Gyeongju

The City for
Conventions
VACTRON

- **Mirror Bender System**

More than sixty mirror bender systems have been working well in PAL(Korea), SSRF(China), BSRF(China) and RRCAT(India).

- **Double Crystal Monochromator**

Fifteen systems have been installed in PAL and RRCAT.

- **Double Multilayer Monochromator**

- **Plane Grating Monochromator**
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Xenocs is proud to introduce you to their latest solutions for characterizing nanostructures. Using Small and Wide Angle X-ray Scattering techniques, the Xenocs solution combines unique ergonomics, ease-of-use and unparalleled performance.

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Xenocs
Exploring the very small

한국나노MSE
16950 경기도 용인시 기흥구 풍덕중앙로 120, 1층 131호 (업덕동, U-TOWER)
Tel.: 070-8822-1203, Fax: 031-212-1203
Mobile: 010-2270-1202, E-mail: hakjun.lee@knmse.co.kr
Global No.1
SKCKOLONPI

SKC코로농피는 국내 유일의 플라마이드 필름 생산 회사입니다. 모기업인 SKC와 코로농의 축적된 기술력과 원가 경쟁력의 바탕으로 국내를 넘어 세계 시장점유율 1위를 차지하고 있습니다.

POLYIMIDE FILM

열적특성
절대온도에 기반한 재고온도의 환경과 400℃ 수준에서의 고온에서도 사용이 가능한 플라스틱으로, 전방산업의 기공 조건 고도화를 지원합니다.

차수 안정성
온도 변화나 물리적 자극과 같은 외부 환경의 영향에도 불구하고 본래의 차수와 특성을 최대한 유지함으로써 적득 제일의 내구성 및 신뢰성을 확보할 수 있습니다.

유연성
PI Film의 우수한 유연성은 높은 수준의 차수 안정성과 더불어 빈번한 변형이 불가능한 온도영역에서의 적응성을 가능하게 하고, 좋은 공간의 활용도를 높여줍니다.

전기적 특성
PI Film이 가진 높은 수준의 절연성과 과전류의 적절한 부피 에너지 전류 순환을 방지함으로써 전기, 전자 기기의 안정성을 확보가 가능하게 합니다.

PI FILM APPLICATION

Cellphone · IT Devices
PI 필름의 우수한 기계적, 열적 특성으로 전자기기의 FPCB소재 및 방열시트의 소재로 적용됩니다.

Display
디스플레이 기기의 구동과 제어를 위한 Drive IC 및 COF(Chip on Film) 소재로 적용됩니다.

Aerospace
최초 우주항공 동체설계 용도로 개발된 PI 필름은 우주항공 이외에도 고전압 기기의 전기 절연, 자동차 소재 등 우리 생활 전반에 널리 사용되고 있습니다.
MAXIMIZE UTILIZATION OF YOUR XRD SYSTEM

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The 3rd generation multipurpose diffractometer now with MultiCore Optics

- Grazing incidence XRD for surface analysis and depth profiling
- Phase identification and quantification to determine composition or monitor purity
- Small-angle X-ray scattering for particle size analysis
- X-ray reflectometry to determine thin film thickness and roughness
- Pole figures for texture analysis
- Residual stress for component and failure analysis
- Transmission XRD for characterization of organic materials
- 2D XRD for microstructural analysis

www.malvernpanalytical.com/empyrean
Scientific Programs (2018 SRPS & 2018 GISAS)

Date/
Time  Sep. 4 (Tuesday)

SRPS-1 (TUE) / Room 201  SRPS-2 (TUE) / Room 202  SRPS-3 (TUE) / Room 203  GISAS-1 (TUE) / Room 204

9:00
Registration (HICO)

9:20
Opening Ceremony (Room 201 & 202)

9:50
Break

10:00
(Chair: Liangbin Li)
Atsushi Takahara
"Synchrotron X-ray Scattering of Polymeric Solids under Various Mechanical Deformation States"

(Chair: Sono Sasaki)
Tiberio.A. Ezquerra
"Nanostructure and Function of Fullerene and Polymer/Fullerene Graftings as Revealed by Grazing Incidence X-ray Scattering and Atomic Force Microscopy"

(Chair: Christine M. Papadakis)
Stephan V. Roth
"Interface formation during rapid coating processes"

10:40
(Chair: Almut Stribeck)
Xuechen Jiao
"In-situ investigation of crystallite structure evolution and its associated anisotropic thermal expansion behaviors in semiconducting polymer thin films"

(Chair: Tiberio A. Ezquerra)
Guoming Liu
"Stress Induced Crystal Transition in Polymers Studied by In-situ Synchrotron X-ray Scattering"

(Chair: Giuseppe Portale)
Michael F Toney
"Morphology in Organic Photovoltaics as Probed by Grazing Incidence X-ray Scattering"

(Chair: Ronald Pandolfi)
Pallavi Pandit
"Comparative in-situ studies of Au sputter growth on homo and di-block co-polymers"

11:20
Lunch

13:30
(Chair: Atsushi Takahara)
Shinji Ando
"Temperature- and Pressure-Induced Changes in Crystalline Structures of Polyimides Analyzed by Synchrotron Wide-Angle X-ray Diffraction"

(Chair: Tiberio Ezquerra)
Ya-Sen Sun
"Effects of Cross-linking density of UV Irradiated Polyethylene Chains on Domain Orientation and Spatial Order of Block Copolymer Nanodomains."

(Chair: Giuseppe Portale)
Wim Bras
"When radiation plays tricks with the sample"

(Chair: Ronald Pandolfi)
Christine M. Papadakis
"Morphologies and Solvent Distribution During Solvent Vapor Annealing of Block Copolymer Thin Films. In situ, Real-time GISAXS Investigations"

14:10
(Chair: Almut Stribeck)
Sono Sasaki
"Preferred Lamellar Orientation in Thin Films of Buta-Block Poly(3-acryloyloxypropionic acid-3-hydroxyhexanoate) Investigated by GISAXS Measurements Using Synchrotron Radiation"

(Chair: Liangbin Li)
J. M. Sungil Park
"Status and Challenges of the Neutron Scattering Facility at HANARO after the Long Shutdown since July 2014"

(Chair: Max Wolff)
Tomyosyu Hirai
"Preparation of novel poly(methyl methacrylate) brush with well-controlled stereoregularity and characterization of its ordered nanostructure"

14:50
(Chair: Almut Stribeck)
Myung Chul Choi
"Nanoscale Assembly Architectures of Tubulin Tubules"

(Chair: Ya-Sen Sun)
Guillaume Fleury
"Nanostructured thin films from block copolymer self-assembly: exquisite symmetries from macromolecular design"

(Chair: Max Wolff)
Max Wolff
"Grazing incidence small angle neutron scattering: The solid-liquid boundary condition in hydrodynamics"

(Chair: Ronald Pandolfi)
Yu-Cheng Chiu
"Intrinsically Stretchable and Healable Semiconductor Polymer for Skin-Inspired Wearable Transistors"

15:30
Break

15:50
(Chair: Almut Strubeck)
Soo-Young Park
"Control of the micellar structures of the block copolymers using solvent selectivity"

(Chair: Ya-Sen Sun)
Eva M. Herzig
"Time-resolved GISAXS/GIXS for control and characterization of structure formation in printed thin films"

(Chair: Max Wolff)
Sung-Min Choi
"Hierarchically Self-Assembled Binary Nanoparticle Superlattices"

(Chair: Stephan V. Roth)
Ronald Pandolfi
"Xi-cam: Flexible High Throughput Data Processing for GISAXS"

16:30
(Chair: Detlev Beeker)
Dae Sung Chung
"Surfactant Engineering to Enhance Crystalline Orientation of Water-Borne Polymer Semiconductors"

(Chair: Giuseppe Portale)
Giuseppe Portale
"SAXS/WAXS/RAMAN/DSC: four techniques in one. Application to the PVDF-co-TiF4 crystalization"

(Chair: Giuseppe Portale)
Zhang Jiang
"Recent Advancement in Grazing-incidence X-ray Scattering for Three-dimensional Structures in Thin Films and Buited Nanostuctures"

16:50
(Chair: Hyungju Ahn)
Dae Sung Chung
"Surfactant Engineering to Enhance Crystalline Orientation of Water-Borne Polymer Semiconductors"

(Chair: Max Wolff)
Peng Zhang
"Long-range ordered crystalline structure in micromolded diblock copolymer ultrathin films via correlated crystal growth at surface and beneath layers"

(Chair: Ronald Pandolfi)
Gennady Pospelov
"Experiment planning, simulation and fitting of GISAXS data using BornAgain framework"

17:10
(Chair: Wonchulm Rungswang)
Yongjin Kim
"Morphological Structure Details and Electrical Memory Characteristics of Poly(3-hexylthiophene) in Thin Films"

(Chair: Marc Gensch)
Marc Gensch
"Optoelectronic properties of metal clusters on polymer thin films during sputter deposition"

17:50
Break

18:00
Poster-1 (TUE)
(SR.P1 & GI.P1)
<table>
<thead>
<tr>
<th>Time</th>
<th>SRPS-4 (WED) / Room 201</th>
<th>SRPS-5 (WED) / Room 202</th>
<th>SRPS-6 (WED) / Room 203</th>
<th>GISAS-2 (WED) / Room 204</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00</td>
<td>(Chair: Shinichi Sakurai) &quot;Unconventional Micromdomains of Block Copolymers&quot; (Chair: Hyunjung Kim) &quot;Principle Investigation of Coherent X-ray Scattering&quot; (Chair: Xiaobing Zuo) &quot;Biological SAXS: advances and perspectives&quot; (Chair: Daniel Söderberg) &quot;Next generation solar cells studied with GISAS&quot;</td>
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<td>10:20</td>
<td>Break</td>
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<tr>
<td>10:40</td>
<td>(Chair: Mari-Cruz Garcia-Gutierrez) Shinichi Sakurai &quot;Ordering Cylindrical Microdomains in an SEBS Triblock Copolymer / Disent Stanice by Application of Temperature Gradient&quot; (Chair: Moonhor Ree) Jaehyun Park &quot;Senal Femtosecond Crystallography Program at the PAL-XFEL Facility&quot; (Chair: Kyoung Taek Kim) Xiaobing Zuo &quot;Structure and Dynamics of Non-coding RNAs by Solution Small Angle X-ray Scattering&quot; (Chair: Daniel Söderberg) &quot;Initial investigations of cellulose thin films using GISAS&quot;</td>
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<tr>
<td>11:40</td>
<td>Break</td>
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<tr>
<td>12:00</td>
<td>Lunch</td>
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<tr>
<td>13:30</td>
<td>(Chair: Kyoung Taek Kim) Veachol Rho &quot;Temperature-dependent structural behavior of polymers containing adenine moieties by simultaneous XRD-DSC measurement&quot; Young Yong Kim &quot;3D Reconstruction of Pt nanoparticle in Operando Condition using Coherent X-ray Diffraction Imaging&quot; (Chair: Mitsunori Shibayama) &quot;Machine Learning for Scattering on Polymers&quot; (Chair: Sigrid Bernstorff) &quot;Critical-Dimension Grazing incidence small angle x-ray scattering&quot;</td>
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<tr>
<td>14:10</td>
<td>Myungeneun Seo &quot;Length Scale Control in Polymerization induced Morphotpe Separation&quot; Hyunjung Kim &quot;Structural Dynamics Probed with Ultrastart Coherent X-Rays from X-Ray Free Electron Laser&quot; Fenggang Bian &quot;Development of Small Angle X-ray Scattering at Shanghai Synchrotron Radiation Facility&quot; Byoung-Ki Cho &quot;Complex Columnar Assemblies and of 1,2,3-Triazole-based Liquid Crystals&quot;</td>
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<tr>
<td>14:50</td>
<td>Toshifumi Satoh &quot;Phase-separated structure of oligosaccharide-based block copolymer&quot; (Chair: Calvin J. Brett) Aurora Nogales &quot;X-ray Photon Correlation Spectroscopy for the study of polymer dynamics&quot; Siriwat Somsanunon &quot;Synchrotron SAXS activities at SRLI to promote industrial and ASEAN user community&quot; (Chair: Marcus Hildebrandt) &quot;Bouguer's-Correlation of PMMA Polymer Brushes - Conformal Brushes&quot;</td>
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<td>15:30</td>
<td>Break</td>
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<tr>
<td>15:50</td>
<td>(Chair: Toshifumi Satoh) Du Yeol Ryu &quot;Directed Self-assembly of High-Molecular Weight Block Copolymers: Lamellar and Cuspidal Structures&quot; (Chair: Alexander Hexemer) Mitsuhiro Shibayama &quot;ID-Pair Distribution Analysis of Uniaxially Deformed Nanocomposite Gea&quot; (Chair: Byoung-Ki Cho) David Babonneau &quot;Real-time investigations of photodynamic Ag/Fe2O3 nanocomposite thin films under UV and visible laser irradiation&quot;</td>
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<tr>
<td>16:30</td>
<td>Kyung Taek Kim &quot;Synthesis of Single Cubic Nanotexts having Large Open-space Lattices Templated by Polymer Cubosomes&quot; (Chair: Calvin J. Brett) Hyotcherl Ihee &quot;Watching reacting molecules by time-resolved X-ray diffraction at synchrotron and XFELs&quot; Jinhwan Yoon &quot;Large Thermal Hysteresis for Volume Phase Transition of Hydrogels Achieved by Hydrophobic Junction of methyl Cellulose&quot; Sigrid Bernstorff &quot;GISAS analysis of three-dimensional Ge nanowire networks&quot;</td>
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<td>17:10</td>
<td>(Chair: Toshifumi Satoh) So Yeon Kim &quot;Microstructure of GO colloids in Polymer Solutions with Small Angle Scatterings&quot; Cheng Wang &quot;Multimodal Resonant X-ray Scattering for Polymer Materials&quot; (Chair: Matthias Schwartzkopf) &quot;Real-Time Monitoring of Morphology and Optical Properties during Sputter Deposition for Tailoring Metal-Polymer Interfaces&quot;</td>
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<td>17:50</td>
<td>Break</td>
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<tr>
<td>18:00</td>
<td>Poster-2 (WED) (SR.P2 &amp; GLP2)</td>
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<td>20:00</td>
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Scientific Programs (2018 SRPS & 2018 GISAS)
<table>
<thead>
<tr>
<th>Date/Time</th>
<th>SRPS-7 (THU) / Room 201</th>
<th>SRPS-8 (THU) / Room 202</th>
<th>GISAS-3 (THU) / Room 203</th>
<th>GISAS-4 (THU) / Room 204</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00</td>
<td>(Chair: Yuka Ikemoto)</td>
<td>(Chair: Kazuhiko Yamamoto)</td>
<td>(Chair: Kazuhiko Omote)</td>
<td>(Chair: Byoungdu Lee)</td>
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<tr>
<td></td>
<td>Paul Dumas</td>
<td>&quot;Synchrotron Infrared spectroscopy: Opportunities and challenges for polymer study&quot;</td>
<td>Ralf Röhlsberger</td>
<td>&quot;Revealing complex magnetic order via nuclear resonant GISAXS&quot;</td>
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<td>Development of Sandwiched Measurements System (THU)</td>
<td>Alessandro Coati</td>
<td>&quot;Supported nanoparticles for catalysis: operando studies of their structural and morphological evolution during reactions by grazing incidence X-ray scattering&quot;</td>
</tr>
<tr>
<td>9:40</td>
<td>Zee Hwan Kim</td>
<td>&quot;Nano-plasmonics: from single-molecule chemistry to infrared nanoscopy&quot;</td>
<td>Mustafah Dallal</td>
<td>&quot;GISAS Study of Nanoporous Block Copolymer Thin Films&quot;</td>
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<tr>
<td>10:00</td>
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<td>Naoko Kawai</td>
<td>&quot;Visualizing the Spatial Distribution of the Nanostructures in Thin Films Using GISAXS-CT&quot;</td>
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<tr>
<td>10:40</td>
<td>(Chair: Paul Dumas)</td>
<td>(Chair: Hyun Hoon Song)</td>
<td>(Chair: Yunlan Su)</td>
<td>(Chair: Hideaki Yokoyama)</td>
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<tr>
<td></td>
<td>Yuka Ikemoto</td>
<td>&quot;Property and Utilization Research of Infrared Synchrotron Radiation&quot;</td>
<td>Kazuhiko Omote (Rigaku)</td>
<td>&quot;Model Tungsten Oxide Nanostuctures for Battery Applications: Structure Characterization during Synthesis and in operando studies of their structural and morphological evolution during reactions by grazing incidence X-ray scattering&quot;</td>
</tr>
<tr>
<td>11:20</td>
<td>Jitraporn (Pimm) Vongsivut</td>
<td>(Chair: Georges Hadziioannou)</td>
<td>Scott Barton (Xenocs)</td>
<td>&quot;The spin structure of highly ordered arrangements of magnetic nanoparticles&quot;</td>
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<tr>
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<td>&quot;High-Resolution Macro-ATR-FTIR Microspectroscopic Technique at Australian Synchrotron IR Beamline and Its Applications for Polymer and Composite Materials&quot;</td>
<td>&quot;Interfacial Effect on Crystallization Behavior of Polymer Nanocomposites&quot;</td>
<td>&quot;Tens. Advantages and Examples of GISAXS in the Laboratory&quot;</td>
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<td>12:00</td>
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<td>12:30</td>
<td>(Chair: Yuya Shihohara)</td>
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<td>(Chair: Peng Zhang)</td>
<td>Giuseppe Portale</td>
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<td>Changwooo Do</td>
<td>&quot;Structural analysis using scattering contrast from SAXS and SANS&quot;</td>
<td>&quot;Mechanism of Block-copolymer self-assembly during spin coating revealed by ultrafast in-situ GISAXS&quot;</td>
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<tr>
<td>14:10</td>
<td>Mitsuhiro Shibayama</td>
<td>(Chair: Kohji Tashiro)</td>
<td>(Chair: Hyun Hoon Song)</td>
<td>Giuseppe Portale</td>
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<td>&quot;SANS Study on Thermoreversible Physical Gels Crosslinked with DNA&quot;</td>
<td>&quot;Effect of Hydration on Corona Layer on Structural Change of Thermo-responsive Polymer Micelles&quot;</td>
<td>&quot;Self-assembly of Calix[4]arene-Based Amphiphiles Bearing Polymethylene Glycol: Another Example of &quot;Platonic Micelles&quot;</td>
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<td>14:50</td>
<td>Jaseung Koo</td>
<td>(Chair: Kohei Tashiro)</td>
<td>(Chair: Kohei Tashiro)</td>
<td>Giuseppe Portale</td>
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<td>&quot;Structural &amp; Dynamic Studies of Confined Polymer Melts near Graphene Oxide Surface Using Neutron Reflectivity&quot;</td>
<td>&quot;Structural Analysis of the Materials and Applications of Neutron Reflectivity&quot;</td>
<td>&quot;Surface-Directed Molecular Assembly of Organic Semiconductor-Based Devices: Insights from X-ray Scattering Analyses&quot;</td>
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<td>15:30</td>
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<td>(Chair: Kohei Tashiro)</td>
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<td>Giuseppe Portale</td>
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<tr>
<td>16:00</td>
<td>Jehan Kim</td>
<td>(Chair: Kohei Tashiro)</td>
<td>(Chair: Peng Zhang)</td>
<td>Giuseppe Portale</td>
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<td>Instrument development to perform In-Situ GISAXS Experiments on 3C SAXS/Brillouin &quot;</td>
<td>&quot;Self-assembly of Calix[4]arene-Based Amphiphiles Bearing Polymethylene Glycol: Another Example of &quot;Platonic Micelles&quot;</td>
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<td>&quot;Microstructural Investigation of butt-arrangements of magnetic nanoparticles&quot;</td>
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<td>16:30</td>
<td>Pham Thi Ngoc Diep</td>
<td>(Chair: Rohit Tashiro)</td>
<td>(Chair: Peng Zhang)</td>
<td>Giuseppe Portale</td>
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<td>&quot;Effects of a Liquid-type Nucleation Agent on the Morphology and Nanostructural Characterization of Poly(methyl Lactic Acid) as Revealed by synchrotron SAXS/WAXS&quot;</td>
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<td>17:10</td>
<td>Rintaro Takahashi</td>
<td>(Chair: Rohit Tashiro)</td>
<td>(Chair: Peng Zhang)</td>
<td>Giuseppe Portale</td>
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<td>Giuseppe Portale</td>
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<td>18:00</td>
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<td>Giuseppe Portale</td>
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</tbody>
</table>

Break

Banquet (Hilton Hotel) & Night Tour (Donggung Palace and Wolji Pond, Cheomseongdae Observatory)
<table>
<thead>
<tr>
<th>Time</th>
<th>SRPS-9 (FRI)/ Room 201</th>
<th>GISAS-5 (FRI) / Room 202</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00</td>
<td>(Chair: Jinyou Lin)</td>
<td>(Chair: Katsuhiro Yamamoto)</td>
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<tr>
<td></td>
<td>Chin Hua Chia</td>
<td>Basab Chattopadhyay</td>
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<tr>
<td></td>
<td>&quot;Silver Nanoprisms Nanocellulose Film as Surfaced-enhanced Raman Scattering Substrate&quot;</td>
<td>&quot;Thin film crystallization: role of substrate and temperature gradient&quot;</td>
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<tr>
<td>9:40</td>
<td>Myungwoong Kim</td>
<td>Keiji Tanaka</td>
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<td>(Chair: Chin Hua Chia)</td>
<td>(Chair: Basab Chattopadhyay)</td>
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<tr>
<td></td>
<td>Jinyou Lin</td>
<td>Katsuhiro Yamamoto</td>
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<tr>
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<td>&quot;Design, Synthesis, and Characterization of Block Copolymers with a High Interaction Parameter&quot;</td>
<td>&quot;Analysis of depth-dependent structures in polymer thin films by GIXAS utilizing tender X-ray&quot;</td>
</tr>
<tr>
<td>10:40</td>
<td>(Chair: Chin Hua Chia)</td>
<td>Katsuhiro Yamamoto</td>
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<td>Jinyou Lin</td>
<td>(Chair: Basab Chattopadhyay)</td>
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<td>&quot;In-situ characterization of SAXS/WAXS in polymer processing&quot;</td>
<td>Katsuhiro Yamamoto</td>
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<tr>
<td></td>
<td>Myungwoong Kim</td>
<td>(Chair: Basab Chattopadhyay)</td>
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Synchrotron X-ray Scattering of Polymeric Solids under Various Mechanical Deformation States

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Synchrotron radiation wide-angle X-ray diffraction (WAXD)/ small-angle X-ray scattering (SAXS) is a powerful tool to characterize hierarchical structure of polymeric materials under deformation. We designed in situ synchrotron WAXD/SAXS system under various mechanical deformation modes. In this presentation, our recent studies on applications of SR-WAXD /SAXS to characterize deformation behavior of polymer soft colloidal crystal nanocomposite, biaxial and uniaxial tensile behavior of poly(styrene-b-ethylenebutene-b-styrene) (SEBS) elastomer, deformation behaviour of Nylon 12 under bulge deformation were presented.

A molded film of polymer-grafted nanoparticles (SPNP), consisting of a spherical silica core and densely-grafted polymer chains bearing hydrogen-bonding side-groups capable of physically crosslinking, was investigated by in-situ ultra-SAXS (USAXS) measurement during uniaxial stretching process. Static USAXS revealed that the molded SPNP formed a highly oriented twinned face-center-cubic (fcc) lattice structure and a [111] plane was aligned nearly parallel to the film surface at initial state. Structural analysis of in-situ USAXS using a model of uniaxial deformation induced by rearrangements of the nanoparticles revealed that the fcc lattice was distorted in the stretching direction being proportional to the macroscopic strain until the strain reached 35% and subsequently changed into the other fcc lattice with different orientations. The lattice distortion and structural transition behavior corresponded well to the elastic and plastic deformation regimes, respectively, observed in the stress-strain curve.

The microdomain structure of SEBS film was investigated during biaxial and uniaxial elongation processes at various rates using in situ small-angle X-ray scattering (SAXS) measurement. Interdomain spacing of the SEBS film increased linearly with an increase in film strain. The strain evaluated from domain spacing exhibited linear relationship with film strain. The slope of the relation between the apparent film strain vs the strain obtained by interdomain spacing decreased with an increase in elongation rate.

