

In this work, we studied the role of bonding and nonbonding atomic interactions in the topochemically controlled solid-state polymerization and assembly of the polymer DCHD (1,6-di(N-carbazolyl)-2,4-hexadiyne). For this we carried out a high brilliance SPring-8 (Hyogo, Japan) synchrotron X-ray study of DCHD monomer and polymer crystals in the temperature range from 20 to 420 K. Since topochemical polymerization is interplay of the monomer and polymer lattices, a comparative analysis of the both monoclinic structures allows us to uncover important insights into the structural machinery controlling formation and stability of polymer DCHD.

For advance details, we examined the structures on a charge density level using Maximum Entropy Method (MEM) upgraded to determine the electrostatic potential, electric field and atomic polarization in structure [1], [2]. The MEM maps based on highly reliable polyDCHD x-ray data viewed the hydrogen bond as electron density path bridging acceptor-donor atoms, linkage of electrostatic potential contour and flux of electric field vector from donor to acceptor sites. They allow us to reveal that polyDCHD assembled by networks of unconventional H-bonds, C-H $\cdots\pi$ (C $\equiv$ C) between sidechain C-H and  $\pi$ -electron clouds of the triple bond segment of nearby backbone in layer and C-H $\cdots\pi$  amongst the interlayer carbazolyl rings packed in a herringbone motif.

In the monomer form, C-H $\cdots\pi$ (C $\equiv$ C) links the monomer's carbazolyl to the triple bond segments of the nearby monomers. The arrangement of the inter-monomer H-bonds is changed from the low-temperature trifurcated (four-centered) to the bifurcated (three-centered) at temperatures above  $T_p \sim 140$ K. As we find, the trifurcated H-bond provides conformational constraint preventing twist of monomer rods to the reactive state for the solid-state polymerization. Supposedly, it makes DCHD non-polymerizable under  $\gamma$ -ray or other radiations below  $T_p$  [3]. Declining of that constraint above  $T_p$  resulted in non-planar bifurcated H-bond arrangement which may accommodate the "monomer rods" to "polymer backbone" switch. In the resulted polymer phase, the chains strengthened by linear (two-centered) H-bonds.

Thus, in the DCHD system unconventional C-H $\cdots\pi$ (C $\equiv$ C) interactions of trifurcated and linear geometries direct the structural stability for the monomer and polymer forms, respectively, while bifurcated one triggers the solid-state monomer-to-polymer reactivity.

[1] M. Takata, *Acta Cryst. A* **2008**, *64*, 232-245. [2] H. Tanaka, Y. Kuroiwa, M. Takata, *Phys. Rev. B* **2006**, *74*, 172105-1-172105-4. [3] V. Enkelmann, *Adv. Polym. Sci.* **1984**, *63*, 91-136.

**Keywords:** electron density, hydrogen bond, polymerization

## MS.04.1

*Acta Cryst.* (2011) **A67**, C28

**Small-angle neutron scattering studies on catalyst ink of fuel cell**  
**Mitsuhiro Shibayama**,<sup>a</sup> Takuro Matsunaga,<sup>a</sup> Takumi Kusano,<sup>a</sup> Kazuki Amemiya,<sup>b</sup> Noriyuki Kobayashi,<sup>b</sup> <sup>a</sup>*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba, 277-8581, (Japan).* <sup>b</sup>*Toyota Motor Corporation, Higashifuji Technical Center Susono, Shizuoka 411-1193, (Japan).* E-mail: sibayama@issp.u-tokyo.ac.jp

Development of fuel cells has been a hot topic in materials science. The performance of fuel cells depends greatly on the microscopic structure of electrodes [1], [2]. Electrodes of fuel cells are manufactured from catalyst ink. Catalyst ink is a multi-component system, consisting of carbon, platinum, water, and ionomers. Contrast-variation small-angle neutron scattering (CV-SANS) is a powerful technique to study the structure of multi-component materials since it allows one to decompose scattering intensity functions to partial scattering functions [3]. In this study, we employed CV-SANS to unveil the structure of

catalyst ink and discuss the relationship between the structure and performance of fuel cells.

Various types of catalyst ink were prepared by varying the size and porosity of carbon in water with various compositions of D<sub>2</sub>O/H<sub>2</sub>O. CV-SANS was conducted at the small-angle neutron instrument, SANS-U, JRR-3 [4]. Contrast-variation SANS revealed the following: (1) The partial scattering functions for carbon-carbon,  $S_{cc}(q)$ , polymer-polymer,  $S_{pp}(q)$ , and carbon-polymer correlations,  $S_{cp}(q)$ , were successfully obtained by CV-SANS. (2) The microscopic structure of the catalyst ink consists of dendric clusters of carbon particles surrounded by ionomers. (3) Ionomers have an ionic cluster peak around  $q \approx 0.1 \text{ \AA}^{-1}$ , which maintain its structure even in the ink mixed with carbon/Pt. (4) The cross term, i.e.,  $S_{c}(q)$ , indicates that ionomers are concentrated on a surface of carbon clusters.

