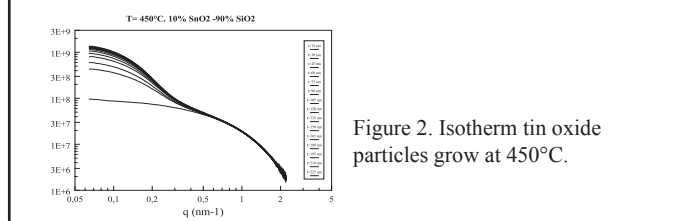

Figure 2. Isotherm tin oxide particles grow at 450°C.

[1] N. Chiodini, A. Paleari, D. DiMarco, G. Spinolo, *Appl. Phys. Lett.* **2002**, *81,* 1702-1704. [2] N. Chiodini, A. Paleari, G. Spinolo, *Phys. Rev. Lett.* **2003**, *90,* 055507. [3] W. Hamd, A. Boulle, E. Thune, R. Guinebretière, *J. Sol-Gel Sci. Technol.*, **2010**, *55*, 15-18. [4] Y.C. Wu, W. Hamd, E. Thune, A. Boulle, C. Rochas, R. Guinebretière, *J. non Cryst. Sol.* **2009**, *355,* 951-959.

Keywords: SAXS, phase separation, tin oxide

MS26.P05

Block copolymer-mediated gold nanoparticles: small-angle scattering studies

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Combined application of small-angle neutron and x-ray scattering studies to characterize block copolymer mediated gold nanoparticles has been reported. These two techniques provide different contrasts for the different components and hence provide complementary information on the system. Neutron scattering sees the hydrogenous block copolymers and their micelles whereas X-ray scattering provides the structure of high-Z gold nanoparticles. We have shown that both gold nanoparticles and block copolymer micelles coexists and synthesis of gold nanoparticles can be controlled by tuning these populations.

The synthesis of the gold nanoparticles was carried out by varying the equi-concentration of gold salt ($HAuCl_4.3H_2O$) and trisodium citrate ($Na_3C_6H_5O_7.2H_2O$) in the range from 0 to 1 wt% for a fixed concentration of block copolymer [1 wt% P85 ($EO_{26}PO_{39}EO_{26}$)]. In the case when both gold nanoparticles and free block copolymer (unimers and/or micelles) coexist, the total scattering is determined by the sum of the individual components as

$$I_t(Q) = I_{np}(Q) + I_{bcp}(Q) \tag{1}$$

where the subscripts *np* and *bcp* correspond to nanoparticles and block copolymer, respectively.

In SANS data of 1 wt% P85 with varying gold salt and trisodium citrate concentration, the contrast with solvent (D_2O) for block copolymers is much higher than for gold nanoparticles. Also gold nanoparticles have much smaller number density (for given wt%, number density inversely depends on the density of the particle). This suggests that the scattering is dominated by block copolymers and no significant scattering occurs from gold nanoparticles [$I_t(Q) \sim I_{bcp}(Q)$ using equation (1)]. The changes in SANS data with varying gold salt concentration are because of the enhanced micellization at higher salt concentrations. Both the block copolymer unimers and micelles coexist in these systems and the fraction of block copolymer micelles increases (30 to 41%) as a result of enhanced micellization (salting out effect) with the salt concentration increase from 0.05 to 1 wt%. The micellar size is found to be almost similar having core radius of 40 Å surrounded by a PEO chain of radius of gyration of 12 Å and aggregation number around 70. Since the number density of gold nanoparticles is very small, the scattering from block copolymers stabilizing nanoparticles is therefore expected to be negligible.

In SAXS data on the same system, the high scattering length density difference between gold nanoparticle and solvent makes the scattering from nanoparticles dominant [$I_t(Q) \sim I_{np}(Q)$] even though the number density of the gold nanoparticles is small. Moreover, there exists almost no contrast for block copolymers in SAXS. The scattering increases as the number density of the gold nanoparticles increases with increasing gold salt concentration. The gold nanoparticles are fitted with polydispersed spherical particles. The particle size is found to increase (11.5 to 21.6 nm) with decrease in polydispersity (0.52 to 0.35) with increasing nanoparticle yield from 0.05 to 1 wt%.

[1] T. Sakai, P. Alexandridis, *Nanotechnology* **2005**, *16*, S344-S353. [2] D. Ray, V. K. Aswal, *J. Macromol. Sci. Part B: Phys.* **2010**, *49*, 810-820. [3] D. Ray, V. K. Aswal, D. Srivastava, *J. Nanosci. Nanotechnol.* **2010**, *10*, 6356-6362. [4] D. Ray, V. K. Aswal, J. Kohlbrecher, *Langmuir*, **2011**, *27*, 4048-4056

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MS26.P06

An examination of the structure of Fe_3O_4 using reverse Monte Carlo refinements

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