Bulge testing equipment for in situ WAXD measurements is designed and used to study the relationship between the molecular aggregation states and the mechanical properties of a crystalline nylon 12 (Ny12) film during bulge testing. Isothermally crystallized and quenched Ny12 films exhibited stress–strain curves similar to those obtained by conventional uniaxial elongation. In situ WAXD measurements during bulge testing revealed that the lattice extension of the crystallites is clearly dependent on crystallinity. Crystallites in the isothermally crystallized film show higher elastic properties than those in the quenched one. The results of the molecular aggregation structure, including the crystal structure and the amorphous chain surrounding the crystallites, of the films during bulge deformation obtained in this study are useful for designing toughened polymer films.

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Thermoplastic polyurethanes (TPUs) are random block copolymer materials whose properties can be adapted to an extremely wide range of applications. This is the consequence of the fact that the materials consist of 3 chemical components which are chosen from extensive classes. Essential for the material properties of TPUs is a morphology consisting of hard domains in a soft matrix phase. Monitoring such systems by SAXS and WAXS serves to gain fundamental understanding of the relationship between the chemical structure and the properties of the material.

First, full analysis of SAXS data from a set of various TPUs of commercial relevance [1] is reported. The morphology evolution under load is resolved. Corresponding mechanisms are identified and quantified. The strengths of these mechanisms relate both to the chemical formulation and to the material properties. The elucidation of these relationships serves to predict the properties of polyurethanes. Chemical structure controls the ability to generate strain-induced hard domains. A hard domain either serves as a filler or as a crosslink. Chemical composition controls the strength of filler-to-crosslink conversion (cf. Figure 1).

Second, qualitative results of monitoring TPU melting and solidification by SAXS and WAXS are presented and discussed. The morphology evolution varies as a function of thermal history, chemical composition and nucleating agents. Figure 2 shows examples. In WAXS several materials exhibit breakdown and recovery of the intensity $I_{\text{WAXS}}(s)$, $0<s<8\text{nm}^{-1}$ after in the melting branch the SAXS long period has vanished. Such inelastic processes are faint with the best nucleating agent. The presented data from ALBA are normalized and calibrated to absolute intensity. In the figure the white level is put to the highest intensity from the heating branch. The development of related evaluation software under Python is reported.

Reference

Stress Induced Crystal Transition in Polymers Studied by In-situ Synchrotron X-ray Scattering

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The plastic deformation of semi-crystalline polymers is a long studied topic, which is crucial for establishing structure/property relationship of polymer materials. By meaning of synchrotron X-ray scattering, it is possible to study the deformation process of polymers in-situ. For some polymorphic polymers, stress can trigger transitions among different crystal modifications. [1] In this talk, stress-induced reversible crystal transition in poly(butylene succinate) was systematically investigated. A “lamellar thickening” phenomenon was observed during stretching, which was shown to mainly originated from the reversible crystal transition. [2] This mechanism was shown to be also valid in poly(ethylene succinate).[3] The critical stress for the crystal transition was measured in a series of PBS-based crystalline-amorphous multi-block copolymers. Interestingly, these PBS copolymers exhibited identical critical stress independent of amorphous blocks. The universal critical stress for crystal transition was interpreted through a single-microfibril-stretching mechanism. [4]

References
Temperature- and Pressure-Induced Changes in Crystalline Structures of Polyimides Analyzed by Synchrotron Wide-Angle X-ray Diffraction

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Variations in the crystalline structures of polyimides (PIs, Fig. a) were analyzed under variable temperature (80°C–300°C) [1–3] or variable pressures (1 atm–8 GPa) [4–7] using synchrotron wide-angle X-ray diffraction (WAXD). Firstly, coefficients of thermal linear and volumetric expansion (CTE, CVE) of crystal lattice for 13 kinds of fully aromatic crystalline polyimides (PIs) were evaluated from the temperature dependence of lattice parameters measured from VT WAXD patterns (Fig. b), and the effects of chemical structure on CTE and CVE are discussed. The smallest CVE (+116 ppm/K) was observed for PMDA-ODA containing an ether linkage (Fig. c) with an extraordinarily negative CTE along the a-axis (~44 ppm/K). The values and anisotropy of the CTEs strongly depended on the crystalline structure, whereas the CVEs were negatively correlated with the weight density, regardless of the PI type (Fig. d). Secondly, variations in the crystalline structures of PIs were analyzed under elevated pressures up to 8 GPa using a diamond anvil cell (DAC). The compressibilities (c) along the polymer chain axis (c-axis) of rigid-rod PIs increased with an increase in the number of phenyl rings in the diamine moiety, which could be due to a pressure-induced deformation of the periodic structure associated with changes in bond angles and dihedral angles. In contrast, PMDA/ODA showed an increase in the lattice parameter along the c-axis up to 0.8 GPa (Fig. e), which could be due to a widening of the ether bond angle. Moreover, PMDA/PPD showed isotropic compression along interchain directions, whereas PMDA/DATP derived from 4,4'-p-terphenylene diamine and PMDA/ODA showed highly anisotropic compression along the cofacial stacking direction, which resulted in the larger volumetric shrinkages of the latter PIs. Consequently, the behaviors of thermal expansion and linear compression of the crystalline lattices of PIs are mutually correlated, and these knowledge can be used to develop novel PIs for electronic and photonic applications, of which the CTE, CVE, compressibility, and their anostropies are precisely controlled.

References:
Studying structural evolutions of polymer under harsh conditions with in-situ synchrotron radiation techniques

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With the development of synchrotron radiation technique, synchrotron technique has been a very important tool in polymer physics and processing of high performance polymer. In general, the high performance is processed or used under harsh conditions, such as intense flow of polymer film during processing, extension of high strength fiber under high vapor pressure, application of rubber under low temperature condition. The above issues refer to flow-induced crystallization, phase separation and other structural evolutions under far from equilibrium condition. In order to study the multi-scale structure evolutions under harsh conditions, we developed series experimental setups, which can combine with synchrotron radiation X-ray scattering techniques for in-situ measurements. Combining the high time resolution of synchrotron radiation X-ray scattering techniques and the setups we developed, we have studied extension induced structure evolutions of polyurethane film, polyacrylonitrile fiber under vapor pressure condition and polydimethylsiloxane rubber under low temperature, which demonstrate the advantages of synchrotron radiation techniques on the studying of polymer physics and processing under harsh conditions.

Key Words: Synchrotron radiation, harsh condition, polymer physics and processing

References
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Nanoscale Assembly Architectures of Tubulin Tubules

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Tubulins are protein building blocks assembling into hollow cylindrical cytoskeletal microtubules (MTs). A variety of cellular functions of MTs such as cell division, intracellular trafficking and maintaining cell shape are attributed to the structural transitions, i.e. the growth and catastrophe of MTs. We present our recent findings on the assembly structures of tubulin tubules in the presence of polycations (MAP Tau and Polylsines) by small angle X-ray/Neutron scattering and electron microscopy experiments. Supported by NRF-2017M2A2A6A01071190, and NRF-2018R1A2B3001690.
Control of the micellar structures of the block copolymers using solvent selectivity

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The effects of the solvent selectivity on the micellar and ordered structures of diblock copolymer were studied. The diblock copolymers studied were PS-b-P4VP, PS-b-PI, and PS-b-SGLCP (side group liquid crystal polymer). The solvent selectivity was controlled by solvent mixtures for PS-b-P4VP, PS-b-PI as well as heating of nematic liquid crystal (5cb) for PS-b-SGLCP. The stable micelle (in the neutral solvent) was studied for PS-b-PI where PI in the core was cross-linked. Solvent mixtures covered a wide range of solvent selectivity from one-block selective, to neutral, and to the-other-block selective and the nematic LC can undergo a first-order transition at the solution’s isotropization point, TNI unlike conventional solvents. We could control a variety of meso-structures and the liquid crystal properties at the step-wise. We believe that these results can be applied to photonic crystals, self-assembled nano-patterning, and functional nanoparticles in which the structural control is most important.
GISAXS on a Multipurpose Laboratory X-ray Diffractometer

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With the advances in thin film engineering, conventional coplanar measurements such as X-ray reflectivity and X-ray diffraction can no longer satisfy the need for comprehensive understanding of materials surface nanostructures. This has motivated a large number of GISAXS studies as well as improvement in instrumentation. GISAXS poses considerable challenges when scaling the method to fit a multipurpose laboratory instrument, including the requirement for good angular resolution at short scattering radius, the reduction of scatter from the direct beam and the observation of low intensity signals. The recent availability of small size pixel (55 μm) photon counting PIXcel\textsuperscript{3D} detectors with very low noise characteristics has enabled the implementation of 2D imaging GISAXS for a standard laboratory diffractometer with a radius of 240 mm. Additionally, when the structural information obtained from the GISAXS data analysis is combined with X-Ray diffraction and reflectometry results, they can provide comprehensive understanding of the engineered nano-objects.

In this work, we present GISAXS results obtained from a series of samples measured on a standard laboratory diffractometer (Empyrean from Malvern Panalytical). Examples include arrays of quantum dots and quantum wires, multilayer thin films as well as nanoparticles and nanoporous surfaces. A comparison of GISAXS results obtained from a laboratory diffractometer and synchrotron beamline will also be presented.

Figure 1: GISAXS images obtained from Empyrean diffractometer using PIXcel\textsuperscript{3D} detector

References
Industrial Applications of Small angle X-ray Scattering Beamline at PAL

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The Small-angle x-ray scattering (SAXS) beamlines of Pohang Light Source-II (PLS-II) at Pohang Accelerator Laboratory (PAL) have offered great opportunities to study the nanostructure and dynamic process of various materials, including polymers, nanoparticles, liquid crystals, and biomolecules.

Recently, the industrial use of SAXS beamlines have rapidly increase, since SAXS can easily offer variety structural information of industrial samples with non-destructive, convenient measuring process and the availability of various in-situ measuring system.

In this presentation, we will describe experimental set-up, including sample stage, data collection and in-situ measuring systems, optimized for the industrial samples. Additionally, we will show the reference results of experiments on industrial samples of fiber, lithium ion battery, rubber-inorganic complex and steel with ex-situ and in-situ measuring system.
Exploring In-situ Synchrotron Investigation for Industrial use

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Synchrotron radiation (SR) has been well known as one of the most intense x-ray source which has been used for in-situ experiments with the environment changes, such as temperature and stress. Here, some examples of in-situ investigation via SR source are demonstrated to fundamentally understand the structure-property relation for the aim of product development in the polyolefins industry. Firstly, the in-situ tensile with small- (SAXS) and wide-angle (WAXS) X-ray scattering measurements trace the structural change of impact resistance polypropylene copolymer (IPC). The impact of the crystal orientation that is related to the elongation properties of the IPC are correlated to the fragmentation and elongation of the lamellar grain. Secondly, the in-situ temperature jumper with SAXS/WAXS was used to investigate the crystallization kinetic and crystal morphology under isothermal crystallization of polypropylene (PP). The effect of molecular weight and tacticity are investigated, and moreover, the tapering of the lamellar width is found. Finally, the in-situ temperature ramp with SAXS/WAXS reveals the structure evolution of polyethylene (PE). The gradually expanding of the lamellar thickness and crystal lattice is traced and this is importantly correlated to the result of dynamic mechanical analysis (DMA).

References
Nanostructure and Function of Fullerene and Polymer/Fullerene Gratings as Revealed by Grazing Incidence X-ray Scattering and Atomic Force Microscopy

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The continuous appearance of emerging applications for organic nanostructured materials makes the controlled generation of micro and nanostructured functional surfaces to be a demanding challenge. Mostly driven by the field of organic electronics advanced lithographic processes are being investigated in order to produce surface nanostructures. The potential interest of avoiding the necessity of stringent environmental conditions like those implied in using clean rooms, high vacuum or complex mask fabrication is one of the driving forces to seek for simpler alternative lithographic procedures as a complement, or even as a substitution, for standard patterning. In particular, laser induced patterning of organic surfaces is a versatile strategy in order to produce functional materials[1]. The formation of Laser Induced Periodic Surface Structures (LIPSS) is a phenomenon which may occur by illumination of solid surfaces by intense either nanosecond or femtosecond laser pulses. In these cases spontaneous formation of periodic structures on the surface takes place. The structures typically consist of ripples although also more complex structures have been described whose periodicities are closely related to the wavelength of the irradiating laser[1,2].

Here we will discuss the nanostructure at the relevant length scales as revealed by grazing incidence X-ray scattering (GIXS) at small and wide angles of LIPSS formed on spin-coated thin films of polymer/fullerene hybrids based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM). In particular we will present a method to produce nanosecond pulsed LIPSS on spin-coated PC₇₁BM films exhibiting a photoinduced resist-free imprinting (PRI) character. PC₇₁BM LIPSS are resist free and can be solvent developed, under certain conditions, leaving the laser illuminated zone as an undissolved residue. A heterogeneous conducting pattern, as observed by Conducting Atomic Force Microscopy (C-AFM), consisting in conducting valleys and less conducting hills is obtained in the LIPSS prepared at 532 nm. On the basis of both GIXS and AFM experiments we propose that laser irradiated PC₇₁BM films suffer a fast heating/cooling process tending to reduce the overall crystallinity of the LIPSS and therefore decreasing the electrical conductivity of the hills while leaving a remnant conducting film underneath the hills. In addition during laser irradiation the heat treatment leads to the development of a buried PC₇₁BM crystalline phase close to the silicon substrate with enhanced electrical conductivity. These results points towards the potential use of the described technology for nanofabrication of organic electronic devices.

References

[Sep. 4 (Tuesday), SRPS-2]
π-conjugated polymers have attracted enormous attention in recent years, thanks to the affordable cost, mechanical flexibility and chemical tunability. Unlike conventional inorganic materials, which usually form highly crystalline structures with long-range order, π-conjugated polymers arrange themselves in a complicated manner with noticeable amount of amorphous and low crystalline aggregates in the solid state. Besides, the crystalline domains in polymer thin films are usually revealed to be imperfect and with finite size (thereafter called crystallites). Within each crystallite, the molecules arrange in distinct ways along each crystallographic axis as a result of the intrinsically anisotropic molecular structure and localized electron distribution within molecules. Accordingly, devices made of π-conjugated polymers exhibit highly anisotropic performance along different directions. For example, organic field-effect transistors (OFET) may exhibit electron mobility as high as 1 cm²/Vs parallel with the substrate, with several orders of magnitude lower mobility perpendicular to the substrate. On the other hand, organic solar cells (OSCs) can exhibit high mobility along direction perpendicular to the substrate while the mobility parallel to the substrate is much lower. The device performance is also revealed to be highly dependent on post-processing condition, such as the thermal annealing temperature. In order to understand the different device performance, investigation and elucidation of the crystallite structure and its thermal expansion behaviors along each crystallographic direction become inevitable. By utilizing synchrotron-based in-situ grazing-incidence wide-angle X-ray scattering (GIWAXS), the diffraction patterns of the crystallites within films as thin as several tens of nanometers can be readily collected in less than 1 s with sufficiently high counts. In this study, two chemically similar semiconducting polymers - Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT) – have been systematically investigated as a function of temperature. Specifically, the linear thermal expansion coefficient (LTEC) along different crystallographic directions were extracted from the plots of d-spacing of lamellar stacking and π-π stacking as a function of temperature. In addition, crystallite size, lattice disorder and thin film texture across wide range of temperature have also been quantified. The finding of varying LTEC across different temperature ranges along π-π crystallographic direction (effective for charge hopping) serves a guideline of determining the optimal thermal annealing temperature for the post-process of organic electronic devices, such as OFETs and OPVs. We believe that the in-situ GIWAXS investigation of semiconducting polymer thin films is an effective way to build meaningful morphology-process-performance correlation as a guideline for further device optimization.
Morphology in Organic Photovoltaics as Probed by Grazing Incidence X-ray Scattering

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Structural and morphological heterogeneity is common in thin film and emerging solar cell absorber layers, including organic photovoltaics (OPV), and this heterogeneity has a significant impact on the (opto)electronic and absorber layer properties. In this talk I discuss the use of grazing incidence X-ray scattering (GIXS) to characterize the nanoscale morphology and in situ formation of OPVs. OPVs consist of blends of an organic electron donor (polymer) and an electron acceptor (often a fullerene derivative, phenyl-C61-butyric acid methyl ester (PCBM)) and are typically formed by solution processing. To ensure a high charge separation efficiency, the donor and acceptor are blended to form a bulk heterojunction (BHJ) and they phase separate into nanoscale domains. The BHJ morphology (domain size and spacing) has a significant impact on the efficiency of the resulting solar cell [1]. There are three distinct phases within a BHJ: pure donor, pure acceptor, and molecularly intermixed donor:acceptor, but the factions and sizes of these phases are poorly known in most BHJs. Here, we quantify the volume-fraction of these phases using GIXS and correlate this to OPV performance with a focus on the X2:PCBM small molecule blend, in order to explain why this BHJ is unusually tolerant to the variations in the ratio of X2 to PCBM: contrary to many polymer:PCBM BHJs, X2:PCBM maintains high efficiency of 6% for 30-60 vol-% of PCBM [2,3]. Importantly, OPV BHJs can be processed from solution, which enables the use of high-throughput techniques such as blade-coating and printing, making this technology ideal for buildings (BIPV). Understanding the BHJ formation process can provide important insight into methods to tailor the printing process to improve the BHJ morphology and consequent efficiency. Real-time X-ray scattering is a sensitive monitor of the BHJ morphology evolution during the drying process and here we use GIXS to understand the morphology development for all polymer BHJs and contrast this to polymer:PCBM BHJs. Specifically, we compare poly(3-hexylthiophene-2,5-diyl) (P3HT):PCBM blends with the all-polymers BHJ P3HT:naphthalene diimide thiophene-based (PNDIT).

References
Effects of Cross-linking density of UV Irradiated Polystyrene Chains on Domain Orientation and Spatial Order of Block Copolymer Nanodomains.

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UV irradiation (UVI) of varied duration caused cross-linking and neutralization of polystyrene homopolymers of molar mass ($M_n$) from 6 to 290 kg mol$^{-1}$ on a silicon-oxide surface. A skin layer of a neutral surface of PS was obtained with an optimum oxidation via brief UVI in air (UVIA). UVI in an inert environment (gaseous dinitrogen) (UVIN) stabilized the PS layers via cross-linking and enabled the PS networks to have an effective adhesive contact with the underlying substrate. Thorough examination of domain orientations and spatial orders of block copolymer via grazing-incident small angle X-ray scattering (GISAXS) and atomic force microscopy (AFM), polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA), thin films in a series on the UVI-treated PS layers yielded clear evidence that a dense layer of neutralized PS chains was required for the perpendicular orientation of PS-b-PMMA nanodomains. In particular, in addition to neutralization[1-2], two factors – the densities of physical entanglements and of chemical crosslinks – both in UVI-treated PS, should be considered for the perpendicular orientation of nanolamellae and nanocylinders in symmetric and asymmetric PS-b-PMMA thin films. The density of physical entanglement in PS depended intrinsically on $M_n$ of the PS whereas the density of chemical crosslinks was controlled with a varied duration of UVIN. Both neutron and X-ray reflectivity (NR/XRR) results indicate that sufficiently large densities of physical entanglements and chemical crosslinks can prevent PS-b-PMMA chains from penetrating through the neutral skin layer. The total density of physical entanglements and chemical crosslinks required for the perpendicular orientation correlated with the dimensions of the PS-b-PMMA chains.

References
Preferred Lamellar Orientation in Thin Films of Biobased Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)
Investigated by GIWAXD Measurements Using Synchrotron Radiation

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Preferred lamellar orientation is one of characteristic phenomena of crystalline polymer thin films with thicknesses below 1 µm. In order to control mechanical/functional properties of polymer thin films, their hierarchical structure should be controlled on the nano- to meso- scales. However, influential factors on crystal orientation in the films haven’t completely been understood. In this study, lamellar orientation of biobased poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) thin films was quantitatively evaluated by grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements using synchrotron radiation. Effect of the 3-hydroxyhexanoate (3HH) content in PHBH on lamellar orientation were investigated for the films.

Samples used in this study were biobased poly(3-hydroxybutyrate) (P3HB) and PHBHs having 3.2, 5.4, 5.8, 7.0 and 10.4 mol% of uncristallizable 3HH (Kaneka Co.). Thin films with thicknesses of ca. 300 nm ~ 1 µm were prepared on Si substrates by a spin-coating method with 1.5 ~ 4.0 wt% P3HB or each PHBH in chloroform. The obtained films were isothermally crystallized at \( T_c = 295, 343, 363 \) and 383 K from the melt under a nitrogen atmosphere. The degree of crystal orientation was evaluated for the films with the azimuthal intensity profiles of GIWAXD measured at BL45XU/SPring-8 (RIKEN, Hyogo, Japan). GIWAXD data indicated that the flat-on type lamellar orientation became more dominant with increasing the 3HH content in PHBHs. Lamellae having the flat-on type orientation, the edge-on type orientation and their mixture were formed depending on \( T_c \). Relationship between the orientation of lamellae grown in the film and thermodynamically-stable orientation of the critical nuclei generated in an interface between the film and the Si substrate will be discussed in my presentation.

This research was partly supported by CREST of JST, JSPS KAKENHI Grant Number 26410135 and the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

Keywords: preferred lamellar orientation, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), thin film, surface tension, interface effect
Nanostructured thin films from block copolymer self-assembly: exquisite symmetries from macromolecular design.

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Block copolymers are a unique class of materials which self-assemble into periodic structures at the nanometer scale with a range of controllable morphologies, including lamellae, cylinders, spheres and unique network morphologies. Their self-assembly into nanostructured thin films offers a promising route to provide a significant advancement in technological applications such as lithography, non-linear optics or ultrafiltration. Over the last years we have developed a first generation of lithographic materials based on the directed self-assembly of PMMA-b-PS and highlights on the use of Grazing Small X-ray Scattering (GISAXS) to probe their self-assembly kinetics and the resulting mesostructures will be presented.[1,2] Following this study, we have designed new block copolymer systems characterized by higher segregation strengths and more complex architectures which allow the definition of sub-20 nm features with exquisite symmetries.[3,4] A few anecdotes related to their thin film self-assembly and their segregation behavior as regards to the processing parameters will be presented.[5,6] In particular, we will show that precise macromolecular engineering allow the formation of complex patterns which can be hybridized to form interesting metallic structures.

References
Time-resolved GISAXS/GIWAXS for control and characterization of structure formation in printed thin films

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The properties of many thin films are closely linked with material performance. For industrial applications printing functional thin films is of high relevance. We have developed a set-up to print functional materials under various controlled deposition environments to understand and influence the structure formation in printed thin films. [1] Using GISAXS and GIWAXS on thin film photovoltaic systems we gain insight into crystallization processes important for device operation. Our controlled deposition process can be carried out in various multi-modal measurement environments to shed light on structure formation processes. We can follow the evolution of thin film morphology with appropriate time-resolution to initially track the solvent removal, followed by the crystallization of the polymer and the aggregation of the fullerene. [2] We observe that the morphological evolution can be separated into several subsequent phases that take place independently of the drying speed of the film. We can manipulate the processing using, for example, different drying times, either by temperature or saturated gas atmosphere and directly observe the changes on the structural development. Furthermore, we can apply this approach to other promising material systems. Such measurements are highly valuable for understanding the structure formation processes in material systems of interest for industry, where stable, reproducible fabrication conditions are essential.

References
Surfactant Engineering to Enhance Crystalline Orientation of Water-Borne Polymer Semiconductors

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In the past, market demands for high performance and appearance were the pace makers in the development of various functional polymers. Consequently, solvent-borne systems were mainly in use. A change has been introduced by the trend to be more environmentally conscious; harsh regulations have been implemented to restrict solvent emissions, especially when polymer coatings are being applied. This trend was led by government regulations like the Clean Air Act in the United States or the German TA-Luft.[1] As a result, there has been a tremendous research effort to make water-borne colloids with the same desirable properties that have been often obtained with solvent-based polymers. Nowadays, in most polymer industries, water-borne polymer techniques have replaced the traditional role of solvent-based polymer techniques. These industrial fields include non-woven fabrics, paper coating, synthetic rubbers, adhesives, toughened plastics, catalytic supports, and the medical diagnostic areas.[2] Nonetheless, there have been no successful reports on the fabrication of water-borne colloids of semiconductors, although there has been a very successful water-borne colloid of the electrode material PEDOT:PSS.[3] Because most organic electronics are assembled by combinations of semiconductors and electrodes, the development of high performing water-borne inks made from semiconductors could be a breakthrough/milestone discovery in the realization of environmentally benign organic electronics. In particular, considering the rapid growth of organic semiconductors in terms of charge carrier mobility, which is now exceeding the minimal industrial requirement, the development of an environmentally benign process is a very urgent task. In this study, we suggest a novel method of fabricating water-borne colloids of semiconducting polymers for use in environmentally benign processes involving organic electronics, without compromising the high charge carrier mobility of the polymeric semiconductors. By developing smart surfactant engineering techniques, we could selectively remove residual surfactants after film deposition, rendering efficient inter-particle charge coupling and thus crystalline orientation.[4] Structural and chemical analyses showed that films consisting of polymer nanoparticles nearly free from surfactants maintained high degree of crystalline orientation, which was enough to render high charge carrier mobility.