[1] G. Gebel, O. Diat, *Fuel Cells* **2005**, *5*, 261-276. [2] M.-H. Kim, C.J. Glinka, S.A. Grot, W.G. Grot, *Macromolecules* **2006**, *39*, 4775-4787. [3] H. Endo, D. Schwahn, J. Cölfen, *J. Chem. Phys.* **2004**, *120*, 9410-9423. [4] S. Okabe, T. Karino, M. Nagao, S. Watanabe, M. Shibayama, *Nucl. Instrum. Methods Phys. Res. A* **2007**, *572*, 853-858.

**Keywords:** small-angle neutron scattering, fuel cell, contrast variation

## MS.04.2

*Acta Cryst.* (2011) **A67**, C28-C29

**Industrial SAS activities at European facilities ESRF and ILL**  
**Jean Doucet**, *Novitom, 6 Allée de Bethléem, F-38610 GIERES (France).* Email: jean.doucet@novitom.com

Large scale synchrotron and neutron facilities offer very efficient tools to analyze the structure of materials using the small-angle scattering technique (SAS). In short, the modern synchrotron rings deliver several million times more intense X-ray beams than those emitted by conventional laboratory sources, allowing the follow-up of real-time evolutions. In addition, the low divergence leads to a sub-micrometer spatial resolution for the micro-analysis and the imaging techniques. SAS using a neutron source opens the possibility to match the contrast for organic materials working with deuterated samples. SAS beamlines at large scale facilities are today used for industry-driven projects, either directly by engineers from companies or by public institutes. The projects concern the various phases of a product life-cycle, mainly for the research and development phases, but also the engineering and the control of quality. A few examples in various domains will be presented, among which: the ageing of the structural components of nuclear reactors under neutron and gamma irradiation, the molecular structure of epidermis and hair in relation with cosmetics, the development of new polymers and composites.

However, despite the obvious interest of the SAS measurements for applied activities using large facilities' equipment, the rate of industrial use is low compared to that of other techniques. The main reasons for this situation are probably: an insufficient communication and commercial effort, the cost and the delays for getting access to the beamlines, the lack of optimized equipment and scientific expertise for industrial issues.

In order to improve the interface between their equipment for the analysis of soft-condensed matter, including SAS, and the communities of users, academic as well as industrial, the ESRF and the ILL have recently launched the *Partnership for Soft Condensed Matter* (PSCM). The PSCM will be established in a step-by-step process, initially as a support facility for the better exploitation of neutron and synchrotron scattering instruments in Soft Matter Research. The PSCM, in the medium term, will provide a platform for promoting the complementary aspects of neutron and synchrotron techniques. The long-term mission

of the PSCM is to streamline neutron and synchrotron based Soft Matter Research to address 21st century challenges in nanomaterials, biotechnology, environmental and energy sciences. New laboratories equipped for sample preparation and characterization will be hosted in the new Science Building to be soon implemented on-site. This structure should permit to bridge the gap between the ESRF and ILL facilities and the European industry in many issues which require SAS measurements.

**Keywords:** SAXS, SANS, industry

## MS.04.3

*Acta Cryst.* (2011) A67, C29

### SAXS in support of industrial research at DuPont

J D Londono,<sup>a</sup> J Meth,<sup>a</sup> B A Wood,<sup>a</sup> P M Cotts,<sup>a</sup> G. Beaucage,<sup>b</sup> S J Weigand,<sup>c</sup> <sup>a</sup>*DuPont Central Research and Development, Wilmington, Delaware (USA)*. <sup>b</sup>*Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio (USA)*. <sup>c</sup>*DND-CAT, Northwestern University, Argonne National Laboratory, Illinois (USA)*.

DuPont offers a wide range of innovative products and services for markets including agriculture, nutrition, electronics, communications, safety and protection, home and construction, transportation and apparel. The SAXS group within the Corporate Center for Analytical Sciences provides support to R&D and businesses throughout DuPont, now in approximately 90 countries. The SAXS technique is unique for the characterization of particle size and agglomeration/flocculation at the nanoscale, providing statistically meaningful information; this technique is particularly powerful when coupled to a synchrotron. Two examples are provided.

