Industrial Utilization of SPring-8 in Polymer Fields

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1. Introduction - Why now SR Beams for Polymers?

2. Examples of Industrial Uses of SPring-8 for Polymer Studies
   (1) Observing curing reactions inside a polymer-modified cement water-proofing coating material.
   (2) Nanostructure of polarizer films consisting of PVA and iodine.
   (3) Nanosurface structure of polyimide films for liquid crystal alignment in LCD.

3. Summary - Not only wider utilization but also higher-quality utilization.
Challenges in Polymer Science

**<Polymer Science in the Past>**
Description of universality that polymers consist of macromolecules connected with flexible covalent bonds
- Shape and size of chain molecules
- Polymerization reactions

**<Polymer Science now and in future>**
Description of features of polymers that have ordered structure in nanoscales.

Controlled syntheses & precision polymerization

Molecular and higher-order structure in nanoscales

Physical properties & Functions
- photonic, electronic, biomedical, environmental,

Nobel prizes in synthetic polymer fields (year)
- 1926-30 H.Staudinger Establishment of polymer concept (1953)
- 1953-55 K.Ziegler-G.Natta Polymerization with coordination catalysts (1963)

As an object of materials science, research trends expand from structural to functional polymers.
Percentage of polymer study in total experiments is about 6% (2003~06) to 10% (2007~). However, there has been so far no BL specified to polymer research at SPring-8.
Experiments by industrial users have increased and become about 20% of total experiments.

Number of applicants still increases, i.e., about 30% of applicants are still rejected due to limited beam time.
Contract Beamline of Industry-Academia Consortium for Advanced Softmaterial Research (FSBL - BL03XU) (Start in Feb. 2010)

Hutch 1: Evaluation of thin film surface structure (GIXD, GISAXS, XR), wide-angle precise diffraction measurements.

Hutch 2: Simultaneous SAXS/WAXS measurements also with DSC, IR, Raman techniques, time-resolved & in-situ measurements of various polymer processes with microbeams.

© FSBL Consortium consists of 19 chemical corporate groups.

© Every corporate group has industry and academia members. Administration Committee of the Consortium is responsible for the management of the beamline.
# General Features of SR Beams and their Uses

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<tr>
<th><strong>SR Beams</strong></th>
<th><strong>Typical Utilization</strong></th>
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<tr>
<td>Ultra-bright</td>
<td>Diffractometry of very small samples, Rapid measurements (time-resolved, during reaction, process)</td>
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<tr>
<td>Highly directional</td>
<td>Microbeam Measurements and Imaging Grazing incidence (GI) XD &amp; SAXS (surface, films)</td>
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<td>High energy</td>
<td>XPS inside samples Inner-orbital excitation of heavy atoms</td>
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<tr>
<td>Spectrally continuous</td>
<td>X-ray absorption (XAFS) Choice of optimal energy condition Effect of anomalous dispersion</td>
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<tr>
<td>Linearly or circularly polarized</td>
<td>Magnetic Properties (MCD)</td>
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(X-ray detects buried structure inside materials.)
Observing Cement Hydration in Polymer-modified Cement Water-proofing Coating Materials

P(E/VAc) Polymer emulsion

Mixing

Alumina cement

Cement hydrates with water in emulsion, forming water-proofing tough coating at a construction site.

Hydration reactions of cement are exothermic, temperature rises, and the reactions inside should be monitored as a function of temperature and humidity.

Water-proofing coating is important at underground construction sites.

SR beam is needed for high resolution, rapid measurements during reactions.
Detecting reactions in buried insides (2)  

K. Miyashita, Ozeki Chemical Industry

Hydration Reactions in Polymer-Cement Water-proofing Coating

CA: CaO \cdot Al_2O_3
C_2AH_8: 2CaO \cdot Al_2O_3 \cdot 8H_2O
C_3AH_6: 3CaO \cdot Al_2O_3 \cdot 6H_2O

Ozeki Chemical Ind. Co. Ltd.: A pioneer of this field, capitalized at 60 million yen, 95 employees.

◎ Realizing a precise method of designing materials and processes suitable for each temperature and humidity in construction environments.

◎ Use of their materials in major facilities in Japan & Overseas; Roppongi hills, Shanghai World Financial Center, Tokyo Nerima Tunnel etc.
Absorption of Iodine into Drawn PVA Films in KI/I2 Solution

SAXS patterns for PVA films, (a) drawn in Pure water, (b) drawn in KI/I2 solution

Crystalline region
Amorphous region

\[ d_{\text{max}} \] - Lamellar thickness
\[ ? \, d_{\text{min}} \] - amorphous or crystalline?

Nitto Denko Co., Ltd.