References
Poly(3-hexylthiophene) (P3HT) is well known as an electron donor material; due to this characteristic, it has been widely investigated for applications in solar voltaic cells. In this study, we have studied its thin film morphology in a quantitative manner by using synchrotron grazing incidence X-ray scattering (GIXS) and X-ray reflectivity (XR). Its lateral ordering in a length scale and orientation were investigated in detail as a function of thin film fabrication parameters. Devices were fabricated with P3HT thin films having various fabrication histories and their electrical memory performances were measured in air ambient by using a semiconductor analyzer and a probe station. Then, the device performances were correlated to the chemical nature and morphological parameters including orientation factor. All results will be discussed in detail. And electrical memory mechanisms will additionally discussed.
Optoelectronic properties of metal clusters on polymer thin films during sputter deposition

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Nanostructured polymer-metal-composites demonstrate great perspectives for optoelectronic applications [1], e.g. as sensors or photovoltaics. To enhance properties of such devices the self-assembly process in the metal layer during fabrication needs to be understood. We therefore studied the insulator-metal transition during sputter deposition of metals on co- and homopolymers by grazing incidence small-angle X-ray scattering (GISAXS) in combination with surface differential reflectance spectroscopy (SDRS) [2]. As templates, solvent annealed ordered diblock copolymer and their corresponding homopolymers were used. Our study reveals both the selective wetting of metals on one of the polymer blocks and the influence of the template on the percolation behavior of the metal layer. In situ GISAXS measurements indicate a difference in the embedding of metal clusters depending on the polymer template, which accompanies selective wetting.

References
When radiation plays tricks with the sample

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Since the early days of research using synchrotron radiation X-ray beams the brightness of the synchrotron sources has grown by many decades. At the same time there is a tendency to reduce the size of the beam often accompanied by a reduction in the size of the sample. Although the amount of energy deposited in the cross section between the X-ray beam and the sample is still not comparable to what one encounters in laser-based research there are several beam-sample interactions that can modify the samples. In soft matter and polymer research this is generally recognized as radiation damage. What is, however, often not known, or maybe ignored, is that radiation influence doesn’t always have to manifest itself as damage but that it can also interfere in other ways with the sample.

In the photon energy range commonly used for X-ray based experiments on polymers the dominant radiation interaction effect is the photoelectric effect. This photon absorption process creates a short-lived electron cloud around the point of impact to come into existence. The electron cloud can generate several radiolysis/radiochemical effects of which the exact nature is somewhat hard to predict but which are partially transient and partially permanent. These effects can generate effects which at first sight might not be recognized as damage but instead give the impressions as being the manifestation of the physical evolution which one hopes to study with the experiment.

So far, the most striking examples of such phenomena have been found in (partially) amorphous materials and solvent containing samples which typically is the domain of soft matter and polymer research.

Examples of unexpected effects are increased chemical reaction rates, induced or inhibited crystallization, changes in pH etc. in the presentation several examples will be given where radiation interfered with the sample evolution in other ways than simply inducing damage.

Fig. 1 Increase in photon flux on SAXS and SAXS-microfocus beamlines over a 15-year period. Data taken from published beam line descriptions. Vertical axis represents total flux divided by beam cross section.

References

Status and Challenges of the Neutron Scattering Facility at HANARO after the Long Shutdown since July 2014

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HANARO, the High-flux Advanced Neutron Application Reactor, is a 30 MW multipurpose research reactor located in Daejeon, Korea. One of the many applications of the reactor is neutron beam utilization. At present, the reactor hosts 19 neutron beam instruments. Among them, 15 are neutron scattering instruments, two neutron imaging, and two activation analysis stations. Combined with the high neutron beam flux produced by the reactor, the neutron scattering facility is one of the major scientific facilities in the country. Unfortunately, the facility had to go through a lengthy shutdown since July 2014. After a long construction effort and regulatory process, the facility is poised to reopen very soon as of writing. The users, who were deprived of neutrons without any backup facility within the country, are eager to come back. There are, however, many challenges to the facility and the users. Many new instruments still need more work before they become available to users, while the operational budget of the facility is only a fraction of many fully serviced facilities overseas. Meanwhile, the only official user program ends soon, and the safety requirements are growing. We plan to meet the challenges through close collaboration with stakeholders.
Gracing incidence small angle neutron scattering: The solid-liquid boundary condition in hydrodynamics

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Neutrons are characterised by a weak interaction for many engineering materials. As a result they can penetrate deeply into matter and are sensitive to light elements. If applied under grazing incidence beam geometry (see figure 1, right panel) neutrons can offer surface sensitivity. If in addition to the specular reflectivity, off-specular scattering or the small angle scattering is collected, correlations in the plane of the interface can be analysed. In this talk I will focus on neutron scattering experiments probing the solid-liquid interface. The talk will cover two parts.

First, it has been demonstrated that the traditionally assumed non-slip boundary condition does not always hold. The discontinuity at the interface can be quantified by a phenomenological number, the slip length (for definition see figure 1, left panel). However, the microscopic origin of slip is still not understood and different scenarios are proposed. Our recent findings, on polymers [1], self assembled monolayers [2], surfactants [3] and simple liquids [4], demonstrate that slip in simple liquids is not explained by a density depleted layer alone. The local structure and dynamics in the liquid at the interface, which are highly sensitive to the interfacial energy, have to be taken into account as well.

Second, the low absorption and brilliance of neutrons beams imposes challenges on the feasibility of depth resolved GISANS measurements. On the example of a micellar surfactant solution we will analyse the limitations and opportunities of the method. For surface layers of micrometer thickness a clear difference in the structure can be resolved [5] and some qualitative depth information can be extracted [6]. However, it turns out that the signal emitted from a specific depth is always limited and as a result extracting specific information form well defined distances from an interface remains challenging [7].

Figure 1: Flow profile for a liquid showing surface slip and definition of the slip length b (left panel). The panel on the right hand side depicts the scattering geometry for gracing incidence scattering experiments from the solid-liquid boundary [8].

References
Hierarchically Self-Assembled Binary Nanoparticle Superlattices

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Synthesis of binary nanoparticle superlattices has attracted attention for a broad spectrum of potential applications. However, this has remained challenging for one-dimensional nanoparticle systems. In this study, we investigate the packing behavior of one-dimensional nanoparticles of different diameters into a hexagonally packed cylindrical micellar system and demonstrate that binary one-dimensional nanoparticle superlattices of two different symmetries can be obtained by tuning particle diameter and mixing ratios [1]. The hexagonal arrays of one-dimensional nanoparticles are embedded in the honeycomb lattices (for AB2 type) or kagome lattices (for AB3 type) of micellar cylinders. The maximization of free volume entropy is considered as the main driving force for the formation of superlattices, which is well supported by our theoretical free energy calculations. Our approach provides a route for fabricating binary one-dimensional nanoparticle superlattices and may be applicable for inorganic one-dimensional nanoparticle systems.

References
Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (P(VDF-co-TrFE)), are recently receiving renewed attention due to their ferroelectric properties and are nowadays incorporated in modern nano-sized electronic devices, expanding their conventional functionalities, thanks to the merits brought by the electroactive nature of these materials. The functional properties of P(VDF-co-TrFE) are dictated by its structure, which, in turns, depends on processing conditions. Usually P(VDF-co-TrFE) films are processed from solution by spin coating and are subjected by an annealing step above their Curie temperature (cold-crystallization) [1,2]. In this work, we explore the possibility to process 70:30 P(VDF-co-TrFE) films from the melt via isothermal melt crystallization. The melt processing is able to produce high quality films with good ferroelectric properties and is able to fine tune the crystallization behavior of the polymer. In particular, the crystallization temperature used in the range 128 - 147 °C has an influence on the order of the ferroelectric structure at room temperature, which in turns influences the ferroelectric properties (i.e. remnant polarization and coercive field). In order to fully explain the crystallization behavior and thermal response of P(VDF-co-TrFE) films and to establish a clear structure-property relationship for melt-crystallized films, we have developed and applied a combined SAXS/WAXS/RAMAN/DSC setup to assess the change in crystallinity, crystal size and phase content in the sample during the isothermal crystallizations steps and the heating/cooling cycles. A clear correlation between the crystal structure of the P(VDF-co-TrFE) and its ferroelectric properties can be established using this multitechnique approach.

References
Long-range ordered crystalline structure in micromolded diblock copolymer ultrathin film via correlated crystal growth at surface and beneath layers

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Polymer crystallization involves molecular assembly at different length and time scales that leads to hierarchical crystalline structure with the atomic chains packing into nanoscale lamellae and mesoscale spherulites. Hierarchical crystalline structure has been widely reported in both traditional polyolefins\(^1\) like polyethylene, polypropylene, and recent functional polymers like poly(3-hexylthiophene-2,5-diyl)\(^2\) and covalent organic frameworks\(^3\). The structural hierarchy and its sensitivity to external fields make polymer crystallization hard to control. To curtail polymer crystal growth to get long-range ordered crystalline structure, some powerful protocols like nanoimprinting and anodized aluminum oxide (AAO) template have been developed, especially the nanoimprinting as a promising technology that can be combined with large-scale continuous production earned great interests in the last decade. However, spherulite structure is usually observed in the nanoimprinted semicrystalline polymer thin films and the growth is via the residual thin layers close to the substrate.\(^4\)

We will present a study that the spherulite structure in imprinted polymer thin film can be inhibited in block copolymers where the crystalline block is chemically bonded with an amorphous block and thermodynamic incompatibility causes the microphase segregation and formation of ordered nanostructures. Autophobic detwetting, resulting from the entropy difference between the adsorbed and free layers\(^5\), inhibited the crystal growth in the trans-channel direction, thus we successfully fabricated the long-range ordered crystalline structure by micromolding the block copolymer thin film.\(^6\) In this work, we studied in situ with AFM and GISAXS the crystal-growth correlations at surface and beneath layers of poly (butadiene)-block-poly(ε-caprolactone) (PB-b-PCL) thin film. We illustrated that a two-step crystal growth process: crystallization occurs first in the surface and crystal growth causes a coarsened surface morphology, and then the surface crystal grows into the beneath layer and induces the crystal growth there. We believe this crystal growth behavior contributed to the formation of long-range ordered crystalline structure in imprinted PB-b-PCL thin film.

References
Unconventional Micrdomains of Block Copolymers

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The microdomains obtained by block copolymer (BCP) self-assembly are mainly decided by the volume fraction of one block. For instance, the lamellar microdomains are expected for symmetric volume fractions, whereas spherical microdomains are obtained for highly asymmetric volume fraction. However, it is very difficult to fabricate highly asymmetric line patterns based on BCP.

We obtained highly asymmetric lamellar morphologies by the use of binary blends of block copolymers [polystyrene-\(b\)-poly(2-vinyl pyridine) copolymer (PS-\(b\)-P2VP) and PS-\(b\)-poly(4-hydroxystyrene) copolymer (PS-\(b\)-PHS)] where P2VP and PHS are capable of the hydrogen bonding. We obtained the asymmetric lamellar microdomains having lamellar width ratio of 4:1. This ratio was even increased up to 6:1 with increasing the degree of hydrogen bonding.

Also, we obtained core-shell double gyroids at highly asymmetric volume fractions by blending of polyisoprene-\(b\)-polystyrene-\(b\)-poly(2-vinylpyridine) (ISP) triblock terpolymer and polyisoprene-\(b\)-polystyrene (IS) diblock copolymer. At overall volume fractions of PI (0.12), PS (0.79), and P2VP (0.09), PI consists of thin core and PS forms thick shell, while P2VP becomes thin matrix. Finally, we observed for the first time the cylindrical and double gyroid microdomains in neat linear block copolymers at the symmetric overall volume fraction by using tetrablock copolymers polystyrene-block-polyisoprene-block-polystyrene-block-polyisoprene (S\(_1\)I\(_1\)S\(_2\)I\(_2\)).

Keywords: Block Copolymer, Unconventional Microdomains, Asymmetric Lamellae, Symmetric Cylinders, Gyroids.
Hierarchical morphology and confinement in nanostructured polymer blends investigated by Nanofocus X-ray beams and Resonant Soft X-ray Scattering

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Arrays of semiconductor polymer nanostructures exhibit an interesting behavior that makes them candidates for use in organic electronics, photovoltaics, and sensor devices. High aspect ratio (length/diameter) one-dimensional (1D) nanostructures are also appropriate for studying size-dependent processes with length scales comparable to the nanostructures’ size [1]. Material properties strongly depend upon molecular order and orientation. Crystallization is one of the simplest molecular-scale self-organization processes capable to control spatially the ordering of molecules and hence to tune the properties of partially crystalline polymer nanostructures, as they will largely depend upon the properties of their crystalline domains. Phase separation and structure confinement are also key factors to take into account in nanostructured polymer blends acting as active layers in organic photovoltaics [2, 3].

This contribution will cover recent research on these phenomena. On one hand, the confinement effects on phase separation, crystal structure and orientation in high aspect ratio (length/diameter) one-dimensional (1D) nanoarrays of the photovoltaic blend poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene)/ fullerene have been studied by Nanofocus X-ray Scattering [4]. On the other hand, Resonant Soft X-ray Scattering at the carbon K edge is shown to be an unambiguous approach to evaluate the phase segregation between donor and acceptor phases across the grooves of a laser induced periodic surface nanostructure on a poly(3-hexylthiophene)/fullerene bulk heterojunction. By taking advantage of the use of polarized soft X-rays, the results provide direct evidence that the formation of the nanostructure on the surface of the heterojunction induces not only additional phase separation of the two components but also a preferential directional arrangement of the different phases [5].

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References
We report experimental results on orientation of the cylindrical microdomains in an polystyrene- block-poly(ethylene-co-butylene)-block-polystyrene (SEBS) triblock copolymer / diluent sheet by application of temperature gradient [1]. For this purpose, cylinder-forming SEBS sample was used where the volume fraction of polystyrene (PS) was 0.16. Diocetylphthalate (DOP) was used as the diluent. Note that DOP has selectivity in solubility for the SEBS; good solubility for polystyrene (PS) while poor solubility for poly(ethylene-co-butylene) (PEB). Due to this selectivity, a lamellar morphology was found at lower temperatures for SEBS/DOP sheets with the compositions of 6/4 and 7/3, as revealed by small-angle X-ray scattering (SAXS). It was further revealed that the morphology changed to be cylindrical at higher temperatures. The order-order transition temperature (Toot) was found 100 °C for both 6/4 and 7/3 compositions, although coexistence of lamellae and cylinders was found in much wider temperature range for the 7/3 composition as compared to the case of the 6/4 composition. These results indicate that the diluent selectivity of solubility at lower temperatures is suppressed at higher temperatures. For the SEBS/DOP (6/4) specimen, we applied the temperature gradient with 86 °C / 143 °C for the 3 mm-wide specimen sheet for 3h. Note here that the order-to-disorder transition temperature was found to be 152.0 °C. The morphology formed in the specimen was then analyzed by SAXS. Figure 1 shows the result. The cylindrical morphology was interestingly found near the cold wall of the sample holder, even though the cold temperature was below Toot and therefore the lamellar phase should be stable. This result implies that the temperature gradient may destabilize the lamellar phase. More interestingly, perpendicularly oriented cylinders (the cylinder axes are perpendicular to the sheet specimen) were formed near the hot wall of the sample cell with a single grain state where (10-10) planes of the hexagonal lattice are parallel to the surface of the hot temperature wall of the sample holder. Since both of the spacing and the cylinder radius becomes larger as the temperature was decreased, such orientational state is considered to accommodate well the cylinders in the confined space under the temperature gradient.

Reference

Recent Advances in Triphenylamine-Based High-Performance Polymers

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This talk will cover a majority of the recent works in our laboratory involving the synthesis and property evaluation of functional high-performance polymers (HPPs) as well as their structural design by using the respective novel arylamine/triphenylamine- (TPA) containing monomers. Solution-processable functional HPPs were successfully prepared as the application of AIE-based PL luminescent and electrochromic materials with interesting color transitions and good electrochromic reversibility in the visible region or NIR range and electrofluorochromic (so called electrochemically photo-switching) devices. The relation between structures and properties of the resulted functional high-performance polymers will be presented in terms of their functionality.

High-performance Transistor memory, electrochromic (EC) and electrofluorochromic (EFC) devices derived from functional polymers with triarylamine units as redox- and AIE-active layer

References:
Temperature-dependent structural behavior of polymers containing adenine moieties by simultaneous XRD-DSC measurement

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We investigated the molecular structure of the polymers containing adenine moieties, poly[oxy(11-(5-(9-adenylethoxy)-4-oxopentanoato)undecanyl-1-thiomethyl]ethylene] (PECH-AS), which showed well-orders multi layered structure with unusual asymmetry thermal hysteresis during heating and cooling processes. PECH-AS and its side-chain-like molecule (ASE) exhibit similar asymmetry thermal hysteresis according to changes in heating and cooling rates. The molecular structure of ASE single crystal reveals correlation between the presence of hydrogen bondings and the complex thermal hysteresis of these adenine-containing materials. The simultaneous XRD-DSC and temperature-dependent IR results showed detailed strong correlation between thermal behaviors of PECH-AS and ASE and their molecular structures including hydrogen bondings.
Length Scale Control in Polymerization-induced Microphase Separation

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Block polymers self-assemble into fascinating nanostructures driven by incompatibility between different polymer chains covalently connected to each other. Advances in controlled polymerization techniques and understanding of block polymer physics allow exquisite control over structure, periodicity, and functionality of the resulting self-assembled material by precise block polymer synthesis. Polymerization-induced microphase separation (PIMS) is an interesting route to self-assemble a block polymer in situ during the synthesis [1]. Typically, reversible addition-fragmentation chain transfer (RAFT) copolymerization of a monomer and a crosslinker in the presence of a macro-chain transfer agent (macro-CTA) is used to yield a crosslinked block polymer consisting of a bicontinuous disordered morphology at nanometer scale with precise control of the domain size. By combining a variety of monomers, crosslinkers, and macro-CTAs, the PIMS process allows us to produce nanostructured polymer membranes composed of functional nanodomains percolating a robustly crosslinked matrix [2-5]. Particularly for synthesis of porous membranes, domain size control is important for attaining desired pores ranging from micropores (< 2 nm), mesopores (2 - 50 nm), and macropores (> 50 nm). I will discuss our efforts to control the domain size in the PIMS process by adjusting molar mass of the macro-CTA and adding additives [6]. While retaining the beneficial bicontinuous morphology, I will demonstrate that spanning three orders of magnitude in length scale from nm to μm is possible as evidenced by small angle X-ray scattering data. The characteristic scattering feature including a broad principal peak followed by a second-order shoulder will be discussed, and the extent of order and the pore stability will be examined based on the scattering and pore characterization techniques.

References
Phase-separated structure of oligosaccharide-based block copolymer

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Self-assembly property of block copolymers (BCPs) to provide microphase-separated structures is of great interest from the viewpoint of various applications. In particular, great effort is focusing on downsizing the microphase-separated structures for use in the next-generation lithography. We recently found that the BCPs consisting of hydrophobic synthetic polymers and oligosaccharide, i.e. oligosaccharide-based BCP, are promising candidate to form microphase-separated structures with domain-spacing in sub-10 nm scale [1-6]. Herein, we demonstrate the synthesis and sub-10 nm scale nanoorganization for linear diblock and miktoarm star polymers consisting of poly(ε-caprolactone) (PCL) and maltoheptaose (MH) (Scheme).

Scheme. Synthesis of MH-b-PCL, MH-b-(PCL)₂, and MH-b-(PCL)₃

miktoarm star polymers (MH-b-(PCL)₂, MH-b-(PCL)₃) were synthesized by click reaction of azido-functionalized PCLs (N₃-PCL, N₃-(PCL)₂, and N₃-(PCL)₃) and N-maltoheptaosyl-3-acetamido-1-propyne (MH-C≡CH). First, N₃-PCL, N₃-(PCL)₂, and N₃-(PCL)₃ were prepared by living ring-opening polymerization of ε-caprolactone (ε-CL) using azido-functionalized alcohol (N₃-OH), diol (N₃-(OH)₂), and triol (N₃-(OH)₃) as the initiators. MH-C≡CH was then conjugated to the azido-functionalized PCLs by click reaction using CuBr/N,N′,N″,N‴,N⁵-pentamethyldiethylenetriamine (PMDETA) catalyst system. The success of the click reaction was confirmed by ¹H NMR, FT-IR, and SEC measurements, and the targeted MH-b-PCL, MH-b-(PCL)₂, and MH-b-(PCL)₃ were obtained in high yields with $M_n$/$M_w$ of less than 1.05. Finally, we studied the morphologies of MH-b-PCL, MH-b-(PCL)₂, and MH-b-(PCL)₃ using small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM). The volume fractions of MH block for the BCPs were 0.18. All the BCPs showed body-centered cubic phase at above 210 °C, and the domain-spacing (d) were determined to be 11.2 nm for MH-b-PCL, 9.8 nm for MH-b-(PCL)₂, and 8.8 nm for MH-b-(PCL)₃ (Figure)

References

Figure. Synchrotron SAXS profiles of bulk samples of MH-b-PCL, MH-b-(PCL)₂, and MH-b-(PCL)₃ at selected temperatures.
Directed Self-assembly of High-Molecular-Weight Block Copolymers: Lamellae and Gyroid Structures

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Block copolymer (BCP) is an excellent candidate to fabricate nanoscopic templates and scaffolds, since the dissimilar polymers linked together covalently self-assemble into the periodic nanostructures with typical feature sizes of 10 - 50 nm. Highly-aligned structure of BCP is currently of interest as a bottom-up or top-down approach for generating templates with well-defined arrays of spherical, cylindrical, lamellar morphologies in nanometer scale. In our study, the ordering and orientation of high-molecular-weight BCP on an intermediate nanometer scale (100–200 nm) has recently been highlighted as being useful in optical applications for photonics and polarizers that require the period sizes exceeding 100 nm. We present a simple approach to fabricating highly stable, perpendicularly oriented lamellae through the self-assembly of high-molecular-weight polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA). Using a SVA process controlled by modulating the temperature gap between the chamber and bottom plate, followed by a subsequent thermal annealing process, the ordering stability of perpendicularly oriented lamellae was investigated. Furthermore, we demonstrate the direct development of gyroid (GYR) nanostructure using high-molecular-weight BCP using controlled solvent annealing methods.

References
Synthesis of Single Cubic Networks having Large Open-space Lattices Templated by Polymer Cubosomes

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Periodic materials having open-space mesoscale lattices, in particular, a diamond lattice, have been pursued as ideal photonic crystals exhibiting large omnidirectional optical bandgaps. The direct creation of such structures, without relying on complex multi-step fabrication, by the colloidal self-assembly and the templated synthesis has been a significant challenge due to the thermodynamic preference to form close-packed lattices and double network structures. In contrast, single networks having open-space cubic lattices are ubiquitously found in biophotonic crystals, although their biogenesis utilizes ordered cellular membranes possessing two non-intersecting cubic pore networks as a template. Here we show that the interfacial topology of polymer cubosomes, finite-sized particles composed of bicontinuous cubic mesophases of block polymer bilayers, force the external guests to enter into only one of two non-intersecting cubic networks embedded within the polymer cubosomes. Consequently, single network structures of diamond and primitive cubic lattices having the lattice parameter up to 200 nm are synthesized by cross-linking of molecular precursors, which showed structural colors arising from the photonic bandgap. While sharing the topological and crystallographic features with lipid cubic mesophases, polymer cubosomes possess structural robustness and scalable lattice dimensions and pore sizes. Therefore, they are suggested as ideal templates for the facile synthesis of single network cubic structures of diverse materials, which could lead to the creation of photonic crystals and metamaterials that are previously unavailable.
Microstructure of GO colloids in Polymer Solutions with Small Angle Scatterings

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Graphene and its oxidized form of graphene oxide (GO) have been of particular interest in material science due to their exceptional physical properties. However, relatively little attention has been paid to the GO dispersions although the state of dispersions directly affect to the material property. For example, GO can be well-dispersed in water due to their hydrophilic functionalities and form liquid crystals (LC); however, they easily form gels or glass around 1 wt%, which often act as an obstacle in GO based composite production. Thus, to understand the structure and dispersing mechanism of GO dispersions is an essential step before reaching the application stage.