The realization of the full potential for polymeric nanocomposites to manifest their entitled property improvements relies, for some properties, on the ability to achieve maximum particle-matrix interfacial area. Well-dispersed nanocomposites incorporating colloidal silica as the filler can be realized in both polystyrene and poly(methylmethacrylate) matrices by exploiting the charge stabilized nature of silica in nonaqueous solvents which act as Lewis bases. We demonstrate that dispersions of colloidal silica in dimethylformamide are charge stabilized, regardless of organosilyl surface functionalization. When formulated with polymer solutions, the charge stabilized structure is maintained during drying until the charged double layer collapses. Although particles are free to diffuse and cluster after this neutralization, increased matrix viscosity retards the kinetics. We demonstrate how high molecular weight polymers freeze the structure of the silica to produce well-dispersed composites. The glass transition temperatures of these composites do not vary, even at loadings up to 50 v%.

An in-situ Study of the pyrolytic synthesis of titania nanoparticles was used to understand the particle growth dynamics in a flame reactor. Particle size (SAXS), chemical speciation (XAS), crystal phase identification (WAXS) were measured as a function of height above the burner to follow the chemical conversion from TiCl<sub>4</sub> to TiO<sub>2</sub> and associated nanoparticle growth and agglomeration dynamics. Much of the observed behavior could be tied to separate hydrolysis and condensation reactions occurring in different lateral and horizontal regions of the flame governed by water concentration and temperature. Crystallization kinetics paralleled the kinetics of particle growth indicating that in some cases single grain particles may form directly from the vapor phase. Due to the lateral distribution of water vapor in the flame and the lateral temperature gradient, hydrolysis and titania conversion had a maximum away from the flame axis, while condensation and nucleation occurred primarily at axial positions. This study

demonstrated that synchrotron SAXS can be used to study pyrolytic synthesis reactions of industrial interest.

**Keywords:** industrial, synchrotron, SAXS

## MS.04.4

*Acta Cryst.* (2011) A67, C29-C30

### SAXS and SANS for industrial materials-by-design

Andrew Allen *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland (USA)*. E-mail: Andrew.Allen@nist.gov

Over several decades, absolute-calibrated small-angle X-ray and neutron scattering (SAXS and SANS) studies of material microstructures, measured over extended length scales, have helped overcome technological barriers impeding advanced materials development for industrial applications. While much work has focused on applications of soft materials (new polymers, biological systems, etc.), SAXS and SANS also make significant contributions in the development of new high-performance “hard” materials of industrial relevance:

Advanced thermal barrier coating (TBC) development has allowed more efficient gas turbine performance to be achieved for jet propulsion and electricity generation. However, the thermomechanical properties of these coating materials depend critically on their highly anisotropic component void morphologies. SAXS and SANS studies have succeeded in distinguishing and quantifying the different components, and have elucidated many of the processing–structure–property relationships for improved materials design [1].

Solid oxide fuel cells (SOFCs) promise major improvements in energy efficiency, clean energy supply and fuel conversion. The small X-ray beams available for SAXS and ultra-small-angle X-ray scattering (USAXS) measurements at 3rd generation synchrotron sources, together with the X-ray energy tunability, enable the microstructure gradients and the state of the electrochemical interfaces close to the electrode–electrolyte boundaries to be interrogated. Anomalous USAXS studies have quantified degradation during SOFC service life such as arises from the presence of sulfur in the fuel [2].

Despite more than a century of research, fundamental aspects of cement hydration, particularly the nature of the nanoscale calcium-silicate-hydrate (CSH) reaction product, remain elusive. For the cement industry, this situation presents a challenge to the development of new cements with advanced curing properties, or for achieving reduced CO<sub>2</sub> emissions in cement manufacture. Carefully calibrated SANS contrast variation measurements have determined the composition and density of the CSH solid phase from first principles. The atomic packing density within CSH is higher than in related mineral analogs – with repercussions both for cement shrinkage and for new cement design [3].

The global coal industry seeks new sorbent materials to select and remove CO<sub>2</sub> from the flue gas streams of coal-fired electrical power plants. Various classes of metal organic frameworks and similar materials exhibit promising sorption properties, but the structure–dynamics–property relationships are complex. SAXS and SANS studies provide a key role in correlating the structural changes measured by small-angle-diffraction both with the observed sorption performance and with the powder morphology or particle surface area [4].

Using these examples the potential of future SAXS and SANS development will be highlighted in the context of new industrial materials design.

[1] A. Flores Renteria, B. Saruhan, J. Ilavsky, A.J. Allen, *Surf. Coat. Technol.* **2007**, *201*, 4781-4788. [2] A.J. Allen, J. Ilavsky, P.R. Jemian, A. Braun, *J. Appl. Phys.* **2011**, submitted. [3] A.J. Allen, J.J. Thoma, H.M. Jennings, *Nature Mater.*