Correlation function \( \gamma(x) \) for meridional slice of a 2D SAXS pattern

Double network model by Miyasaka
T. Miyazaki, S. Sakurai et al., Polymer, 46 7436 (2005)
Absorption of Iodine into Drawn PVA Films in KI/I₂ Solution

T. Miyazaki, Nitto Denko Co.

WAXS patterns for PVA films,
(a) drawn in Pure water, (b) drawn in KI/I₂ solution

Azimuthally integrated intensity profile for a 2D WAXS pattern

Crystallinity index vs. draw ratio

T. Miyazaki, S. Sakurai et al., Polymer, 46 7436 (2005)
Observing nanostructure of polarizer films with SAXS/WAXS (3)

Crystalline region
Amorphous region

\[ d_{\text{max}} \quad \text{Lamellar thickness} \]

\[ d_{\text{min}} \quad \text{amorphous thickness} \]


1. The increase in \( d_{\text{min}} \) with increasing DR up to 4 in KI/I\(_2\) solution suggests the PVA-iodine complexes are formed in amorphous regions in PVA films.

2. The increase in crystalline thickness for DR>4 drawn in KI/I\(_2\) solution should be attributed to the stress-induced crystallization.

3. Further, simultaneous SAXS/WAXS measurements of PVA films during drawing in water clarified the mechanism of strain-induced crystallization taking place in the interfibrillar extended amorphous regions, and proposed a new model for nanostructure of drawn PVA films.

\[ \text{(a) drawn in Pure water, (b) drawn in KI/I}^2\text{ solution} \]

A new model by Miyazaki et al. (Macromol. 40, 8277 (2007))

T. Miyazaki, S. Sakurai et al., Polymer, 46 7436 (2005); Macromolecules, 39, 2921 (2006); 40, 8277 (2007)
LC aligning power of the film is controlled by rubbing the film surface.
Relationship between LC Aligning Power and Nanosurface Structure

What happens by rubbing the surface?

**GIXD Measurements**
- X-ray energy: 10keV
- Incident angle ($\alpha_i$):
  - 0.12° (surface sensitive)
  - 0.16° (bulk sensitive)
- Beamline: SPring8 BL19B2

GIXD (grazing incidence X-ray diffraction) is sensitive to scattering from sample surface (~8nm)

<table>
<thead>
<tr>
<th>Samples</th>
<th>LC align. power</th>
<th>Supposed crystallinity</th>
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<tbody>
<tr>
<td>SP-PI1</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>SP-PI2</td>
<td>△</td>
<td>△</td>
</tr>
<tr>
<td>SP-PI3</td>
<td>◎</td>
<td>○</td>
</tr>
<tr>
<td>SP-PI4</td>
<td>×</td>
<td>×</td>
</tr>
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What is the origin of LC aligning power?
GIXD Measurements of LC Aligning Polyimide Films

A film with good LC align. Power

A film with poor LC align. Power

LC aligning power depends on surface crystallinity.

Summary 1: Reasons of Good Results in Industrial Utilization of SPring-8

1. Stable SR beams of a world top level are constantly supplied.
   - Ultra-bright, Highly directional, Top-up operation.

2. R & D people in industries have been trying to find out new nano-scale techniques for solving their problems.
   - Action (giving information) of people in Analytical & Evaluation Technology Division to people in R & D Division is important.

3. Technical staffs in JASRI Industrial Application Division have been supporting industrial users in sample preparation, measurements at SPring-8, and sometimes also in analyzing the data.
   - Financial support from Government on number of staffs for promoting industrial uses. (Trial Use Program, Strategic Activation Program)
   - A change in professional morals of BL technical staffs has been needed.

4. The quality of research has been improved by industry-academia collaboration.
   - Industry: consideration based on basic theories, Use of new techniques, Improvement in data analyses.
   - Academia: Finding new basic subjects from the discussion with industry, Advances of technology in SR measurements.
Summary 2: Challenges in Industrial Utilization at SPring-8 --- Towards More Advanced Quality of utilization

© Trails of wider utilization in polymer fields

- **XD, SAXS**
  - Crystalline polymers
  - Fibers

- **XD + SAXS, GI, MB, Time-resolved, Imaging**
  - Crystalline polymers, Fibers → Dynamics
  - Nanosurface & buried interface in Polymer films, Organic devices.
  - Higher-order structure (phase-separated polymers, composites)
  - Gels, Micelles, cell membranes

© Towards not only wider utilization, but also more advanced quality of utilization.

1. Good subjects are brought about by active participation of R & D people.
2. Closer collaboration between industry and academia(*) and closer international collaboration between SR facilities in the world.
3. Bring up young scientists in SR fields.

*e.g. Industry-Academia Consortium for Advanced Softmaterial Research (FSBL) consisting of 19 chemical corporate groups including academic members. (BL03XU)