In this talk, the detailed structural and rheological studies for GO dispersions are introduced with extensive scattering and rheology experiments. The use of small angle x-ray scatterings is discussed in detail to investigate the microstructur e of GO colloids. We first systematically investigate the phase behavior and structural evolution of GO LC suspensions under various experimental conditions and disclose how the glass transition of GO dispersions is affected particularly in the presence of strongly interacting polymers. An intriguing observation was that adding polymer can effectively retard glass transition of GO in water. Furthermore, by varying polymer type, functionality, and molecular weight, the GO structures and LC properties can be changed significantly, suggesting the possibility of controlling the process conditions in GO employed applications.

References
Principle Investigation of Coherent X-ray Scattering

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Since the concept of X-ray free electron lasers (XFELs) was developed in the early 1970s [1] and self-amplified spontaneous emission (SASE) was proposed as an XFEL operating mechanism in the 1980s [2,3], several XFEL facilities constructed: LINAC coherent light source (LCLS) in USA, SPring-8 Angstrom compact free electron laser (SACLA) in Japan, PAL-XFEL in Korea, Euro-XFEL in Germany, PSI-XFEL in Switzerland, and so on [4]. These FEL facilities have opened up new methods for the investigation of nanostructures and femtosecond molecular dynamics. In particular, coherent X-ray scattering gains great attraction for getting more information on structures of materials including molecules and their assemblies. In this study, coherent X-ray scattering was considered for some model structure systems. In addition, coherent X-ray scattering with XFELs was further considered for single molecules. The results and perspectives will be discussed.

References

XFEL Performances achieved at PAL-XFEL and a Plan of New Hard X-ray Undulator Line

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The hard X-ray free-electron laser at the Pohang Accelerator Laboratory (PAL-XFEL) has achieved unprecedented performances of XFEL. The use of electron-beam-based alignment incorporating undulator radiation spectrum analysis has allowed reliable operation of PAL-XFEL with unprecedented stability in terms of orbit, energy, and timing. A timing jitter of smaller than 15 fs for the FEL photon beam, a transverse position jitter of smaller than 10% of the photon beam size, and a variation of FEL intensity of smaller than 5% are consistently achieved due to the use of a state-of-the-art design of the electron linear accelerator and electron-beam-based alignment. The low timing jitter of the electron beam makes it possible to observe Bi(111) phonon dynamics without the need for timing-jitter correction, indicating that PAL-XFEL will be an extremely useful tool for hard X-ray time-resolved experiments. In order to make a full use of this high performance of FEL, we propose a new hard X-ray undulator line to generate a hard x-ray FEL with pulse duration down to one-hundred atto-second. It will enable us to open a new atto-science as well as to increase the user beam time because two hard X-ray undulator lines are available to users.
Serial Femtosecond Crystallography Program at the
PAL-XFEL Facility

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Pohang Accelerator Laboratory X-ray Free Electron Laser (PAL-XFEL) facility has finished the commissioning successfully and started user operation from 2017. The NCI experimental hutch, which is one of the hard X-ray experimental stations, has been designed and prepared to perform serial femtosecond crystallography (SFX) experiments. I will present the current status of the sample environments (including sample delivery and dedicated sample chamber), beamline optics and experiment preparation facilities, which are related with SFX.
Single Particle Imaging at PAL-XFEL

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Pohang Accelerator Laboratory X-ray Free Electron Laser (PAL-XFEL) is a research facility that provides ultrabright (4x10^11 photons/pulse at 9.7keV) and ultra-short (20-30 femtosecond) X-ray pulses. The NCI (Nano-Crystallography and Imaging) beamline, which delivers hard X-ray pulses (2-20keV), is designed to measure diffraction signals with forward scattering geometry. Not only does it offer imaging studies of biological, chemical and physical samples by the ‘diffraction-before-destroy’ technique, but is also helpful in high field hard X-ray physics and material science. The scientific programs are currently aimed at Serial Femtosecond Crystallography (SFX) for macromolecular systems and Coherent X-ray Imaging for bio-specimen and nano-structures. In this talk, we will describe the details of the beamline layout and sample delivery system for single particle imaging experiment. After that, we will introduce recent experiments performed at NCI beamline as well.
We aim to follow changes in the shape, atomic structure and spatial configuration of Pt nanoparticles during catalytic CO and CO/O2 (2:1 ratio) oxidation under continuous gas flow using coherent X-ray diffraction. These structural properties are directly related to catalytic activity and deactivation, which remains crucial for the design of future stable industrial catalyst materials with extended lifetimes. In this experiment, we investigated substrate-supported a single Pt nanoparticle, grown by evaporation on (100)-oriented STO single crystal surfaces using Bragg Coherent Diffraction Imaging (BCDI) in a 8.5 keV energy X-ray beam focused to 150 nm × 300 nm. After measuring 3D Bragg diffraction under Ar, CO and CO/O2 (2:1 ratio) conditions, 3D Pt nanoparticles were successfully reconstructed using phase retrieval algorithm[1-3]. Therefore, we were able to track subtle strain changes of the Pt nanoparticle during catalytic reactions under mild conditions.

References
Structural Dynamics Probed with Ultrafast Coherent X-Rays from X-Ray Free Electron Laser

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The recent advent of hard x-ray free electron lasers (XFELs) opens new areas of science due to their exceptional brightness, coherence, and time structure. In principle, such sources enable studies of dynamics of condensed matter systems over times ranging from femtoseconds to seconds [1].

In the first part of my talk, I present the results obtained in LCLS on the relaxation dynamics of gold nanoparticles suspended in polymer melts using X-ray photon correlation spectroscopy, while monitoring eventual X-ray induced damage. In spite of inherently large pulse-to-pulse intensity and position variations of the XFEL beam, measurements can be realized at slow time scales. The X-ray induced damage and heating are less than initially expected for soft matter materials [2].

In the second, I show the recent studies of optically induced ultrafast atomic scale structural response of multilayers of Bi$_2$Se$_3$ by laser pump - x-ray probe experiment using hard x-ray pulses at XSS station at PAL-XFEL [3]. In the initial stage from 0 to 6 ps after laser excitation, the lattice contracts due to modulation of van der Waals force between quintuple layers (QLs) resulting from the carrier excitations. The resultant compressive strain propagates through the whole sample and its reflection from the surface and interface observed in the period of 10 ps. We compared the results from the density functional theory with the determination of the excited free carrier localized layers.

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References
X Ray Photon Correlation Spectroscopy for the study of polymer dynamics

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X Ray Photon Correlation Spectroscopy, XPCS, is a novel technique developed for the study of slow dynamics in condensed matter. The principle of this technique is based on the time variations of the speckle pattern originated by the scattering of coherent light from a material with spatial inhomogeneities. Although laser photon correlation spectroscopy was long established, XPCS has only been possible with the advent of new synchrotron radiation X-ray sources that can provide sufficient coherent flux. In this presentation we will review our contributions on the study of polymer dynamics by XPCS, and future perspectives in the field of polymer science will be highlighted.

References
High-Resolution X-ray Coherent Surface Scattering Imaging

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At the center stage of the scientific topics, surface/interface phenomena are of great interest to scientists in a variety of fields. Imaging techniques provide ideal tools to directly observe surface/interface structures and monitor their dynamic evaluation responding to changes in external conditions. Much progress has been made in the development of hard x-ray sources and tools, including the development of storage-ring sources and x-ray free-electron-laser sources. Among all, grazing-incidence x-ray scattering and x-ray photon correlation spectroscopy (XPCS) exhibit unique advantages for exploring the surface/interface problems that are challenging to solve using other imaging techniques dynamics probes. The APS Upgrade (APS-U) will increase brightness by a factor of 100 to 1000 – clearly high-brightness and coherence are the cornerstones of the upgraded source. The x-ray beams from the upgraded source possesses a large coherent fraction, which is well suited for measuring the spatiotemporal evolution of structures in complex systems with the highest precision at surfaces and interfaces. A new beamline for coherent surface-scattering imaging (CSSI) [1,2] takes advantage of the much improved x-ray beam coherence and is ideal for probing and understanding mesoscopic spatial-temporal correlations by integrating the coherence-based surface x-ray probe with state-of-the-art coherence-preserving optics and advanced x-ray detectors. The spatial resolution of the method is determined to be better than 5 nm to probe 3D structures and dynamics at surfaces and interfaces.

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References
Watching reacting molecules by time-resolved X-ray diffraction at synchrotrons and XFELs

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The pump-probe X-ray diffraction and scattering techniques have now been fully established as a powerful method to investigate molecular structural dynamics [1-5]. We have employed the techniques to study structural dynamics and spatiotemporal kinetics of many molecular systems including diatomic molecules, haloalkanes, organometallic complexes and protein molecules (biopolymer) over timescales from ps to milliseconds. X-ray crystallography, the major structural tool to determine 3D structures of proteins, can be extended to time-resolved X-ray crystallography with a laser excitation and X-ray probe scheme, but has been limited to a few model systems due to the stringent prerequisites such as highly-ordered and radiation-resistant single crystals. These problems can be overcome by applying time-resolved X-ray diffraction directly to protein solutions rather than protein single crystals. To emphasize that structural information can be obtained from the liquid phase, this time-resolved X-ray solution scattering technique is named time-resolved X-ray liquidography (TRXL) in analogy to time-resolved X-ray crystallography where the structural information of reaction intermediates is obtained from the crystalline phase. We will present our recent results from both synchrotrons and X-ray free electron laser (XFELs) including the achievement of femtosecond TRXL by using an XFEL.

References
Multimodal Resonant X-ray Scattering for Polymer Materials

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An improved understanding of fundamental chemistry, morphology, and dynamics in polymers and soft materials requires advanced characterization techniques that amenable to in situ and in operando studies. Soft X-ray methods are especially useful in their ability to non-destructively provide material or chemical moiety specific information. Recent development of resonant soft x-ray scattering (RSoXS) at the Advanced Light Source (ALS) has enabled its applications to many critical research areas of materials research. Combining conventional x-ray scattering with soft x-ray absorption spectroscopy, RSoXS is a unique chemical sensitive structure probe that provides a novel route to unambiguously decipher the complex morphologies of mesoscale materials. Tuning x-ray photon energies to match the absorption spectrum of the different chemical components, the scattering contributions from the different components can be selectively enhanced, enabling a glimpse into these complex morphologies with unprecedented details. Applications of RSoXS have been extended to the areas of structured polymer assemblies, organic electronics, functional nano-composites, liquid crystals, as well as bio/bio-hybrid materials. Recent development of customized instrumentation, multimodal characterization methods, as well as complementary theory and modeling for the extraction of the chemical distribution and spatial arrangement at multiple length scales in the application of soft materials will be discussed.
Biological SAXS: advances and perspectives

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SAXS is a powerful method to study biological macromolecules providing information on their overall structure in near-native conditions [1], and it can be easily combined with other technics such as macromolecular crystallography or cryo-electron microscopy. The sample contains dissolved macromolecules in solution, and different experimental conditions can be easily and rapidly screened. SAXS is also very well suited for time resolved measurements: different methods can be employed to trigger a biomolecular reaction in solution and data can be collected within ms-range on modern synchrotron sources.

At the same time biological SAXS can be experimentally challenging: biological samples are often fragile, available in limited quantities and particular care should be taken to obtain aggregate-free specimens. Biomolecules are also weak scatterers because they are composed of light atoms and their electron density is only slightly higher than the one of the surrounding aqueous buffer. Radiation damage induced by the high flux beam is also an issue, particularly on modern synchrotron sources, where the sample can be damaged in less than a second [2]. This presentation describes how these challenges are tackled on modern synchrotron SAXS beamlines; how the weak scattering signal from the biological molecules can be collected using beam collimation/focusing, advanced detectors and dedicated sample environment; how does a robotic sample handling allow to precisely handle small sample volumes and speed up the operation; how can in line-purification and spectroscopic characterization be achieved by coupling chromatographic devices to the beamline; and also, which strategies can be employed to mitigate radiation damage.

Significant progresses has also been made over the last decade in the automation of SAXS data collection and analysis [3, 4]. This automation does not only allow a better reproducibility and higher throughput of the measurements, but it also makes SAXS accessible to users with little to no previous experience of the technique. On many dedicated beamlines, BioSAXS measurements can be performed by novices users, who just need to put their samples in the robotic machine, provide basic information such as the sample name and its concentration and start the data collection. Within a minute after the SAXS curves are collected, the data are automatically processed and overall parameters are computed and a first ab initio shape is built.

All these improvements contributed to the success of BioSAXS that became an important part of the structural biologist toolbox. Further perspectives for BioSAXS, for example capitalizing on the high flux of modern synchrotron for time resolved experiments will be also be discussed.

References
Small Angle X-ray Scattering Studies on Structures of Biological Macromolecules in Solution

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The fundamental aim of structural studies in molecular biology is to establish a relationship between the structure (or, more precisely, structural changes) and function of biological macromolecules. Over the past years, a tremendous amount of structural information has been obtained using macromolecular crystallography and nuclear magnetic resonance (NMR). These high-resolution methods apply only in rather specific conditions: it is often difficult to grow crystals of high molecular weight (MW) assemblies that are suitable for diffraction, and the application of NMR is fundamentally limited to small (MW < 30 kd) proteins. Investigation of structure of biological macromolecules in solution remains one of the most important fields of application of small angle X-ray scattering (SAXS) technique. SAXS permits analysis of biological macromolecules and their complexes in nearly physiological environments and direct study of structural responses to changes in physical and chemical conditions. Recent remarkable progress in instrumentation, in particular thanks to high-flux dedicated X-ray synchrotron radiation has significantly improved the quality of the experimental SAXS data. This method is an important complementary tool to the high-resolution techniques (X-ray crystallography and NMR). The fundamental aim of this study is to obtain more detailed information on the structure and structural differences of a variety of biological macromolecules in solution under various conditions by using SAXS technique. Ultimately, the structural evidence presented here will contribute to a better understanding of relationship between structures of macromolecules and their function, from a biophysics point of view. In this talk, current status of 4C SAXS beamline, long-term plan for advanced beamline, SAXS data processing, overall parameters, and recent research results of biomacromolecules (DNA, protein) will be discussed in more detail.
Structure and Dynamics of Non-coding RNAs by Solution Small Angle X-ray Scattering

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The past two decades have witnessed many great discoveries on new functions of non-coding RNAs (ncRNAs), which had been considered as junk materials for long time. Comparing to proteins, RNA molecules are intrinsically more flexible, which makes structural study on RNA very challenging. However, a well-folded RNA is typically modular: its secondary structure can often be precisely predicted; A-form duplex is the major building block of the RNA structure; and the three-dimensional structure of the RNA can be approximated as the packing of those A-form duplexes. In this presentation, I will present structural studies that utilize solution small-angle X-ray scattering and RNA structural characteristics to solve structures of a few non-coding RNAs with important biological functions, such as Rev-response element in HIV-1 RNA genome.

In addition to the 3D structure, the structural dynamics is also important to RNA function. Using solution X-ray scattering, we have studied the structures and thermodynamics of the aptamer domain of Adenine-riboswitch (another type of non-coding RNA) under various conditions, including a range of temperatures and concentrations of Mg2+, Urea, and adenine ligand, and revealed that Mg2+ and the ligand can greatly stabilize the RNA folding, while temperature plays an important role on the RNA folding when the stabilizers are absent.

In this presentation, I will also discuss the capabilities of beamline 12-ID-B of the Advanced Photon Source at Argonne National Laboratory.

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Pneumolysin and Its Domains: Structural Characteristics in Biomimic Solutions and Adhesion Characteristics to Biomimic Brush Polymer Films

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Pneumolysin and its truncated fragments (domains 1–3, and 4) as recombinant proteins were cloned and over-expressed in *Escherichia coli* and then purified. Their three-dimensional (3D) structures were examined in phosphate buffered saline by synchrotron X-ray scattering and data analysis. The 3D structure of pneumolysin was obtained and compared with that in crystalline state which was determined by X-ray crystallography. The 3D structures of the domains were additionally obtained; then we have tried to understand their structures. The structural parameters were extracted from these analyses. In addition, adhesion characteristics of these proteins were tested onto nanoscale thin films of biomimetic brush polymers consisted of cholesterol and phosphorylcoline moieties. The adhesion results could be understood with considering 3D structures of the proteins as well as chemical nature, specific interaction, surface characteristics of the biomimetic polymers.
Topology Effects on Single Macromolecular Structures in Solution and Morphological Structures in Thin Films of Star Polymers

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Single molecule structure of three groups of star-shaped polymers (star-PMMAs, star-PMAs and star-PnBAs) with a same molecular weight and different arm numbers were examined in solutions from the view of molecular topology effects by using synchrotron X-ray scattering method. The quantitative scattering data analysis found the individual star polymers behave either prolate or oblate ellipsoidal shape rather than spherical shape, depending on the topologies and arm numbers. In particular, the degree of distortion from spherical shape was dependent strongly on the topologies, arm numbers and arm lengths. The overall size and segmental dimension with density variation were quantitatively determined though the quantitative analysis. The size of blob was shortened with increasing arm length but increased with arm number. The radial electron density profile was also affected by the molecular topology. The star polymers were further investigated in nanoscale thin film state by synchrotron X-ray reflectivity analysis.
Machine Learning for Scattering on Polymers

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With the increase in flux and brightness we experience a tremendous increase in data and the need to further increase the speed of analysis. In addition to the advanced in synchrotron technology we also experience a revolution in computer science with the arrival of machine learning in every aspect of science and computing. In this talk we will highlight our results from applying machine learning to scattering data on polymers. The proposed analysis schemes employ Convolutional Neural Networks as the core algorithm in the reconnaissance of expected events from data gathered in two regimes: experimentally and by simulation. At the interface of physical and digital datasets, we propose classification schemes that exploit complex geometrical structure from scientific images through different machine learning packages, such as MatConvNet and TensorFlow. Our results show correct classification rates over 90% considering thousands of samples from two image modalities: simulated X-ray diffraction and simulated X-ray scattering. Our main contributions are: (a) developing algorithms designed for data that stem from physical experiments; (b) building new software to constrain parameter space, particularly given new hardware; and (c) testing different CNN models for classification of scientific images.
Development of Small Angle X-ray Scattering at Shanghai Synchrotron Radiation Facility

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Small angle X-ray scattering (SAXS) is an important technique in polymer research, so here I introduce the development of SAXS technique at Shanghai Synchrotron Radiation Facility (SSRF). SSRF is briefly introduced at first. There are two SAXS beamlines (BL16B1 and BL19U2) at SSRF currently, which are being operated and are open to users from all over the world. One of both (BL16B) is from bending magnet for general application. Another one (BL19U2) from undulator is mainly served for liquid field, such as proteins and colloid, which can also provide beam time for other fields. The parameters, techniques and devices on the end stations of the two beamlines are introduced. An ultra-small angle X-ray scattering (USAXS) beamline is being constructed and will be completed in 2020, which will be very longer (about 120m) and have larger and higher experiment hall outside the main building of SSRF and can be used more in industry. USAXS beamline will also develop the micro-beam SAXS with smaller beam size and higher flux. On the base of the first two beamlines some techniques have been developed, including simultaneous SAXS/WAXS, GISAXS, GIWAXS and micro-beam SAXS. SAXS-CT and USAXS/SAXS/WAXS/Raman/IR/UV-Vis multi-technique in situ are being developing at SSRF. Those experimental techniques are discussed here. Several examples of polymer science are also presented.
Synchrotron SAXS activities at SLRI to promote industrial and ASEAN user community

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Beamline 1.3W: SAXS/WAXS is dedicated to small/wide angle x-ray scattering experiments at the Synchrotron Light Research Institute (SLRI), Thailand. The beamline has capabilities for nano-structural characterization of materials such as polymer, biological samples, liquid crystals and nano particles, including some limited capability for shape determination of biological macromolecules. The beamline is opened for general users, both from Thailand and abroad. In particular, several programs have been carried out to promote the utilization of the beamline for users from the Association of Southeast Asian Nations (ASEAN) community. The ASEAN workshop on small angle x-ray scattering, the ASEAN synchrotron science camp, the special lectures on the topics of synchrotron radiation applications given at several universities in ASEAN countries are among the activities regularly organized for this purpose. Since the SAXS/WAXS technique is very useful in polymer science, polymer-related industry has been approached and has become regular users of the beamline. Recently, SCG chemical Co. Ltd., one of the largest companies in polymer industry in Thailand, has agreed to co-invest with SLRI for the upgrade of the SAXS/WAXS station. As part of the user support program, a tensile machine as well as temperature controlled sample holder have been developed at the beamline for in-situ experiments. An in-house Matlab-based data processing and analysis software, SAXSIT, has also been developed to support users. The program is freely available and contains several modules for data manipulation such as standard pattern calibration, data normalization and background subtraction and circular averaging of the profile, as well as some fitting modules for data analyses, such as paracrystalline model for lamella structures, WAXS peak profile analyses and liquid crystal phase analyses. The program is continuously developed following the requirement from the users.
2D-Pair Distribution Analysis of Uniaxially Deformed Nanocomposite Gels

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We are very pleased to announce that the 7th SRPS and 4th GISAS will be held at the Gyeongju Hwabaek International Convention Center (HICO), Gyeongju, Korea during September 4-7, 2018. Gyeongju, historically known as "Seorabeol", is a coastal city in the far southeastern corner of North Gyeongsang Province in South Korea [1]. It is the second largest city by area in the province after Andong, covering 1,324 km² with a population of ~260,000 people [2] and numerous low mountains - outliers of the Taebaek range - are scattered around the Gyeongju city [3]. Gyeongju was the capital of the ancient kingdom of Silla (57 BC - 935 AD) which ruled about two-thirds of the Korean Peninsula between the 7th and 9th centuries. A vast number of archaeological sites and cultural properties from this period remain in the city. Gyeongju is often referred to as "the museum without walls". Among such historical treasures, Seokguram grotto, Bulguksa temple, Gyeongju Historic Areas and Yangdong Folk Village are designated as World Heritage Sites by UNESCO [4]. Tourism remains the major economic driver, but manufacturing activities have developed due to its proximity to major industrial centers such as Ulsan and Pohang.

The SRPS and GISAS conference have become one of the world’s leading international events in the field of synchrotron radiation in polymer science. These conferences will cover recent advances in the applications of synchrotron radiation in a broad range of advanced sciences and technologies. For more information, we warmly invite you to visit this conference website: http://www.2018srps-gisas.org. We are looking forward to meeting you in September of 2018 in Gyeongju, Korea.

References
Large thermal hysteresis for volume phase transition of hydrogels achieved by hydrophobic junction of methyl cellulose

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Poly(N-isopropylacrylamide) hydrogel undergoes a reversible volume phase transition from a swollen hydrated state to a shrunken dehydrated state at the critical temperature that called lower critical solution temperature (LCST). To optimize the temperature responsiveness on demand, the modified thermal behavior including shifting of transition temperature, 1-2 stepwise transition over wide temperature range, 3 and large thermal hysteresis 4 was achieved by modifying the chemical structure. In order to achieve a hydrogel capable of programmable volume change, poly(N-isopropylacrylamide)graft-methylcellulose hydrogel (PNIPAm-g-MC) was prepared through the grafting of PNIPAm onto a MC backbone and simultaneous cross-linking of the chains. PNIPAm-g-MC exhibited large thermal hysteresis in its volume change, which results from the stable hydrophobic junctions between the MC strands formed during heating. By combining photothermal magnetite nanoparticles as a heat transducer with the prepared hydrogel, programmable volume phase transition between the shrunken and swollen state could be triggered by visible light irradiation and excessive cooling, respectively. The developed programmable hydrogels are expected to provide a platform for the next generation of origami, microvalves, and drug delivery systems.
Development a combined method of molecular dynamic simulation and synchrotron X-ray absorption spectroscopy (MD-EXAFS) to investigate the atomistic nanostructure of polymer/salt complexes

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The Thailand Synchrotron project was approved by the government in 1996 to develop the Siam Photon Source (SPS). Later, the Synchrotron Light Research Institute (SLRI) was established as a Public Organization under the supervision of the Ministry of Science and Technology. SLRI [www.slri.or.th] is located in Suranaree University of Technology. X-Ray Absorption spectroscopy was one of the very first beamlines which was used by most Thai researchers especially material science. In this work, a novel characterization technique that combines molecular dynamics (MD) simulation and the extended X-ray absorption fine structure (EXAFS) spectroscopy called "MD-EXAFS" method has been developed to investigate the solvation local structure of polymer/salt complexes. These samples were composed of mono- and bi-valence (K⁺ and Ca²⁺) cations mixed with oxygen containing polymers either at side chain or backbone i.e. poly(vinyl alcohol) (PVA), poly(acrylic acid (PAA) and poly(ethylene oxide) (PEO). This method gives useful information at the atomistic scale including the average distance between atom pair around the probed cation and its coordination number. Comparison between MD-EXAFS with the experimental spectra gave overall good agreement for both frequency and amplitude of the signal oscillations. For PVA and PAA systems, it is obvious that there is only one dominant shell from oxygen atoms around cations. The distance between the ions and oxygen atoms in the first shell is in good agreement with experiment within ± 0.1 Å. For the cation K-edge EXAFS spectrum of PVA/salt and PAA/salt samples, there is no evidence for the formation of contact ion pairs. These cations can induce the conformational changes of PVA and PAA backbone. On the other hand, PEO/salt complexes exhibit quite different behavior. Cations can coordinate with anions as well as coordinated to ether oxygen and the conformation around C-C bond prefer the gauche state and PEO becomes more compact shape. This MD-EXAFS technique should be a powerful method to elucidate the detailed solvation structure of the probed ion in polymer matrix at the atomistic scale.

References
Synchrotron Infrared spectroscopy: Opportunities and challenges for polymer science

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Many breakthrough advances that are often at the cutting edge of technological development take place at synchrotron facilities. In the case of IR spectroscopy, the last decade has seen important developments in infrared instrumentation incorporated to and developed at synchrotron facilities to take advantages of the characteristics of the bright synchrotron source.

In this presentation, we will describe the origin and nature of synchrotron infrared micro-spectroscopy and nano-spectroscopy, highlighting some of the key developments that have made an impact in the study of macromolecular materials, and illustrating several applications in the area of polymer science.

Most of the study so far have been concentrated in using an infrared microscope, with a micron-scale resolution only limited by diffraction. There have been many applications extending from the study of compositional heterogeneity in multicomponent systems to the study of structured materials or dynamic processes. Some examples will be shown during the presentation.

Imaging is a key property, which is exploited at synchrotron facilities. 2D spectroscopic images have been exploited to identify interphase transition, and the advent of two-dimensional (2D) focal plane array (FPA) detectors with synchrotron source has allowed the study of dynamic processes such as phase separation or degradation.

Infrared tomography is also very potential in polymer science, even though poorly exploited up to now. We will show some example showing the attractiveness of such a technique, that combines the high brightness source (synchrotron), and Focal Plane Array detector.

The recent coupling of synchrotron radiation with AFM-based technology is an exciting new field, since nanoscale domains can be studied, as this is reported on Ref. 1. There are two approaches for nanoIR spectroscopy and imaging (scattering effect and thermal effect) and both approaches will be detailed.

Even though infrared lasers are becoming more and more available for spectroscopy in the mid infrared, synchrotron infrared light display unraveled properties such as very wide energy domain, and extreme beam stability, both are crucial in the study of polymer materials.

References
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Nano-Plasmonics: from single-molecule chemistry to infrared nanoscopy

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My research group at SNU focuses on gaining deeper understanding of nanoparticle plasmonics, and widening its application to single-molecule chemistry and nano-imaging. First, I will show that surface-enhanced Raman spectroscopy (SERS) of single molecules can reveal angstrom-scale surface structures: a common wisdom of nano-plasmonics is that the optical property is completely determined by the overall geometry of nanostructures (sizes, shapes, and gap-distances), despite the fact that real metallic surfaces have atomic surface defect structures and diffuse electron densities extending beyond metallic boundaries. This classical picture of plasmonics leads to the belief that plasmonic length-scale (size of localized field distribution) cannot usually go below ~10 nm. I will present spectroscopic evidences that the plasmonic hotspots can be as small as 1 angstrom, and discuss its implication in molecular spectroscopy, photochemistry, and nano-scale imaging. Second, I will demonstrate the use of infrared plasmonics to visualize the crystallographic structures of 2D-materials and its electro-optical properties. Specifically, I will show that infrared near-field microscopy reveals stacking-domains of few-layer graphene, and also show that differently stacked graphene domains have drastically different infrared plasmonic properties.
Property and Utilization Research of Infrared Synchrotron Radiation

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More than 20 infrared beamlines are available in many synchrotron facilities in the world, and they have contributed to the science in various fields. Important features of the infrared synchrotron radiation are a high brilliance and a broadband property. At the infrared beamlines, a representative measurement technique is micro-optical spectroscopy. Recently, some advanced techniques have developed, namely, infrared near-field spectroscopy[1,2] and infrared tomography[3].

Usually a thermal radiation source such as a ceramic heater is used as a conventional broadband infrared light source, and it is equipped in a commercial infrared spectrometer. Figure 1 shows the brilliance estimation and the spot size at the focus point of the microscope. In the estimation, parameters of BL43IR, infrared beamline at SPring-8, are used for synchrotron radiation and the formula of black body radiation are used for the thermal radiation. The brilliance of the synchrotron radiation is more than two order of magnitudes higher than that of the thermal radiation. Owing to the high brilliance, the synchrotron light can be focused on a smaller area with a higher peak intensity as seen in Fig. 1. The compatibility of the high brilliance and the broadband properties is also an important feature of the synchrotron radiation. BL43IR covers from 10000 to 100 cm⁻¹. At BL43IR, we prepare the apparatuses for doing micro-optical spectroscopy under various conditions, for example, high temperature, low temperature, high magnetic field, high pressure, humidity-controlled condition, wet condition, UV irradiation, electric field, and their combinations. Science fields at BL43IR include polymers, physics, biology and medicine, industrials, archeology, materials, pharmacy and instrumental development. I will briefly introduce recent studies at the conference.

Figure 1  Brilliance estimation and spot size of the synchrotron radiation and the thermal radiation.

References
High-Resolution Macro ATR-FTIR Microspectroscopic Technique at Australian Synchrotron IR Beamline and Its Applications for Polymer and Composite Materials

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Two models of macro ATR-FTIR devices were developed at Australian Synchrotron IR Beamline. The use of Ge and ZnSe hemispheres as ATR elements essentially reduces the beam focus size and the mapping step size relative to the stage step motion, resulting an improved lateral resolution critical for high-resolution mapping capabilities. At this stage, macro ATR-FTIR measurements at Australian Synchrotron IR Beamline can be performed at minimum beam focus sizes of 1.2 μm with 32× objective (NA = 0.65) and 1.9 μm with 20× objective (NA = 0.60), and a minimum mapping step size of 250 nm [1,2].

The first available model, “hybrid macro ATR-FTIR” (Fig. 1A), uses Ge ATR elements with different contact facet sizes (i.e. 1 mm, 250 μm and 100 μm in diameter) – each offers a different pressure level to suit both fragile, soft and hard materials [3–5]. The hybrid macro ATR-FTIR device can be coupled to a temperature control unit for temperature-dependent study such as analysis of dairy products at 4 °C (Fig. 1B).

The other model, “soft-contact piezo-controlled macro ATR-FTIR”, was designed specifically for analysis of very delicate and sensitive surfaces, such as polymer multilayer films (Fig. 1C). This device uses a unique combination of piezo-controlled linear translation stages to achieve precise positioning and gentle approach of the sample towards the ATR sensing facet, which can be set as small as 50 nm [1].

The development of these two macro ATR-FTIR devices has led to successful surface characterisation of samples from a diverse range of research. Successful applications in polymer and composite material science include biolubricant multilayer films, single fibres, surface coatings, and biodegradable polymer composites.

References
Structural analysis using scattering contrast from SAXS and SANS

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Various nanostructure and nanoscale building blocks are being fabricated using soft-materials targeting unique physical, chemical, and mechanical properties by controlling orientations, densities, or locations of constituting molecules via self-assembly. Especially, by taking advantage of the temperature dependent phase behavior of block copolymers in water, thermos-responsive self-assembled structures of conjugate polymers are demonstrated. Small angle x-ray scattering combined with small angle neutron scattering provided structural information on these self-assembled and ordered systems that is much more than just periodic length scales. The scattering contrast provided by the neutron and x-ray, without the need of deuterating polymers, helped identify the distribution of conjugate polymers in the template, which showed unique thermos-reversible conductive property.
SANS Study on Thermoreversible Physical Gels Crosslinked with DNA

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We developed a “physical Tetra-PEG gel”, in another word, a “DNA-module gel”. As shown in Figure 1, tetra-functional PEG modules are crosslinked with end-modified double-stranded DNA. This gel has two features; (1) the structural heterogeneity is expected to be significantly reduced compared to general physical gels, and (2) because of the specificity of the double helix of dsDNA, the aggregations on the crosslinking point, which is a general feature for physical gels, can be reduced. DNA-module gel could be an ideal material to understand the physical properties of physical gels. Dynamic viscoelasticity (DVE) measurements showed that the DNA-module gel underwent a reversible sol-gel transition around 72 °C by heating/cooling. Changes in the structure and dynamics were investigated by small angle neutron scattering (SANS) and dynamic light scattering (DLS), respectively. Firstly, two Tetra-PEG solutions carrying sense and anti-sense DNAs were mixed at 90 °C, and SANS/DLS were measured. The SANS showed a distinct peak as shown in the figure. By decreasing temperature, sol-to-gel transition occurred and the peak disappeared, and the SANS functions became similar to those of Tetra-PEG chemical gels as shown in the lower-most curve. By re-heating, the scattering peak re-appeared above the gel-sol transition temperature. The details of the SANS as well as DLS analysis will be given in the presentation.

Fig 1. An illustration of (a) tetra-PEG gel crosslinked with covalent bonding and (b) tetra-PEG gel physically crosslinked with double stranded DNA.
We investigated the diffusion dynamics of entangled polymer thin films confined between graphene oxide (GO) sheets by using neutron reflectivity\(^1\). We prepared the bilayer of polymethylmethacrylate (PMMA) and deuterated PMMA sandwiched between GO monolayers by employing a Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques\(^2\). We found that diffusion coefficient of the PMMA became 30 times slower when the polymers were near the GO surface. This is due to the attractive interaction between the polymer matrix and the GO. The dynamics of polystyrene was reduced only 3 times by the GO confinement, compared to the bulk PS. This is in a good agreement with dewetting results where the dewetting of the PMMA thin films were completely prevented by the GO\(^3\), and assembled block copolymer results where the PS-b-PMMA block copolymer domains were vertically oriented on the GO surfaces\(^4\).

References
Real-space molecular motion of water observed with inelastic X-ray and neutron scattering

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Viscosity is a fundamental property of liquid; and yet, the understanding of its microscopic origin is insufficient despite an immense amount of studies. Recent progress in inelastic x-ray/neutron scattering makes it possible to obtain inelastic scattering spectra over a wide range of energy transfer ($E$) and momentum transfer ($Q$) with a high $E$- and $Q$-resolution, thereby converting dynamic structure factor, $S(Q,E)$ into the time-dependent pair correlation function, called the Van Hove function, $G(R,t)$ [1] via double Fourier transformation. With this novel approach, we have determined the spatial and temporal correlations of molecular motions of water [2] and its temperature variation [3] on picosecond in time scale and sub-nanometer in length scale. The results show that the time-scale of the decay in the Van Hove function is directly related to the Maxwell relaxation time, $\tau_M$, which is defined by macroscopic viscosity and instantaneous shear modulus. The results validate our earlier finding that the topological changes in atomic/molecular connectivity govern the viscosity of liquids. The approach used in this study offers a powerful experimental technique for investigating local real-space dynamics of liquids and can be used for various liquids and non-crystalline samples.

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References
Instrument development to perform In-Situ GISAXS Experiments on 3C SAXS1 Beamline of PLS

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The grazing incidence small-angle X-ray scattering beamline 3C of the Pohang Light Source (PLS) was used to investigate the structure of surface and interface of thin film. During recent years, the in_situ instruments at this beamline has developed in order to investigate structural change of thin film under a wide range of well defined and controllable environments and the details of a newly constructed instruments are presented.

The major in_situ devices are a cryo_device, a high temperature device, and a solvent vapor adsorption device. They were designed considering environment adjustment possibility, user accessibility and safety. The cryo_device for observing the crystal growth and phase change at low temperature was adjusted from -180 °C to 150 °C using liquid nitrogen and heater for temperature control. The high temperature device is applied to the observation of the pore formation of inorganic substances or the structure of nanoparticles and it was allowed to raise to 1000 °C.

The solvent vapor adsorption device for adsorbing solvent vapor on porous coordination polymer films or for solvent annealing of organic thin films can inject solvent an amount of several ul. Each device has a control system and program that enables In_Situ GISAXS experiment (Fig.1) The performance of the instrument is illustrated through several different measurements, including (1) GIWAXS for polymer crystallization at low temperature, (2) GIWAXS for polymer blends in the solvent vapor, (3) GISAXS for pore formation in inorganic film at high temperature.

We confirm that various studies such as the following can be performed through in_situ GISAXS experiments: (1) phase transition of crystallite in organic film (2) pore formation in inorganic films with temperature, (3) structural changes of self-assembled organic thin film with solvent annealing.

References
Development of Simultaneous Measurement System of FTIR, WAXD and SAXS Data for the Study of Hierarchical Structure Change of Polymers Subjected to the Various External Fields

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The simultaneous measurement of a variety of characterization data is important when the so-called soft materials like synthetic polymers are studied from the various hierarchical structure levels. We have developed the simultaneous measurement systems in which the experimental data of the synchrotron wide-angle and small-angle X-ray scatterings and transmission FTIR spectra are collected at a high time-resolution for polymer substance subjected to such various kinds of external field as temperature, tensile force, solvent vapor atmosphere, high electric field and so on [1]. One example is shown in Figure 1, where the temperature jumping cell is set on the sample stage. A miniature FTIR spectrometer surrounds the sample stage, the 2D WAXD (wide-angle X-ray diffraction) is detected with a flat panel detector located at about 5–10 cm from the sample, and the 2D SAXS (small-angle X-ray scattering) is measured using a CCD detector with an image-intensifier. The temperature jumping cell is useful for the study of isothermal crystallization of the molten polymer sample at a constant temperature. The SAXS data gives us the information of higher-order structural evolution process: the creation of small domains consisting of short helical chain segments, the increasing correlation between these domains and the final formation of crystalline lamellar stacking structure. The WAXD data clarifies the formation of crystal lattices in the crystalline lamellae. The transmission FTIR spectra tell the appearance and growth of regular helices in the melt. Figure 2 shows the evolution process of isotactic polypropylene from the molten state to the constant crystallization temperature [2]. Another type of the simultaneous measurement system developed by us is to detect the effect of high electric field on the hierarchical structure change of poly(vinylidene fluoride) film. The application of high electric field causes the inversion of polar polymer chains and the structure transformation between the different crystal forms [3]. Some details are presented in the lecture.

References
DSC and Simultaneous SAXS/WAXS studies on Crystallization of Poly(L-Lactic Acid) Based Nanocomposites

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Poly (L-lactic Acid) (PLLA) is the most frequently used biobased polymer due to its biodegradability and favorable mechanical properties. However, some properties such as slow crystallization and low crystallinity restrict its industrial applications. In order to overcome these limitations, a number of fillers from organic and inorganic origin have been investigated over the past few decades to reinforce the PLLA materials. In view of this, the current work has been focused on silk nanocrystals (SNC) as a filler to reinforce the PLLA matrix. SNC used for this investigation was prepared in the laboratory from the Muga Silkworm by the acid hydrolysis treatment [1]. The PLLA/SNC nanocomposites were prepared by solution-casting method with dichloromethane as the solvent. The effect of SNC content on the crystallization behavior of PLLA was investigated by differential scanning calorimetry (DSC) and simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements. For the isothermal crystallization, the samples were melted at 200°C for 5 minutes and immediately cooled to 120°C and allowed to crystallize for 60 min. The kinetics of isothermal crystallization is described by the well-known Avrami equation. Fig. 1 shows the DSC analysis for the PLLA and PLLA/SNC nanocomposites isothermally crystallized at 120°C. It indicates that the addition of SNC increased the crystallization rate of PLLA. The Avrami exponent n does not change with the inclusion of SNC. The results of synchrotron SAXS/WAXS simultaneous measurements will be discussed in detail in the presentation.

Figure 1. Results of the DSC isothermal crystallization measurements at 120°C upon quenching the specimen from 200°C (a) Heat flow as a function of time, (b) the Avrami plots, and (c) the crystallization rate constant (k) as a function of the loadings of SNC.

References

Synthesis and Self-Assembly of Cyclic Polymers and Structural Analysis of the Molecular Aggregates

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Cyclic polymers with a variety of chemical structures were synthesized, and self-assembly was performed. The formed molecular aggregates were investigated using various measurement techniques finding unique characteristics arising from the topology.
Structure and Properties of Complex Coacervate Core Micelles

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Complex coacervation is a liquid-liquid phase separation when two oppositely charged polyelectrolytes are mixed in aqueous solution. It has been known that the complex coacervation is driven by entropic increase due to counter-ion release and by electrostatic interaction between oppositely charged moieties. Because of low interfacial tension and hydrophilicity, complex coacervate has been applied to the field of pharmacy and food industry. In particular, it is appropriate for the storage and release of charged or hydrophilic drugs. Complex coacervate core micelles (C3M) are formed by simple mixing of AB and A’B diblock copolyelectrolyte solutions in aqueous solution where A and A’ are oppositely charged blocks, and B is neutral and hydrophilic block (e.g., PEO). In this study, we investigate the structure of C3M as a function of molecular weight of charged block, pH, and salt concentration by dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS). Since the charged moieties are introduced by post modification of mother block copolymers, charge imbalance issue can be neglected. The results reveal that the relatively monodisperse C3Ms are formed by simple mixing, and overall micelle size and core radii reduce as salt concentration increases, and followed by C3Ms disappears above a critical salt concentration. In particular, we observed scaling relationship between core dimension and molecular weight of charged block, which is analogous to traditional block copolymer micelles.
Effect of Hydration in Corona Layer on Structural Change of Thermo-responsive Polymer Micelles

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Amphiphilic block copolymers are well-known to self-assemble into polymer micelles consisting of hydrophobic core and hydrated corona in aqueous solution. Polymer micelles are expected to be drug vehicles in drug delivery system (DDS) owing to their suitable size, stability, and so forth. For the drug targeting in DDS, to introduce stimuli-responsiveness, such as thermos- and pH-responsiveness, to polymer micelles has been required. Thermo-responsiveness should be given by introducing phase transition, such as LCST and melting, to polymer micelles. In the case of thermos-responsive polymer micelles made by introducing a phase transition in hydrophobic core, if the hydration in corona layer is robust, it should be have significant effects on structural change in the micelles. Thus, in this study, we investigated effects of hydration in corona layer on structural change in thermo-responsive polymer micelles consisting of strongly hydrated corona and hydrophobic crystalline core.

Poly(N-vinyl pyrrolidone)-block-poly(n-octyl acrylate) (PVP-b-PODA) synthesized RAFT polymerization was used as an amphiphilic block copolymer. The melting temperature of PODA ($T_m$) is 40 ºC. Aqueous solution of PVP-b-PODA micelles is prepared by dissolving PVP-b-PODA in nano-pure water at 1.0 mg/ml and homogenizing with ultrasonic homogenizer. For the resulting PVP-b-PODA micelle solutions, small-angle X-ray scattering (SAXS) measurements were performed at BL-40B2 of SPring-8, Japan. Two-dimensional SAXS images obtained by an imaging plate were concerted to one-dimensional scattering intensity $I(q)$ versus the magnitude of scattering vector $q$ profiles by circular averaging.

Figure 1 shows change in SAXS profiles of PVP-b-PODA micelles with elevating temperature. SAXS profile measured at 25 ºC ($< T_m$) shows $q^2$ dependence of $I(q)$ in $q < 0.1$ nm$^{-1}$, suggesting that the PVP-b-PODA micelles take disk-like shape. The SAXS profile at 25 ºC well agree with the solid line which is the scattering curve calculated for core-shell disk. Therefore, PVP-b-PODA micelles take disk-like shape owing to crystallization of PODA. On the other hand, in SANS profile at 60 ºC ($> T_m$), $q^2$ dependence of $I(q)$ in low $q$ region is disappeared. The dashed line on the SAXS profile at 60 ºC is the scattering curve calculated for oblate particle. Therefore, it is considered that melting of PODA causes structural change of PVP-b-PODA micelles from disk to oblate. However, taking molecular characteristics of PVP-b-PODA into account, structural change from disk-like to spherical shape has been predicted. Hence, it seems that the memory of disk-like shape still remains at 60 ºC. The shape memory effects should be caused by robust hydration of PVP chains in corona layer. It has been known that PVP is dehydrated at 70 ºC. As shown in Figure 1, SAXS profile at 70 ºC is much different from that at 60 ºC. The dotted line on the SAXS profile is calculated for core-shell sphere. Therefore, PVP-b-PODA micelles take spherical shape at 70 ºC, indicating that dehydration causes second structural change. Inevitably, it is concluded that robust hydration in corona layer causes shape memory effect on structural change in polymer micelles and the memory is erased by dehydration.

Figure 1 SAXS profiles of PVP-b-PODA micelles measured at 25, 60, and 70 ºC in heating process. Solid, dashed and dotted lines are theoretical scattering curves calculated for core-shell disk, oblate and sphere, respectively.
Quantitative X-Ray Scattering Studies on Micellar Morphologies of Topological Amphiphilic Block Copolymers

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Synchrotron X-ray scattering measurements were conducted on the polymer micelle of a cyclic poly(n-butyl acrylate-b-ethylene oxide) and its diblock and triblock counterparts formed in aqueous solutions. The obtained X-ray scattering data were treated with all available quantitative analytical methods: Guinier analysis, indirect Fourier transformation analysis, two phase sphere model analysis, two phase ellipsoid model analysis, and three phase ellipsoid model analysis. In addition, the validity and limitation of each method were evaluated with respect to the range, precision, and accuracy of the obtainable structural parameters. All scattering data analysis methods considered in this study were found to be able to provide information on the formation and morphological structure of micelles formed by the topological polymer amphiphiles. The range, precision, and accuracy of the structural information, however, varied significantly depending on the analytical methods. The rigorous evaluation identified that the recently developed three phase ellipsoid model analysis could provide a much wider range of information with higher precision and accuracy levels regarding the micellar morphology based on the cyclic amphiphile and its linear diblock and triblock counterparts, compared to the other analytical methods.

Overall, the molecular topologies of the amphiphilic block copolymers have been identified to heavily impact the shape of micelle and the structural composition of micelle corona, in which the differences in the micellar morphologies of the cyclic amphiphile and its linear diblock and triblock counterparts have been parameterized and made clear by the three phase ellipsoid analysis scheme whereas the other analytical methods have been unable to do so with high precision and accuracy. Additionally, the three phase ellipsoid method has specified in more detail the influence of the molecular topology to the micelle size, aggregation number, and core stability (i.e., micelle stability).

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Solvent size dependent structure of diblock copolymer micelles in \( n \)-alkanes

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Block copolymers can self-assemble into micelles in selective solvents. Generally, theoretical description for the micelle structure considers the balance between the chain stretching of core and corona block (i.e., entropic contribution) and the unfavorable interaction between core block and solvent (i.e., enthalpic contribution) with the assumption that the core is melt. In practical, solvent molecules can penetrate into the core by the solvent entropy effect.

In this research, we investigate the detailed micelle structure of poly(styrene-\( b \)-ethylene-\( alt \)-propylene) (PS-\( b \)-PEP) in \( n \)-alkanes (C\(_n\)H\(_{2n+2}\), \( n = 8, 10, 12, 14, 16 \)) as a function of solvent size and temperature to tune the unfavorable interaction between PS core and alkane systematically. Solubility parameter calculation shows that smaller solvent results in more unfavorable interaction. The combination of small-angle X-ray scattering (SAXS) and static light scattering (SLS) were used to investigate detailed micelles structure such as core radius, solvent fraction in the core area, and aggregation number.

We observed that the critical micelle temperature (CMT) decreases as the solvent size becomes smaller, which indicates that the solvent entropy effect becomes significant to control micelle structure rather than solubility parameter (i.e., enthalpic contribution). For the micelles the core radii in all solvents are nearly similar to two times of \( <R_g> \), where \( <R_g> \) is the unperturbed radius of gyration of the core block, which indicates that the core block conformation has nearly fully relaxed. In addition, the solvent fraction in the core of a smaller size solvent, which is more easily penetration into the core, appears larger at all temperatures. In addition, we observed that all data is overlapped when properties are plotted versus CMT-T, indicating that micelle structure is systematically controlled by solvent size of the same unit. The results are discussed in terms of current understanding of block copolymer micelles.

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Micelles have been widely used for many applications in daily life, including cosmetics, soups, detergents, and drug delivery, as well as them being key materials in nanotechnology. Spherical micelles are one of the various types of micelle that have been extensively studied over the past hundred years. The aggregation number ($N_{agg}$) of micelles is not typically fixed but instead varies across a certain distribution, which depends not only on the molecular structure and its concentration but also on the environment, including solvent conditions and temperature. In contrast to the conventional micelle system, we recently identified no variation of $N_{agg}$ of spherical micelles composed of calix[4]arene-based amphiphiles, in which electrolyte functional groups are attached to the upper rim and alkyl chains are added to the lower rim. Owing to the presence of a triazole ring between the calix[4]arene moiety and the electrolyte group as a spacer, the conformation of the surfactants would be cone-shaped due to the electrostatic intramolecular repulsions in the headgroup, which satisfies the geometric balance needed to form spherical micelles. In addition, $N_{agg}$ varies depending on the functional group in the hydrophilic part and the length of the alkyl chains, being one of a range of numbers including 2, 6, 8, 12, 20, and 32.[1] Since some of these numbers coincide with the vertex numbers of Platonic solids (regular polyhedrons), we named these micelles “Platonic micelles.”

In this study, we attached polyethylene glycols (PEGs) as non-ionic hydrophilic groups to the upper rim of calix[4]arene-based amphiphiles (denoted by PEGₘCaL₅, as shown in Figure 1: $m$ indicates the molecular weight of PEG and the suffix number is the number of carbons in each alkyl chain) in order to discuss the effect of the non-ionic functional groups on the aggregation behavior into Platonic micelles. The amphiphile conformation would be cone-shaped, which is necessary for the formation of spherical micelles, owing to the high flexibility of PEG and the large exclusion volume in water. We also characterized the structures of the micelles bearing PEGs and investigated the effects of the molecular weight of PEG on the aggregation behavior of the micelles.

Figure 2 shows the small angle X-ray scattering (SAXS) profiles of PEGₘCaL₅ micelles in 50 mM aqueous NaCl solutions. At the low-$q$ region of all SAXS profiles, the asymptotic behavior satisfies $I(q) \sim q^{l}$, indicating that the micelles are isolated without the formation of secondary aggregations. The first minimum position of the scattering profiles is shifted to the low-$q$ region with increasing molecular weight of PEG, suggesting an increase of micellar size. In fact, the gyration radius ($R_g$) of the micelles determined by a Guinier plot increases with increasing PEG molecular weight. The weight-averaged molar mass ($M_w$) of the micelles determined from the intercept values [$I(0)$] extrapolating the scattering intensity to zero angle were $3.90 \times 10^4$, $4.18 \times 10^4$, and $2.99 \times 10^4$ g mol⁻¹ for PEG₅₅₀CaL₅, PEG₁₀₈CaL₅, and PEG₂₅₆CaL₅, respectively. The $N_{agg}$ values were calculated from the respective $M_w$ values, giving $N_{agg} = 12$, 8.0, and 3.5 for the micelles of PEG₅₅₀CaL₅, PEG₁₀₈CaL₅, and PEG₂₅₆CaL₅, respectively. These values indicate that the formation of Platonic micelles.

References
Microstructural investigation of butt-fusion joint in HDPE pipes using wide and small-angle X-ray scattering

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Polyethylene pipes in gas and water applications have proven to be reliable over their 70 years of successful use. The obvious advantage of polyethylene over the conventional metal-based pressure pipes is that they maintain exceptional resistance to corrosion and chemical attacks. In recent times, the application of polyethylene pipes has extended into areas where their safe performance is critical to maintaining the structure integrity of the piping system. Such applications include safety class pipes in nuclear power plants and large diameter pipes for conveying and/or storing greater scale volume of water. In designing a sound polyethylene piping system, the structural integrity of the joints between pipes is of importance. There are variety of joining methods available for polyethylene pipes that include butt-fusion, electro-fusion, mechanical joint, etc. Among them the butt-fusion method is the most widely used for joining larger diameter pipes. During butt fusion, a melt fusion zone (MFZ) is formed, which contains various morphologies due to the difference in flow behavior within MFZ. It has been reported that in polyethylene and polypropylene pipe butt-fusion joints, cracks were seen to initiate in the zone between the oriented crystallinity and fine spherulites. Through various studies it was observed that the ordering between crystal lamella and amorphous region as well as molecular orientation are crucial in giving rise to butt-fusion joint integrity.

In this work for the first time 2D wide and small angle X-ray scattering (WAXS/SAXS) techniques were applied to investigate the microstructure of MFZ in butt-fusion joint of HDPE pipes.
Effects of A Liquid-type Nucleation Agent on Isothermal and Non-isothermal Crystallization Behaviors of Poly(L-Lactic Acid) as Revealed by synchrotron SAXS / WAXS

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INTRODUCTION
Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible polymer. Moreover, PLLA can be synthesized from renewable sources such as sugar, carbohydrate, etc. In recent several decades, scientists are interested in PLLA because of environment-friendly characteristics. However, there existing some big problems of PLLA, which are low crystallization rate and low crystallinity. In order to overcome such drawbacks, nucleation agents have been incorporated into PLLA. In this study, we added a special liquid-type nucleation agent (organic acid monoglyceride; OMG) into PLLA in order to increase the crystallization rate and to reduce the induction period, and we conducted time-resolved small and wide-angle X-ray scattering (SWAXS) to follow crystallization of PLLA/OMG.

EXPERIMENTAL
There are two types of neat PLLA samples such as PLLA4032D (1.4 % D-content: D1.4) and PLLA2500HP (0.5 % D-content: D0.5) from Nature Works and PLLA with OMG (1% addition) such as D1.4/OMG and D0.5/OMG specimen. The time-resolved SWAXS measurements in each 5s step were conducted at BL-6A beamline in KEK, Tsukuba, Japan upon temperature jump from 200°C to 110.2°C (cooling rate was approximately 385°C/min, T-jump was completed within 14s). The wavelength of the X-ray (λ) was 0.150 nm. In order to determine the induction period of crystallization, we examined temporal evolution of the most intense reflection peak which is overlapping (200) and (110) reflections. Computational peak decomposition was conducted to separate the peak from the amorphous halo peak.

RESULTS AND DISCUSSION

WAXS results
The crystallinity is plotted as a function of time in Fig. 1. The plots of crystallinity show a tendency such that PLLA/OMG has higher crystallization rate in an early stage. The crystallinity increases up to 42% finally, excepting for D0.5/OMG. Although this specimen showed the most rapid crystallization, the ultimate crystallinity was lowest (at t = 2500s). It is speculated that the morphology of the higher-order structure for D0.5/OMG is different from those for the other specimens, as a result of the very rapid crystallization which may induce self-termination of the crystallization around t = 300s. Namely, very quick crystallization may induce higher order structure which automatically terminate the further crystallization.

SAXS results
The lamellae thickness (L) and long period (D) are evaluated from the 1d-SAXS profiles by using correlation function γ(r):

\[ \gamma(r) = \frac{\int_0^\infty I(q)q^2 \cos(qr)dq}{\int_0^\infty I(q)q^2dq} \]

As clearly seen in Fig. 2, the lamellar thickness increases as a function of time. The lamellar thickness increases in early stage (<500 s) and turns to stabilization. The linear fitting of the increasing tendency in the early stage was made to evaluate the rate of growing of the lamellar thickness. The rate was found in the following order: D1.4 < D1.4/OMG < D0.5 < D0.5/OMG. Thus, the thickening rate of lamellae is found to be affected by the nucleation agent OMG and the amount of D-content. Furthermore, by focusing on the ultimate value of the lamellar thickness, the specimens with OMG have thinner lamellar thickness. This result shows a good agreement with the DSC result that...
the specimens with OMG have lower melting temperature than the neat PLLA specimens.

Grain Coarsening on the Free Surface and in the Thickness Direction of a Sphere-Forming Triblock Copolymer Film

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Control of block copolymer “grain”, in which the microdomains regularly order in a single lattice, is significant to develop high-performance polymeric materials. This is because the grain, of which size is several micrometers, is considered to affect properties directly. In this regard, we focus on the grain coarsening on the free surface and in the thickness direction of a sphere-forming triblock copolymer film. We evaluated the grain size on the free surface using atomic force microscopy combined with the image processing1, and in the thickness direction using the small-angle X-ray scattering edge-view measurements2. The significant findings of our study is that the grain coarsening was found to be independent for both cases with different values of the growth exponent (alpha), as the grain growth follows a power-law behaviour with the thermal annealing time (t): (Grain size ~ t^alpha). For the case of the grain coarsening on the free surface alpha = 0.7 and for that in the thickness direction alpha = 1.8 are found, as shown in Fig. 1. Another notable finding is that the thickness of the oriented layer near the free surface or near the surface contacting to the substrate is as large as 3 µm, which is even larger or comparable with the reported values3 of the propagation distance of the surface-induced orientation of the spherical microdomains. It is speculated that the grain growth plays an important role as a propagator of regular ordering of spherical microdomains.

Fig. 1 Double logarithmic plots of the grain size on the free surface and in the thickness direction as a function of the thermal annealing time. \(d_{tot}\) denotes the total film thickness.

References

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Amphiphiles, such as surfactants, lipids, and copolymers, spontaneously assemble to form micelles in aqueous solutions with a well-defined size or shape and a certain number of molecules, so-called aggregation number ($N_{agg}$). According to the thermodynamics of micelles, it has been suggested that there are multiple equilibria between the $N$-mer and the $N+1$-mer. For spherical micelles, the standard chemical potential for the amphiphile $\mu_N^{\theta}$ has a minimum at a certain value $N$, which is determined by the balance between the volume and/or repulsion among the hydrophilic groups and the hydrophobic coagulating attraction among the hydrophobic groups.

We recently found that calix[4]arene-derived surfactants form spherical micelles with a defined, monodisperse $N_{agg}$ value of 4, 6, 8, 12, or 20, corresponding to the Platonic solids. We had postulated that $\mu_N^{\theta}$ may not be a continuous function of $N$ when $N$ is sufficiently small, and this may be the reason for the appearance of micelles with Platonic numbers in $N_{agg}$. The $N_{agg}$ number can be controlled by the solution conditions. For example, it has been reported that QACaL5 (Figure 1) exhibits $N_{agg} = 12$ at a NaCl concentration ($C_{NaCl}$) of 50–100 mM and $N_{agg} = 20$ at $C_{NaCl} = 200$ mM. This $N_{agg}$ change may be caused by a decrease in the volume of the hydrophilic moiety (the green part in Figure 1), which is due to reduced electrostatic repulsion at higher $C_{NaCl}$. In the present study, we investigated how $N_{agg}$ changes when $C_{NaCl}$ is abruptly increased in the QACaL5 micelles through time-resolved small-angle X-ray scattering (TR-SAXS) combined with rapid mixing by a stopped-flow device.

Figure 1 shows the time evolution of $N_{agg}$ after the rapid increase in $C_{NaCl}$, determined from the SAXS profile at each time. An abrupt increase in $N_{agg}$ was observed after an induction time of approximately 60 s, and that such a long induction time was not observed in other studies on micelles. Usually, time evolution of $N_{agg}$ in micelle formation can be described by a stepwise insertion model involving only micelles and unimers without intermediate states. For such a model, the molar fraction of the amphiphile is a continuous function of $N$. However, our previous study showed that QACaL5 can adopt only one state: $N_{agg} = 12$ at the low $C_{NaCl}$ and $N_{agg} = 20$ at the high $C_{NaCl}$. Therefore, one can assume that there are only three equilibria when we increase $C_{NaCl}$, namely, 12-mer $\rightleftharpoons$ unimer $\rightleftharpoons$ 20-mer. We tried to reproduce the induction period by choosing an extreme rate constant between two species, but no combinations of the parameters gave an induction time.

Hence, we consider another kinetic pathway: fusion and fission. That is, two micelles of $N_{agg} = 12$ fuse to form a micelle of $N_{agg} = 24$, followed by a fission process. We have found that this kinetic model can reproduce the long induction time. In the presentation, we will explain the theoretical model in detail and show experimental results of the dependence of $C_{NaCl}$ on the induction time.

Figure 1. Chemical structure of QACaL5 and a cone model to represent its shape (upper) and time evolution of the aggregation number (bottom).
Silver Nanoprism Nanocellulose Film as Surfaced-enhanced Raman Scattering Substrate

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The features of templates, such as physical dimensions or functional groups, often affect the in situ growth process of nanoparticles. In this study, a rapid thermal synthesis method was adopted for the synthesis of Ag nanoprisms (AgNPRs) on cellulose nanofibrils (CNF), which were obtained via defibrillations of holocellulose. The produced nanocomposites were examined for their optical and physical properties using ultraviolet-visible spectroscopy, transmission electron microscopy and X-ray diffraction. The results demonstrate that the reduced of the fibres into nanosize and carboxylate functional groups presented on the cellulosic template promote the formation of AgNPRs. The surface-enhanced Raman scattering (SERS) activity of the CNF-AgNPRs composite was studied and exhibited a higher enhancement, compared to the spherical AgNPs-anchored CNF. The CNF prepared from carboxylated holocellulose not only served as nanoparticles support for the SERS application, it also facilitated the formation of AgNPRs that resulted in a better enhancement SERS signal.
Design, Synthesis, and Characterization of Block Copolymers with a High Interaction Parameter

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Nanotechnology and semiconductor industries have embraced a directed self-assembly of block copolymers as one of next-generation lithographic tools to access sub-10 nm technical node.[1-2] To achieve the ultimate goal, tailoring properties and structures in block copolymer materials is required, which has been one of significant and challenging aspects in polymer science. In this talk, we will discuss the design of block copolymers that can extensively push the limit of a critical dimension to sub-10 nm regime.

In order to achieve the ultimate goal, the structure of the copolymer should be designed to exhibit high interaction parameter ($\chi$) for microphase separation at low degree of polymerization.[3] In addition, it is equally important to find effective synthetic routes.[4] We will first discuss the design principle to desire a high interaction parameter. In the designs, one of the blocks was selected from various conventional polymers, polystyrene, poly(hydroxystyrene), and poly(vinyl pyridine), which have been widely utilized in a number of applications.[5-7] In synthetic aspects, living anionic polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization are focused as a tool to achieve well-defined block copolymers with target molecular weight and narrow dispersity.

Finally, we will discuss the use of small angle X-ray scattering (SAXS), which is a powerful tool to closely examine periodic patterns in soft materials. The characterization approaches for the synthesized block copolymers will be emphasized for the reduction of the periodic pattern size, which is directly correlated to lithographic performance, and also for the estimation of effective interaction parameters to gain insights on structure-property relationship of synthesized block copolymers.

References
In-situ characterization of SAXS/WAXS in polymer processing

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Clearly knowing the structural responses of polymers to the treatment conditions is essential to regulate their final properties during industrial processing such as spinning, extrusion, injection, and blow molding. In this work, we report on the changes of hierarchical structure in poly(butylene succinate-co-terephthalate) (PBST) copolymer upon application of synchronous stimuli via uniaxial stretching at varying temperatures. The lamellae melting and the transition of crystal structure from α to β form in PBST copolymer always presented at the early stage of the deformation at different temperatures. The lamellae oriented to about ± (40-50)o direction as the yielding response to the stimuli. Upon further stretching, the oriented lamellae were freshly and progressively formed at high temperature, whose morphology was controllable by regulating the synchronous stimuli. Furthermore, a schematic for the structural responses to the synchronous stimuli was proposed. The structural responses of PBST copolymer under such synchronous stimuli is beneficial to tailor the final properties of the products in the form of fibers, films, plastics, etc., which also can provide new insights into the design and development of other copolymers. [1, 2]

References
Pore structure analysis and physical properties of nanoporous thin films

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Within the last years, grazing incidence small-angle X-ray scattering (GISAXS) emerged to a versatile and frequently used analysis technique in the field of nano-structured thin films and surfaces. In this study, we focused on nanoporous thin film analysis and shows the complementarities of two experimental techniques: GISAXS and X-ray reflectivity (XRR). The scattering technique is applied to characterize randomly distributed pore structures in the films and reflectivity technique is conducted to evaluate the physical properties of the film such as electron density and roughness. We prepared two sacrificial pore generators, trimethoxysilylxyitol (TMSXT) and core-shell nanoparticle composed of thermally labile polymethylmethacrylate/divinylbenzene (PMMA/DVB) core and polymethylsilsesquioxane (PMSSQ) shell, to imprint pores within a silsesquioxane-based matrix. This presentation will discuss the pore structures and physical properties of the nanoporous thin films depending on porosity by combining GISAXS and XRR analysis.
Poster [Sep. 4 (Tuesday)]

Influence of process parameters on the formation of crystal-crosslinked network and crystal scaffold during film blowing of polyethylene: an in-situ synchrotron radiation small- and wide-angle X-ray scattering study

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Film blowing is an important processing technology extensively used in producing packaging, protective and agriculture films [1, 2]. During the film blowing of polyethylene (PE) film, since the influences of flow and cooling rate on crystallization kinetics are coupled with each other [3, 4], it is a challenge to study their specific roles on crystallization, bubble stability as well as the final properties of film products. In this sense, a combination of in-situ homemade film blowing machine and simultaneously synchrotron radiation small- and wide-angle X-ray scattering (SAXS and WAXS) measurements is employed to investigate structural evolution of PE at different blow-up ratio (BUR) during film blowing in this work. The evolution of crystallinity, lamellar long period and orientation are studied at different positions of PE bubble, which are divided into four zones with different features from the die exit to the positions above the frost line. Based on these results and our previous works, the polymer entanglement network gradually evolves to the crystal-crosslinked network and the non-deformable crystal scaffold from Zone I to III, which are important structures to determine the stability of film blowing and the product properties. Moreover, the crystallinity for the formation of crystal-crosslinked network keeps constant with different BUR, which seems to be mainly controlled by molecular parameters of the PE material. However, as the lamellar orientation is weakened with the increase of BUR, increasing BUR causes the increase of the critical crystallinity for the formation of crystal scaffold, which is determined by both processing and molecular parameters of PE material. This study of multiscale structure evolutions during film blowing is important to understand the non-equilibrium physics during film blowing, which may supply a guidance for improving stability of bubble and properties of products.

References
Directed self-assembly of sub-10 nm perpendicular lamellar pattern by fluorine copolymerized block copolymer

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Directed self-assembly of block copolymer is one of the most promising candidates for sub-10 nm scale lithography due to its cost effectiveness and outstanding pattern resolution. However, further improvements of line edge fluctuation and etching selectivity of Poly(styrene-\textit{b}-methyl methacrylate) (PS-\textit{b}-PMMA) block copolymer remain as critical challenges. Here, we suggest a newly designed block copolymer that can form sub-10 nm perpendicular lamellar pattern and aligned by graphoepitaxy template. The block copolymer was synthesized by reversible addition-fragmentation chain-transfer polymerization copolymerized with fluorine containing monomer, which has hydrophobicity. The modified block copolymer showed increased pattern resolution than conventional PS-\textit{b}-PMMA due to two times higher Flory-Huggins interaction parameter ($\chi$). Increased $\chi$ value was proven by bulk small angle X-ray scattering measurement. Even though it had a high $\chi$ value, the polymer could form perpendicular lamellae morphology by short thermal annealing. Also, synthesized BCPs were vertically aligned on non-selective surface, which means neutral brush does not required for formation of perpendicular lamellar morphology.
Comparison between NDP and SIMS Analytical Methods to Determine the $^{10}$B and $^6$Li Depth Profiles

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In this study, the comparison of the analytical results between SIMS (Secondary-ion mass spectrometry) [1] and NDP (Neutron Depth Profiling) [2] methods have been carried out with LiCoO2 and BSi samples. The NDP is an analytical method that can analyze the component nuclide concentration versus depth distribution in a sample by detecting the charged particles emitted after the neutrons are absorbed. The $^{10}$B and $^6$Li depth profiles in the BSi and LiCoO2 samples were also analyzed by using a CAMECA IMS 7f SIMS instrument at the National Nanofab Center (Republic of Korea). The results from NDP analysis have been performed at the CN-NDP system (HANARO, Republic of Korea). In comparison results for the samples, the peak depth, peak concentration, and total dose of the NDP results are consistent with the SIMS results to within 2, 6, and 11 %, respectively. The NDP is useful for analyzing light elements with high neutron cross-sections for particle-producing reactions.

Keywords: SIMS, NDP, Neutron Depth Profiling, Analysis.

References
Thin Film Morphology Details of Crystalline-Amorphous Brush Diblock Copolymers Bearing Alkyl and Phosphonic Acid Moieties

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A series of crystalline-amorphous brush diblock copolymers bearing alkyl and phosphonic acid groups (poly(propylthiopropyl glycidyl ether-b-glycidyl 7-phosphonoheptanoate) (PGPSHP-b-PGPPH)) were newly synthesized by low-temperature metal-free anionic ring-opening copolymerization of glycidyl derivatives and subsequent selective postfunctionalizations. As the volume fraction of PGPSHP block increased, the degradation temperature ($T_d$) was increased from 218 °C (PGPSHP$_{20}$-b-PGPPH$_{60}$) to 250 °C (PGPSHP$_{60}$-b-PGPPH$_{20}$). These block copolymers were found to undergo phase-separation, forming nanostructures. PGPSHP$_{20}$-b-PGPPH$_{60}$ films revealed hexagonal cylinder packing (HCP) structure, whereas PGPSHP$_{60}$-b-PGPPH$_{20}$ showed lamellar structure. The crystal lattices in the crystalline phases were identified. The PGPPH block chains formed densely packed phase, showing orthorhombic lattice of fully extended bristles; the PGPSHP block chains formed randomly entangled amorphous structure. Overall, the results collectively inform that the diblock copolymers in this study are suitable for applications as electrolytes in fuel cells.
Industrial Application of Neutron Reflectometry to the Interfacial Structures between Si-containing and Organic Thin Films

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Si-containing polymer has been widely used in many industrial applications, such as OLED (Organic Light Emitting Diode), OPV (Organic Photovoltaics) and other electronic devises. In such applications, Si-containing polymer was frequently stacked on organic polymer layers. Therefore, it is important to investigate the interface between Si-containing and organic polymers. The interface of such polymer stacks has been investigated by several methods, such as time-of-flight secondary ion mass spectrometry (TOF-SIMS), cross sectional transmission electron microscopy (TEM) and X-ray reflectometry. Among these methods, reflectometry was suitable to determine the interfacial thickness at the sub-nanometer scale. Here, we used neutron reflectometry to determine the interfacial thickness between Si-containing and organic polymer layers, whose interface could not be distinguished by X-ray reflectometry.

Fig.1(a) shows the X-ray reflectivity profile of Si-containing and organic polymer stack on silicon wafer with Cu-Kα radiation. Si-containing and organic polymers used in this experiment were organo polysiloxane and acrylate polymer, respectively. This reflectivity data could be fitted as one layer with the sum of polysiloxane and acrylate layer thickness because there was little difference in electron densities between two layers. Fig.1(b) shows the neutron reflectivity of the same sample measured at BL-17 beamline at J-PARC and the fitted result is shown as the scattering density profile in Fig.2. This result shows neutron reflectometry could be used to investigate the interfacial thickness of Si-containing and organic polymer layer without deuteration of any polymers. It is very important to industrial applications because deuteration of developing products is difficult in many cases. In this work, the effects of surface treatments of the organic polymer layer on the interfacial thickness are compared.

Fig.1. Reflectivity profiles of organo polysiloxane / acrylate polymer stack on silicon wafer. (a) X-ray reflectivity with Cu Kα radiation, (b) Neutron reflectivity (left) and scattering length density profile obtained from neutron reflectivity (right).
Characterization of Biocompatible HPMA Copolymers Designed for DDS

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Introduction

Poly[N-(2-Hydroxypropyl)methacrylamide] (PHPMA) is a good candidate carrier owing to its excellent biocompatibility. When an anticancer drug is connected to PHPMA with a hydrazine bond, the drug can be released at by pH atmosphere provided by tumor tissues. We have synthesized two types of copolymers of HPMA and HPMA5tB (Chart 1) and their monomer reactivity solution properties have been investigated. Our final aims are to clarify relationship between sequence structures and aqueous solution properties and correlated their physical properties to biological activities.

Experimental Section

The monomer-reactivity ratio (r_{HPMA}, r_{HPMA5tB}) of P (HPMA-co-HPMA5tB) was calculated from the copolymer composition curve, and conformation or the aggregate morphology in aqueous solution was investigated by small angle X-ray scattering (SAXS).

Results and Discussion

Fig.1 shows the copolymer composition curve of P(HPMA-co-HPMA5tB), which determined the monomer reactivity ratios for HPMA and HPMA5tB to be r_{HPMA} = 1.00 and r_{HPMA5tB} = 0.56, respectively. Fig. 2 shows the SAXS profiles of P(HPMA-co-HPMA5tB) of different monomer composition in an aqueous solution (no salt and no buffer). I(q) denotes the excess scattering intensity as a function of magnitude of the scattering vector (q). The steep slope at the low q region in the SAXS profiles indicated that aggregates were formed.

Fig. 1. Copolymer composition curve of P(HPMA-co-HPMA5tB)

Fig. 2. SAXS profiles of P(HPMA-co-HPMA5tB) of different composition in water.
**Introduction**

An amphiphilic block copolymer consisting of hydrophilic portion and hydrophobic portion in a molecule, self-assemble into a micelle in aqueous solution. Recently, stimuli-responsive block copolymers have caught a great deal of attention for their ability of control release of drugs as nano-carriers for DDS application. pH is one of the most important stimuli for prospective drug delivery systems because the pH value inside cells and around tumor tissues is distinctly lower than the physiological pH (~7.4). We chose pH responsiveness as a trigger of drug release, then we incorporate ionic-hydrophilic block including carboxyl group into block copolymer in order to provide pH responsiveness to the polymer (Figure 1). Since the middle block chain is ionic, the influence of interaction between block chains on micelle is considered to be important. Therefore, in this study, we examined how the micellar structure changes by changing the interaction between ionic block chains due to pH change.

**Experimental Section**

We synthesized PEO_{42}-b-PAGE_{12,COOH}-b-PrBGE_{22} according to the previous report. We dissolved this terpolymer completely in THF. SAXS measurement and FFF-MALS measurement were performed under various pH condition. We also investigated the micellar structure of triblock terpolymer adding naphthalene or 1-amino-naphthalene as model drugs.

**Results and Discussion**

Sharp minimums are observed in the SAXS profiles at pH = 4 and 5, and the minimum diminished with the pH increased from 5 to 8 from each SAXS profile (Figure 2). It is suggested that a size distribution of micelle became wider with increasing pH. Further, both the z-average radius of gyration (R_g) and the aggregation number (N_{agg}) vales of the micelles from Guinier plots are drastically changed by increasing pH. We considered that the change in the interaction of the middle block chain influenced on the micellar structure. The obtained SAXS profiles could be fitted by spherical and ellipsoidal core-corona model. From cryo-TEM measurement, spherical objects were clearly observed at pH = 4. However slightly distorted spherical micelles were observed at pH = 8. It is suggested that a morphological change was induced by pH increase. In addition, the SAXS profiles of terpolymer were greatly changed by adding naphthalene or 1-amino-naphthalene as model drugs at pH = 4 (Figure 3). The power low, I(q)\propto q^{-2}, in SAXS profiles suggested the micellar formation of vesicles, and the TEM observations confirm the formation of vesicles. It is considered that the interaction between the amino group of the model drug and carboxyl group of terpolymer changed the packing parameters and the morphological change from spherical to vesicle shape on micelle occurred.

**References**

Creation of highly stable micelles using hydrosilylation reaction

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Introduction
Amphiphilic compounds self-assemble into micelles in aqueous solution. Because hydrophobic compounds such as a hydrophobic drug can be encapsulated into micelles, micelles are expected to use as a useful platform for DDS carriers. Although micelles are the candidate of DDS carrier, their structures are easy to change by the influence of environment conditions such as the pH, salt concentrations and composition of the solution. In addition, there is another problem in practical use, which is that the concentration of the drug encapsulated in the micelle in blood immediately decreases due to the partial dissociation of the micellar structure after the administration into blood stream. This is called “initial burst”. As Polyethylene glycol (PEG) has a high biocompatibility and a stealth character, it is considered that the retention of a micelle composed of PEG-bearing amphiphilic compounds in blood may increase. Furthermore, if the micelle could maintain their structure even if the surrounding environment changes, the range of the applications of micelle is drastically expanded as a nano-carrier for DDS.

In this study, we have synthesized a PEG-bearing amphiphilic compound containing a vinyl group in the end of the alkyl chain (C11), and tried to immobilize the micellar structure using the hydrosilylation reaction.

Experiment
We newly synthesized an amphiphilic compound named as PEO-DiUndecene (PDU) (Figure 1). This compound was dissolved in 150 mM NaCl aqueous solution to obtain a micelle solution. SiH-containing cyclic siloxane (D4H), vinyl group-containing cyclic siloxane (D4V) and Karstedt catalyst were added into the micelle solution and subjected to a hydrosilylation reaction inside the micelle core by ultrasonic treatment with a probe type ultrasonic homogenizer for 1 min. The progress of the hydrosilylation reaction was confirmed by 1H-NMR measurements and the particle size of the core cross-linked micelle was measured with dynamic light scattering (DLS) measurements.

Results and discussion
In 1H-NMR spectra of the micelle after the hydrosilylation reaction, the peak assigned as the vinyl group of PDU disappeared, indicating the reaction worked. The hydrodynamic radius (Rh) of micelles determined with DLS increased from Rh = ~ 6 nm to Rh = ~ 100 nm. The particle size of the core cross-linked micelle prepared by the hydrosilylation reaction inside the micelle core by ultrasonic treatment with a probe type ultrasonic homogenizer for 1 min. The progress of the hydrosilylation reaction was confirmed by 1H-NMR measurements and the particle size of the core cross-linked micelle was measured with dynamic light scattering (DLS) measurements.

Figure 1 Chemical structure of PDU

Figure 2 The size distribution histogram of the core cross-linked micelle before and after the addition of methanol.

References
Dilute-solution properties of biocompatible PHPMA for drug delivery use

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Abstract
Dilute-solution properties of HPMA homo-polymer for drug delivery system (DDS) were examined by use of small-angle X-ray scattering (SAXS) and gel permeation chromatography (GPC) coupled with static light scattering.

Introduction
Anticancer drugs used in chemotherapy do not have any targeting ability to cancer cells and may be equally distributed into healthy organs. This is the main reason for side effects. Therefore, drug delivery using enhanced permeability and retention effects (EPR effects) has been payed attention in recent years. For such DDS particles, the particle size is the most important. In previous studies, HPMA polymer bearing an anti-cancer drug acts efficiently on cancer cells. However, the particle size and its relationship with the EPR effects was not studied. We synthesized HPMA polymer with various molecular weights and studied its dilute-solution properties by use of scattering techniques.

Experiments
A series of HPMA polymers were synthesized with free radical polymerization and fractionated. The weight-averaged molecular weight ($M_w$), radius of gyration ($\langle S^2 \rangle$) and intrinsic viscosity ($[\eta]$) were measured by GPC-LS-VISCO and SAXS.

Result and Discussion
Conformation plot and Mark-Houwink-Sakurada Plot ware constructed (Fig. 2, 3) As are result, PHPMA was found that it takes a form close to a random coil. Also, it was suggested that the molecular weight of 200,000 [g/mol] to around 1,000,000 [g/mol] would take the good size for EPR effects.

References

Fig. 1 PHPMA

Fig. 2 Conformation plot

Fig. 3 Mark-Houwink-Sakurada Plot
Iron oxide nanoparticles (IONP) are promising in applications of magnetic drug delivery, magnetic separation and magnetic resonance imaging. Two general high temperature reactions include thermolysis of iron-oleate complex and solution reaction of iron (III) acetylacetonate, 1,2-hexadecanediol, oleylamine and oleic acid were developed to produce monodisperse IONP. In the first reaction, prior to the synthesis of IONP, the preparation of iron-oleate complex is susceptible to sodium impurities and different structures of complex. In the second reaction, the reflux temperature of the unstable solvent, benzyl ether is difficult to be maintained. By merging the advantages of both reactions, the synthesis of monodisperse IONP was revised. The iron-oleate complex were prepared in the reaction mixture of iron (III) acetylacetonate, 1,2-hexadecanediol, oleic acid and 1-octadecene. Subsequently the mixture was heated to 320°C and refluxed for 30 min under argon atmosphere. The production of monodispersed 6 nm IONP was collectively confirmed from the structural analyses of synchrotron solution X-ray scattering, grazing incidence X-ray scattering, and transmission electron microscopy. The magnetic properties of iron oxide nanoparticles were additionally examined.
Microphase-separated structure change of styrene-based triblock copolymer elastomer during mechanical deformation

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Polystyrene (PS)-based ABA type triblock copolymer is one of the most important thermoplastic elastomers. The reason would be the mechanical properties can be easily tuned by changing fraction of each component and its high recyclable property. However, improvement of mechanical strength need to be immediately solved. To do go, the change in a microdomain structure during deformation process should be clarified based on in-situ analytical method.

In this study, the change in the microphase-separated structure of poly(styrene-b-ethylene-butylene-b-styrene) (SEBS) films was investigated under biaxial deformation using small-angle X-ray scattering (SAXS) measurement.

SEBS (13 vol% of polystyrene fraction, number-average molecular weight ($M_n = 180,000$) were annealed at 170 ºC for 168 h in vacuo to attain the equilibrium sphere structure. A microdomain structure during biaxial deformation process were investigated using a SAXS method. SAXS patterns were obtained at the synchrotron radiation facility, SPring-8 Japan. Initial length was 10 mm and elongation rates were controlled at 0.04, 0.2 and 1 mm/s.

The diffraction peaks were observed at 2.54, 3.61, and 4.37 nm$^{-1}$ in SAXS pattern. These peaks can be assigned (110), (200) and (211) planes of body centered-cubic (bcc) lattice of PS domains in the SEBS film. Figure 1 a) shows relationship between film strain and strain obtained by domain spacing ($d(\varepsilon) - d(0)/d(0))$ of the SEBS films ($\varepsilon_{SAXS}$) for crystal plane. $\varepsilon_{SAXS}$ linearly increased with increasing film strain. In addition, $\varepsilon_{SAXS}$ obtained from each domain spacing exhibited the same manner. These trends were observed for SAXS data obtained at all elongation rates (not shown). Figure 1 b) shows relationship between film strain and $\varepsilon_{SAXS}$ of the SEBS films at various elongation rates. $\varepsilon_{SAXS}$ linearly increased with film strain, however, the relationship were dependent on the elongation rate, that is, slope decreased with increase in elongation rate. This might be related to the molecular mobility of rubbery EB chains cannot follow the deformation at highest elongation rates.

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Calix[4]arene based spherical micelles in aqueous solution form the monodispersed micellar structure. We can control the morphology transition via electrostatic interaction between head groups of calix[4]arene. Interestingly, the control of ratio of calix[4]arene were provided the variety morphology change in the cylinder from sphere to vesicle. The morphology changes were investigated small-angle X-ray scattering (SAXS), light scattering (LS), and isothermal titration calorimetry (ITC).
Creation of a polysaccharide-based DDS career reducing immunogenicity

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Introduction
Amphiphilic molecules, containing both hydrophilic group and hydrophobic one in one molecule, self-assemble into micelles in aqueous solutions mainly due to the hydrophobic interactions. Micelles can encapsulate drug molecules into its hydrophobic core, which is generally expected as a carrier in drug delivery system (DDS). Polyethylene glycol (PEG) is well known as a hydrophilic and highly biocompatible macromolecule. DDS particles bearing PEG on their surface have been extensively studied so far, and it has been reported that all of them exhibit very high retention in the blood. However, recently, a phenomenon in which rapid clearance from the blood occurs in frequent administration of PEG-containing DDS particles, namely accelerated blood clearance (ABC) phenomenon, is reported as a problem. Although various causes have been reported so far, it is believed that PEG, which is a non-natural substance, causes an immune reaction in vivo.

In this study, in order to overcome the ABC phenomenon, a lipid modified with a natural biocompatible polysaccharide, dextran, have been prepared (Figure 1). Another lipid bearing PEG whose structure is similar to that bearing dextran is also prepared. We compare the biocompatibility of dextran with PEG by testing the retention of blood of particles bearing the macromolecules.

![Chemical structure of a lipid bearing dextran (Dex-D) and lipid bearing PEG (PEG-D)](image)

Experiment
Dextran-modified lipid (Dex-D) and PEG-modified one (PEG-D) were synthesized by click chemistry, and the structure of the obtained compound was confirmed by 1H NMR. Cy5-containing lipid was added in the preparation of the micelle of the synthesized lipids, and their complexation was confirmed by asymmetrical flow field flow fractionation coupled with multi-angle light scattering (AF4-MALS) measurements. Mice were intravenously injected as a fluorescent and the blood fluorescent concentration at each time was measured by UV measurement.

Results and discussion
The physical properties including the particle size, shape, and critical micelle concentration (CMC) of the Dex-D micelle and the PEG-D one were almost similar to each other. Fig. 2 shows blood circulation profiles of the micelles bearing dextran or PEG including Cy5-lipid after first and second administration. There is no difference between the first administration and the second one in the profile, indicating that the ABC phenomenon did not occur in this system. This is presumably because the particle size of the micelle used in this experiment was 10 nm, resulting in no recognizing by the immune system.

![Blood circulation profiles of Dex-D micelles vs. PEG-D micelles after first administration (purple: PEG-D and green: Dex-D) and second administration (blue: PEG-D and red: Dex-D).](image)
Phase behaviors of self-assembled structures of amphiphilic block copolymer in aqueous solution

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The amphiphilic molecules form a micellar structure in aqueous solution. Their shape and size can be easily controlled by external conditions such as temperature, concentration and additives. The amphiphilic block copolymer, has hydrophilic and hydrophobic block, also was followed with the same mechanism. However, for the phase transitions of amphiphilic block copolymer have not been fully exploited yet. Therefore, we present a new method for inducing phase transition of amphiphilic block copolymers in aqueous solution. In this study, we present to a phase control method of the diblock copolymers in aqueous solution, which is depend on the control of the mass fraction of the hydrophilic part with temperatures. In addition, the small angle neutron scattering (SANS) intensities was reproduced by the model functions. The self-assembled structures of block copolymers can provide a broad spectrum of potential applications in nano-building blocks and drug delivery systems.
Off-specular neutron reflectivity analysis for buried interfaces: arbitrary vertical interfacial profile approach

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Off-specular neutron scattering (OSNS) enables in-situ probing of buried layers and interfaces providing the information on their in-plane structure. In a combination with specular neutron reflectometry (SNR) delivering the depth resolved density profile, OSNS is able to record the 3D density distribution in thin films and layered heterostructures. Although the technique has been used for many years and exploited mainly with X-ray scattering, it is more challenging for neutron studies of soft interfaces. In the latter case, a great advantage of the use of isotope contrasting may only partially compensate for lower neutron beam intensity hence requiring a more complex data analysis. This complexity is due to the fact that OSNS is mainly detectable in close proximity to the total reflection angle where Born approximation is not applicable.

The distorted wave Born approximation (DWBA) has been formulated \cite{1} to analyse the intensity scattered in the off-specular direction, both from a single interface and multiple interfaces \cite{1, 2, 3}. In the DWBA, the scattering potential is generally decomposed into two parts: the first one is represented by a 1D ideal reference potential with an exact solution, while the other one describing small 3D deviations from the reference potential is taken into account as a perturbation. In most cases, the DWBA formalism is applied to scattering from the self-affine statistical roughness of interfaces. Then the reference 1D potential is chosen as the mean value laterally averaged over such roughness. As a result, interfaces are in the basic approximation smeared out in accordance with the error function (erf). Local deviations of scattering potential caused by deviations of interfaces from their nominal positions are treated as a perturbation which is reduced to the height-height in-plane correlation function.

In this work we present a generalisation of the DWBA method to interfaces with arbitrary density profiles. Instead of focusing on the perturbation of a smooth interface, we changed the ideal potential part by first modelling the interface as an analytical function and then breaking it up into stratified sublayers \cite{4}. For such a system the calculation of SNR and wave field inside each sublayer is fairly straightforward. Furthermore, the perturbation part which, through the density-density correlator, describes the lateral features could be of any form (form factor) and distribution (structure factor). We have applied this method to the study of buried polymer interfaces.

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Miktoarm Architectural Effect on the Phase Behavior of PS-b-PLA Block Copolymer

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Block copolymer (BCPs) are widely used in materials science due to their unique ability to be self-assembled into various nanostructures. Recent advances in BCPs focused on the development of new systems that can overcome the size limitation of traditional BCPs. Such efforts have been demonstrated with design and synthesis of new type of BCPs having high interaction parameter (χ). Although many previous studies have been mainly focused on linear BCPs, it was also suggested that non-linear architecture such as star BCPs can further promote the phase segregation. Herein we synthesized well-defined miktoarm PS-b-PLA BCPs to compare the segregation behavior with linear PS-b-PLA BCPs having similar molecular weights and volume fraction. As a control sample, linear PS-b-PLA BCPs of similar volumetric ratio were synthesized. The samples were thermally annealed in thin film and bulk state, and characterized with SEM, TEM, and SAXS. The phase behaviors were also compared with SCFT simulation performed.
Graphene Oxide (GO) can form liquid crystals (LC) in aqueous solution, which can be employed in many applications that require orientations of materials. One of the most attractive applications of GO is the GO based polymer nanocomposites where GOs are employed as an effective nanofiller in semicrystalline polymer matrix. Previous research showed that polymer can be crystallized onto GO surface and thus adding GO helps to develop the polymer crystalline structures and change the property of materials. However, less attention has been paid to how adding crystallizable polymers can alter the liquid crystallinity of GO. Herein, we show that liquid crystallinity of GO can be correlated with polymer crystallization such that adding polymers significantly reduce the liquid crystallinity of GO suspension when they are crystallized. Conversely, the liquid crystallinity of GO can be enhanced with high degree of polymer crystallization. The microstructures of GO LC and polymer crystallization were investigated with small-angle X-ray scattering, wide-angle X-ray scattering and differential scanning calorimetry.
Initial solvent induced out-of-equilibrium behavior of polymer nanocomposites

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The good degree of particle dispersion is essential to achieve the desired physical properties in polymer nanocomposites (PNC). Controlling the size of particle/polymers, surface chemistry of particles, and grafting/adsorption polymer density on nanoparticles is often suggested to make particles and polymers interact favorably, thus enhance miscibility between them; however, PNCs can be kinetically trapped at an out-of-equilibrium state during the solution processing of PNCs because of the slow dynamics of polymers compared to the rapid evaporation of initial suspending solvents.

In this study, silica nanoparticles are mixed with poly(ethylene glycol) in different dispersing solvents, where we vary the polymer chain length, particle volume fraction and solvent quality for polymer. The detailed microstructure of particles was examined with small angle X-ray scattering. We show the microstructures and rheological property of PNC can be strongly dependent on the solvent-mediated interactions, which are only present in the initial step of PNC production. Finally, we reveal that it is quantitative difference in adsorbed polymers in PNCs that affects predominantly to the different final structures and properties of PNCs.
Self-Assembly Behaviors of Amphiphilic Zwitterionic Brush Polymers at Air-Water Interface

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Self-assembling characteristics of a series of amphiphilic zwitterionic brush polymer were investigated at an air–water interface by using surface pressure–area isotherms, infrared spectroscopy, and X-ray reflectivity analysis. In this study, two different type brush polymers, homopolymers (poly(oxy(n-dodecylthiomethyl)ethylene) (PECH-C_{12})) and poly(oxy(11-phosphorylcholineundecylthiomethyl)ethylene) (PECH-C_{11}-PC) and random copolymer(poly(oxy(11-(3-sulfonyl)propyltrimethylglycinyl)undecylesterthiomet hyl)ethylene-co-oxy(n-dodecylthiomethyl)ethylene)s (PECH-DMAPS_m where m is the mol% of DMAPS end group), were used. The brush polymers were found to favorably form molecular assemblies at the water interface. They initially formed a monolayer assembly in which the hydrophilic backbones were in the extended conformation and the zwitterionic functional group ends were anchored at the water interface and the hydrophobic alkylenyl linkers were present over the water surface. These phases underwent a surface pressure-driven structural transformation path way, ultimately forming highly ordered Langmuir mono or bilayer structures. These Langmuir film formations and their ordering and orientation might be driven by positive, cooperative efforts of several factors such as the compositional balance of hydrophobic and hydrophilic zwitterionic bristles, the air- and water-induced segregations of the bristles and backbone, the lateral ordering capabilities of the alkyl groups and the alkylenyl linkers in the bristles under the assistance of surface pressure.
Facilitating Phase Transfer of Polymer Semiconductor in Mini-Emulsion Synthesis via Molecular Affinity Engineering

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A synthetic approach has demonstrated to enhance coalescence phenomenon during solidification of water-borne colloids so that thin, even, and continuous film morphology of polymer semiconductors can be realized. From theoretical study of complex colloids, it is shown that small-sized and uniform colloid particles are essential to minimize depletion contact energy between colloid particles and thus to enhance coalescence. Therefore, the newly synthesized polymer semiconductor is designed for better molecular affinity with surfactants, so that phase transfer of polymer semiconductors from organic phase to water phase can proceed more efficiently during mini-emulsion synthesis. This is achieved by substituting a Si atom to the branching C atom of the alkyl solubilizing group of a conventional donor-acceptor polymer semiconductor. Such a chemical modification increases the volumetric portion of hydrophobic alkyl chains and thus enables higher solubility as well as higher hydrophobicity, all of which are closely related with enhancing molecular affinity between polymer semiconductor and surfactants. As a result, the performance of organic field-effect transistors fabricated from water-borne colloids can be improved to a level similar to the case of organic solvents. More importantly, the reproducibility of transistor performance is also greatly improved due to the small and uniform water-borne colloidal particles. [1]

References
Poster [Sep. 5 (Wednesday)]

Effects of Side Chain Length and Inter-Chain Interaction on the Thin Film Morphologies of Poly(n-alkyl isocyanate)s

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PAIC(poly(n-alkyl isocyanate)) series having different alkyl side chain length were synthesized using anionic polymerization[1]. The thin films supported on Si wafer have formed various nanostructures in different annealing conditions. The driving force of various nanostructures was a result of harmony and equilibrium between force for forming curvature and force of inter-chain interaction with neighboring chains. Poly(n-butyl isocyanate) (PBIC) have formed variously oriented multilayer structure as the most stable conformation and poly(n-hexyl isocyanate) (PHIC) showed mixed structure of variously oriented multilayer, multilayer and hexagonal close packed cylinder (HCP) in various annealing conditions[2]. Poly(n-octyl isocyanate) (POIC) showed variously oriented multilayer structure and multilayer and mixed structure of multilayer and HCP according to annealing solvent. Additionally, poly(n-pentanoxycarbonylaminohexyl isocyanate) (PPEAHI) introduced urethane linker in the middle of side chains was investigated and it stably showed multilayer structure because of strong interaction from hydrogen bonding between urethane linkers. Thermal stability and the extent of inter-chain interaction were studied by differential scanning calorimetry(DSC) and thermogravimetric analysis(TGA). Then the morphological information was investigated through atomic force microscopy(AFM) and grazing incidence X-ray scattering (GIXS) analysis.

References
Structure and Biocompatibility Characteristics of Ionic Polymer Nanoparticles

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A series of ionic polymer nanoparticles were synthesized by in-situ copolymerizations with varying compositions in solutions. The chemical compositions and characteristics of synthesized particles were characterized by using nuclear magnetic resonance and infrared spectroscopies, thermogravimetry, and differential scanning calorimetry. They were further examined by synchrotron solution X-ray scattering and grazing incidence X-ray scattering in order to get structural shape, structural parameter details, and size distribution. Biological assays were carried out for the ionic nanoparticles for their biocompatibilities. The results will be discussed in the views of chemical composition, shape and size, morphology, surface characteristics, ionic characteristics, and biocompatibility.
Reverse micelle formation of lactone type sophorolipids in organic solvent

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Reverse micelles formed by amphiphilic molecules in organic solvent have been used as reaction fields for protein separation and chemical reaction. Since the properties of reverse micelles as a reaction vessel is related to their structural features, such as size and shape, it is important to control the structure of reverse micelles. It has been known that amphiphilic molecules having cyclic moiety at hydrophilic groups show unique associating behavior in aqueous solution [1]. Therefore, it should be expected that amphiphilc molecules having cyclic moiety at hydrophobic groups also show characteristic associating behavior in organic media. Then, we focused on lactone type sophorolipid (LSL), which is a glycolipid consisting of hydrophilic sophorose cyclized with a long hydrophobic chain. It is interested to reveal how the feature of molecular structure of LSL is reflected in the associating behavior or structure of reverse micelle in organic media. Thus, in this study, associating behavior of LSL in organic solvent is investigated with synchrton small-angle X-ray scattering (SAXS).

Reverse LSL micelles were prepared by dissolving in toluene at various concentrations. The structural analyses of reverse LSL micelles were carried out by SAXS measurements at BL-40B2 of SPring-8, Japan. 2 dimensional SAXS images obtained by an imaging plate were converted one-dimensional \( I(q) \) versus \( q \) profiles by circular averaging. Here, \( I(q) \) is scattering intensity at \( q \), \( q \) is the magnitude of scattering vector defined by \( q = (4\pi/\lambda) \sin \theta \), \( 2\theta \) is scattering angle, and \( \lambda \) is the wavelength of incident X-ray.

Fig. 1 (a) shows SAXS profiles reverse LSL micelles in toluene at various concentration. These profiles indicate that LSL forms spherical shape because the characteristic power law was not found in low \( q \) range. Fig. 1 (b) shows the Guinier plots of SAXS profile for the reverse LSL micelles. The radius of gyration of reverse LSL micelles was estimated to 0.84 nm from the slope of Guinier plots. In addition, the association number of reverse LSL micelles was estimated to 16 from the scattering intensity at \( q = 0 \) [1]. From these results, it was considered that the reverse LSL micelle has a structure in which the hydrophilic field is covered with a large cyclic hydrophobic chain.

References
Inclusion of water-soluble polymer into nanotube with hydrophilic interior consisting of amphiphilic cyclic peptide

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Surfactin sodium salt (SFNa) is an amphiphilic cyclic peptide having two carboxyl groups on the peptide ring and a long alkyl tail. Owing to ring structure of SFNa and inter-ring hydrogen bonding, SFNa molecules spontaneously assemble into supramolecular hollow fiber with unimolecular width in non-polar organic media, such as cyclohexane (CHx). Since carboxyl groups are oriented toward to the inside of the SFNa nanotubes, it should have hydrophilic interior. Therefore, it is considered that the SFNa nanotubes should include a water-soluble polymer in their inside. Thus, in this study, we investigated inclusion of poly (ethylene glycol) (PEG) as a water-soluble polymer into the SFNa nanotube in CHx.

To examine the formation of inclusion complex of SFNa nanotube and PEG, desired amount of aqueous solution of PEG (PEGaq) was added to CHx solution of SFNa (SFNa/CHx). The mixture was vigorously stirred at 60 °C, and allowed to cool to room temperature. Homogenous mixtures of SFNa/CHx and PEGaq were obtained, whereas aqueous solution of PEG is almost insoluble in CHx. In order to investigate the formation of inclusion complex of SFNa nanotube with PEG, small-angle X-ray scattering (SAXS) measurements for SFNa/CHx containing PEGaq were carried out at BL-40B2 of SPring-8, Japan. 2 dimensional SAXS images obtained by an imaging plate were converted one-dimensional \( I(q) \) versus \( q \) profiles by circular averaging. Here, \( I(q) \) is scattering intensity at \( q \), \( q \) is the magnitude of scattering vector defined by \( q = \frac{4\pi}{\lambda} \sin \theta \), \( 2\theta \) is scattering angle, and \( \lambda \) is the wavelength of incident X-ray.

Fig. 1 shows change of SAXS profile from SFNa/CHx by adding PEGaq. SAXS intensities of the SFNa/CHx containing PEGaq show \( q^{-1} \) power law at low \( q \) region regardless of the presence of PEGaq. This result indicates that fiber-like structure of SFNa nanotube in CHx is maintained even when PEGaq is added. On the other hand, the shoulder around 2 nm\(^{-1} \) of \( q \) in SAXS profile is shifted to low \( q \) side and the scattering amplitude around 4 nm\(^{-1} \) of \( q \) becomes clear by addition of PEGaq. The former change in SAXS profiles means that cross-sectional diameter of SFNa nanotube is expanded, and the later suggests radial electron density distribution is changed due to the presence of PEGaq. As mentioned above, both PEG and H\(_2\)O are almost insoluble in CHx. Further, the hydrophilic region is only the inside of SFNa nanotube. Therefore, it is considered that these changes of SAXS profiles by addition of PEGaq to the SFNa/CHx are caused by the formation inclusion complex of SFNa nanotube with PEG.

![Fig. 1 SAXS profile from SFNa/CHx in PEGaq. The ratios shown on the right of the SAXS profiles are molar ratios of SFNa to repeating unit of PEG.](image)

Synchrotron X-ray Scattering Studies of Protein A, Immunoglobulin G, and Their Mixtures in Buffered Solutions

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Staphylococcus protein A (pA), immunoglobulin G (IgG) protein, and their mixtures in phosphate buffered saline were investigated from the view of three-dimensional (3D) structures by using synchrotron X-ray scattering analysis. 3D structures of pA and IgG were identified. In particular, the 3D structure in solution of IgG was compared with that obtained by X-ray crystallography. The structural stabilities of these proteins were monitored in various pH conditions. In addition, the mixtures of pA and IgG in various compositions were examined. The scattering analysis results will be discussed with considering the chemical natures and structures of pA and IgG.
A series of functional polymeric nanoparticles were synthesized by in-situ copolymerizations with varying compositions in solutions. The particles were characterized by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies, thermogravimetry (TGA), and differential scanning calorimetry (DSC). They were further examined by synchrotron solution X-ray scattering and grazing incidence X-ray scattering in order to get structural shape, structural parameter details, and size distribution. Their biocompatibilities were investigated by using human cells. All results will be discussed in the views of chemical composition, shape, size and distribution, morphology, surface characteristics and biocompatibility.
Detailed atomistic structures and x-ray scattering structure factors of amorphous vinyl polymers: A multiscale molecular modeling approach

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This work reports the recent development of multiscale simulations of amorphous polymeric materials based on some commercial vinyl polymers [CH2–CH(X)], e.g. polypropylene (PP, X=CH), polyvinylchloride (PVC, X=Cl) and polystyrene (PS, X=C6H5) at the bulk density. The model starts from determination of the conformational energy maps of polymer segments, using semi-empirical quantum chemistry calculation (AM1), to obtain the statistical weights matrices based on the rotational isomeric state (RIS) theory [1]. The lowest energy conformers were selected from these energy map to be geometrically optimized by ab initio quantum chemistry calculation at MP2/6-311+g**. The refined RIS models for PP, PVC and PS with first- and second-order neighbor interactions were validated by comparing the characteristic ratio (Cn) as well as its temperature coefficient (d ln<R2>/dT) for chains having the probability of meso diads (Pm) from 0.0 to 1.0. The predicted results for large degree of polymerization are in good agreement with experimental data. Next, polymer chains were then mapped to coarse-grained models using the modified RIS model onto the second nearest neighbor diamond (2nnd) lattice. The average non-bonded interactions were treated by the discretized Lennard-Jones (LJ) potential [2-3]. Bulk amorphous PP, PVC and PS were generated and equilibrated. Finally, fully atomistic amorphous PP, PVC and PS models were then obtained by the reverse mapping procedure to recover the missing carbon and hydrogen atoms. After an energy minimization step, properties including torsion angle distribution, solubility parameter and static x-ray scattering structure factors were determined and in good agreement with experimental scattering results.

Figure 1. Example of conformational energy map of meso diads for PP segments calculated by semi-empirical (AM1) method.

Figure 2. Example of static normalized coherent structure factor I(Q) from scattering experiment of fully atomistic PS model after a reverse mapping and energy minimization.

References
Relationship between alkyl chain length and aggregation number of calix[4]arene-based micelles bearing primary amines

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Introduction
Amphiphilic compounds such as lipids self-assemble into micelles in aqueous solutions. The micellar structures including the morphologies, size, and aggregation number (N_{agg}) are very important in the function in some practical application such as drug delivery system carriers. We have recently found that the primary amines bearing calix[4]arene-based micelle [PACaLₙ (ₙ is the carbon number of the alkyl chain)] demonstrate monodispersity in the N_{agg} which agree with the vertex number of regular polyhedra: Platonic solids (1, 2, 3).

Micellar structures generally depend on the balance between the hydrophilic and hydrophobic volume. For the Platonic micelle system, we have so far not investigated the effect of the alkyl chain length on the aggregation behavior. In this study, we have synthesized the series of the calix[4]arene micelles with various alkyl chain length to investigate the effect on the structure and the monodispersity.

Experiments
We synthesized the series of the PACaLₙ micelles with various alkyl chain. The structure of PACaLₙ was confirmed by ¹H NMR. The micellar structure including the aggregation number and the distribution were investigated with small angle X-ray scattering (SAXS) measurements and multi-angle light scattering coupled with asymmetrical flow field flow fractionation (AF4-MALS) measurements, and analytical ultracentrifugation (AUC) measurements.

Results
Fig. 1 shows the SAXS profiles of PACaLₙ at pH = 3 in 50mM aqueous NaCl. The slope of low q regions of PACaL₄-₆ almost close to zero, indicating the presence of spherical micelles. The slope of low q regions of PACaL₇ and PACaL₈ satisfy I(q) ∝ q⁻¹, indicating the formation of cylindrical micelles.

The aggregation number of PACaL₄ and PACaL₅ determined by Guinier plot (fig 2) to be 12 in both system. The aggregation number determined with three independent experiments (SAXS, AF4-MALS, and AUC) agree with each other and shows monodispersity. The aggregation number of conventional micelles including CTAB gradually increasing with increasing the carbon number of alkyl chain. However, PACaL₄-₆ demonstrated the constant aggregation number while the carbon number increases. This is presumably due to the high coverage density of the hydrophobic core in the dodecamer system.

Reference
Structural stable nano-balls bearing polyethylene oxide for the application as DDS carriers

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Introduction

Amphiphilic compounds having both a hydrophobic part and a hydrophilic one in one molecule form micelles in an aqueous solution by hydrophobic interactions. Micelles are widely studied as one of the drug carrier candidates in drug delivery system (DDS) because they can encapsulate hydrophobic drugs in inside core of micelles. However, the micellar structure easily changes because its structure is very sensitive to external stimuli such as changes in solution compositions, temperature, and pH. For this reason, micelles collapse due to dilution effects and interaction between micelles and bio-macromolecule in the blood when it is administrated into blood stream. This phenomenon causes quick release of drugs from micelles after administration, which is called “initial burst”. This is a problem for micelle as DDS carriers. Due to the this, it is required to stabilize micellar structures so as to withstand surrounding environmental changes. In this study, we prepared core cross-linked nano-balls using a radical polymerization reaction in order to achieve improvement of the stability of the micellar structure, whose structures have been investigated using small angle X-ray scattering (SAXS) measurements.

Experiment

We newly synthesized the amphiphile containing polyethylene oxide ($M_n = 2,000$ g/mol) and methacryloyl group at the end of dodecyl chains of hydrophobic parts (PEO-BDMA shown in Figure 1). In the preparation of the core cross-linked nano-ball, PEO-BDMA was dissolved in 150 mM NaCl aqueous solutions, then we added divinylbenzene (DVB) and bis(2-methacryloyl)oxyethyl disulfide (DSDMA) dissolved in acetonitrile and initiator. The polymerization reaction was carried out by ultrasonic treatment using a probe-type ultrasonic homogenizer for 1 min, and then put in a hot water bath at 65 °C for 5 minutes. The proceeding of the cross-linking reaction is confirmed by $^1$H-NMR measurements. The micellar structures were characterized SAXS and dynamic light scattering (DLS) measurements.

Results and discussion

The results of $^1$H-NMR measurements showed the proceeding of the polymerization reaction. We also confirmed that the particle size of the core cross-linked nano-ball did not change even in methanol solutions which is good solvent for PEO–BDMA. Based on these result, we concluded that the micellar structure is captured in nano-balls by polymerization reaction in its core. Fig. 2a shows the SAXS profiles before and after the polymerization reaction of PEO-BDMA micelles. The SAXS profile of the PEO-BDMA micelles can be reproduced by the theoretical curve calculated using the core-shell spherical model. It was also suggested that the polymerization reaction proceeded keeping the micellar morphology in sphere since the slope at the low $q$ region in the SAXS profile remain in flat. For the nano-ball composed of DSDMA, we added Glutathione (GSH) which exists in cytosol and can cleave the disulfide bond. Fig. 2b shows the SAXS profiles of the nano-ball in different conditions. After addition of GSH, the SAXS profile in low and high $q$ region slightly changed, indicating something happened in their structures, probably suggesting the cleaving disulfide bond in the nano-ball.
Self-assembly Behavior of Heteroarm Core Cross-Linked Star Polymers

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Self-assembly Behavior of Heteroarm Core Cross-Linked Star Polymers Nam Young Ahn1, Myungeun Seo*1,2 1Graduate School of Nanoscience and Technology, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea, 2Department of Chemistry, KAIST, Daejeon 34141, Republic of Korea, *seomyungeun@kaist.ac.kr Heteroarm core cross-linked star (CCS) polymers, in which two chemically different arm emerging from a densely cross-linked core, have been received considerable attention due to different self-assembling behaviors compared to linear block copolymers.1 We have developed a facile synthetic route to heteroarm CCS polymers containing polylactide (PLA) and polystyrene (PS) arms by utilizing reversible addition-fragmentation chain transfer (RAFT) copolymerization of 1,2-bis(maleimidoethane) (BMI) and styrene (S) that proceeds in an alternating fashion. We have observed that heteroarm CCS polymer PLAnPSn exists as individual nanoparticles in a neutral solvent, and also self-assembles to form microphase-separated structures in a selective solvent and in bulk presumably via intramolecular segregation of PLA and PS arms within the star architecture.2 In this presentation, we discuss self-assembly behavior of PLAnPSn with various compositions in solution and in bulk. We will particularly focus on small angle x-ray scattering (SAXS) analysis of PLAnPSn films. Microphase separation behavior of PLAnPSn at different compositions and temperatures will be examined by temperature-dependent SAXS experiments and presented in comparison with PLA-b-PS linear diblock copolymers.

References
Microphase Separation Behavior of a Diblock Copolymer upon Selective Metal Ion Binding

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Microphase Separation Behavior of a Diblock Copolymer upon Selective Metal Ion Binding

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Well-defined and periodic nanostructures generated by microphase separation of block copolymers provides fascinating opportunities towards advanced applications such as next-generation lithography.1 It is increasingly important to develop a methodology to combining block copolymer self-assembly with inorganic components such as ions and nanoparticles in a selective fashion to bestow target functionality to specific microdomains in the block copolymer nanostructures. Here we present synthesis and characterization of a new block copolymer system where one of the blocks contains carboxylic acids in the side chain. We synthesized the target block copolymer by utilizing thiol-yne reaction of an alkyne-containing block polymer precursor2, and characterized its microphase separation behavior by temperature-dependent small angle X-ray scattering (SAXS) experiments. We will further discuss how selective binding of the metal ion to the carboxylic acid-containing block affects the microphase separation behavior of the block copolymer.

References
Specular and off-specular neutron reflectivity to probe the effect of irreversible polymer adsorption

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We have used specular neutron reflectivity (NR) to probe the connection between the adsorption of polymer chains at a solid substrate and the interface with another immiscible polymer. Irreversible polymer chains adsorption onto a silicon substrate has been studied with ellipsometry and it has been shown that it proceeds via different steps via a chain pinning process with a linear behaviour for the adsorbed amount for shorter time and, as the annealing time increases, with a logarithmic dependence [1]. The adsorbed chains may have an influence on the formation of the interface between this first layer and another thin immiscible polymer film. This effect may impact the intrinsic interfacial width and, in particular, the capillary wave component [2] of the full interface between the two polymers.

To probe this effect, NR is ideal, since one of the two polymers can be deuterated, thus creating a contrast between the two phases. The first step was to apply NR to study in detail the profile of the polymer/polymer bilayer where the bottom polymer layer had been pre-annealed prior to the deposition of the second layer: this allowed the macromolecules to adsorb at the surface (we have also considered the case where no pre-annealing step was performed). We used a bilayer of polystyrene (PS) and poly(methyl methacrylate) (PMMA) where one of the layers was deuterated. The experiments were performed using the reflectometers D17B at ILL (France) and SOFIA at J-PARC (Japan). By pre-annealing the first layer at temperature above the glass transition and at different annealing times, we observed a complex structure of the film for longer annealing time. This effect has an influence on the width of the interface with the other polymer lying above. To gain more information on the effect of the multilayer structure, we then applied off-specular neutron scattering to the annealed systems allowing to investigate the thermal fluctuations at the interface via the Distorted Wave Born approximation (DWBA) formalism with the in-plane correlation function equal to the modified Bessel functions of the second kind of 0th order [3]. Analysing the off-specular scattering signal, the intensity in the off-specular direction differs depending on the adsorption of the macromolecules. This study was performed as a function of interface-substrate distance.

References
Synthesis and characterization of highly soluble phenanthrol carbazole-based copolymer: Effects of thermal treatment on crystalline order and charge carrier mobility

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Herein, we report a novel semiconducting polymer with 6H-phenanthro[1,10,9,8-cdefg]carbazole as building block. The polyacene system underneath the carbazole core increase the effective conjugation length of the polymer and also contribute to the planarity of the polymer backbone. Furthermore, the electron rich amine functional group on the PCZ molecule ensures electron donating capability, making it a good candidate for donor moiety for donor-acceptor (D-A) configuration. The planar structure of the acceptor unit can further contribute to the planarity of the building block while the electron deficient benzothiadiazole effectively reduce the electron density, which induces broad light spectrum absorption. Due to the high coplanarity of both donor and acceptor moiety, the resulting polymer, PPTBTT will benefit from strong intermolecular interaction with nearby polymer chains which would be advantageous for effective charge transport. To confirm its high solution processability and charge transport characteristic, we have fabricated OFET device which showed a compact film from a simple spin coating technique, and exhibited a hole mobility of 0.009 cm² V⁻¹ s⁻¹ with current on/off ratio of 10⁴.
Self-assembled structures of boron nitride nanotubes by hydrophobic interaction: A small angle X-ray scattering study

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Due to the excellent mechanical and thermal properties, boron nitride nanotubes (BNNTs) have been of interest for a wide range of potential applications such as materials for reinforcements or for thermal dissipation. For the practical use of BNNTs, it is essential for the control of the morphologies of BNNTs, leading to the enhancement of their properties. Since the synthesis of BNNT is very difficult and it is rather focused in the synthesis until now, the related studies are very rare and in early stage. Therefore, we report various self-assembled structures of boron nitride nanotubes by controlling the hydrophobic interaction upon heating, which is analyzed by the small angle X-ray scattering technique.
Small angle x-ray scattering study of comonomer composition on the segregation behaviour of poly(butyl acrylate)-b-poly(methyl methacrylate-r-styrene)

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Block copolymers, composed of two or more chemically different polymer blocks connected by covalent bond, can self-assemble into periodically segregated nanostructure. The phase behavior of block copolymer is dictated by the Flory-Huggins interaction parameter between dissimilar blocks (χ), volume fraction (f), and degree of polymerization (N). In this study, we investigated the segregation behavior of a molten diblock copolymer, poly(butyl acrylate)-b-poly(methyl methacrylate-r-styrene) (PBA-b-P(MMA-r-St)) where styrene is incorporated as a comonomer in the second block for controlling the incompatibility between two blocks. Poly(butyl acrylate)-b-poly(methyl methacrylate-r-styrene) (PBA-b-P(MMA-r-St)) was synthesized by atom transfer radical polymerization (ATRP). The PBA block has a relatively narrow molecular weight distribution (MWD: 1.06) and the P(MMA-r-St) block has a relatively polydisperse molecular weight distribution (MWD: 1.2 ~ 1.5). To examine the effect of styrene comonomer fraction (φ) on the segregation behaviors of PBA-b-P(MMA-r-St), the bulk morphologies of PBA-b-P(MMA-r-St) with different φ were characterized by transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS). The effective χ parameter between PBA block and P(MMA-r-St) block was estimated by analyzing SAXS profiles with the random phase approximation (RPA), which allows us to quantify the degree of incompatibility of PBA-b-P(MMA-r-St) diblock copolymer as a function φ.
Nanoscale Thin Film Morphology and Electrical Memory Characteristics of Copolymers Bearing Phenyl, Thiophenyl, and Dipropargyl Malonate Units

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It is well known that fully conjugated polymers can form well-defined nanostructure via self-assemblies. There are strong correlations between electrical properties and nanostructures of conjugated polymers [1-2]. In this study, we report thin-film morphology and electrical memory characteristics of poly(p-phenylene)-block-polythiophene (PPP-b-BT), and poly(dihexyl dipropargyl malonate) (PDHDPM). Nanoscale thin films of these polymers were investigated by synchrotron grazing incidence X-ray scattering and X-ray reflectivity analyses. The block copolymers in thin films did behave phase-separations in the block chains, forming lamellar structures. Within such lamellar structures, the polymer chains formed edge-on and face-on structures in a mixed mode. In contrast, the aliphatic polymer in thin films showed featureless morphology. With these polymers, electrical memory devices were fabricated and their device performances were tested. We tried to understand the device characteristics from the views of chemical compositions and natures as well as thin film thicknesses, morphologies and orientations.

References
Programmable volume phase transition of hydrogels for adaptive solar control windows

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Active switching glazings driven by electrical energy have been widely used for the on-demand control of the optical transmittance of smart windows; however, continuous electrical energy consumption is necessary to maintain the optical state. In this work, to minimize the energy consumption during operation of switchable windows, we have developed an optically bistable switching glazing based on the memory function in the volume change of the hydrogels. By grafting a multi-component copolymer that has a chemical composition gradient of three different monomers1 onto the methyl cellulose backbone,2 the prepared hydrogel exhibits a smooth transition during heating and a large thermal hysteresis in the swelling behavior during cooling. Based on the novel thermal behavior of the triangular shape in volume phase transitions, an optically bistable window capable of retaining a switched state as well as stepwise activation, depending on the applied current, can be prepared. The developed bistable glazing is expected to provide energy-saving devices for on demand solar control and variation in visibility.

References
Much of the focus on block copolymer/nanoparticle (BCP/NP) nanocomposites has been on the passive dispersion of NPs inside the BCP matrix. However, recent studies have looked into the active role of enthalpically neutralized NPs in controlling the orientation of BCP thin film microdomains by an entropy-induced segregation of the NPs to the substrate and/or free surface. Notwithstanding the recent progress in understanding such systems, these nanocomposites are yet to be fully elucidated because of the complex mechanisms that arise when these two moieties meet. The appropriate conditions for the segregation of NPs in BCP matrices and thus the reorientation of microdomains are reported in this study. Organic NPs with ~30, 21, 6, and 0 (single chain NP) arms are incorporated into cylinder-forming PS-b-PMMA thin films to produce perpendicular microdomains on native silicon substrate. While ~30-armed, 21-armed, and single chain NPs bring forth perpendicular cylinders, 6-armed organic NPs do not due to the lack of entropic penalty incurred on the host BCP chains.
Domain Structures of P3DDT-based Block Copolymers Depend on Regioregularity

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Microphase-separation behavior of conjugated–amorphous block copolymers (BCPs) is driven by a complex interplay between Flory–Huggins interaction ($\chi$), liquid crystalline (LC) interaction and crystallization. Herein, in order to elucidate the influence of LC interaction on the morphology of the BCPs, we report the effects of regioregularity (RR) on the morphology and molecular packing structures of poly(3-dodecylthiophene)-block-poly(2-vinylpyridine) (P3DDT-b-P2VP). To decouple the effect of LC interactions from crystallization kinetics, we investigate the morphological behavior of the P3DDT-b-P2VP at above the melting temperature of P3DDT (~160 °C). Both electron microscopy and X-ray scattering show an abrupt reduction in the domain spacing of both lamellar and cylindrical phases as the RR of P3DDT block increases. Specifically, lower RR (i.e., 85, 79, 70%) BCPs have larger domain spacings than high RR (94%) by 50% (lamellar) or 80% (cylindrical), even though the overall molecular weights and P2VP volume fractions were similar for each morphology. We propose that the RR-driven transition in domain spacing is caused by a change in P3DDT conformations and interchain interactions. When RR is low, the system assembles into a typical bilayer structure like other semiflexible and flexible block copolymer systems. When RR is high, the less flexible P3DDT chains are extended, driving their assembly into an LC monolayer. Significantly, this study demonstrates that tunable RR provides a simple route to manipulate melt state self-assembly of conjugated-amorphous materials.
THE 7TH SYNCHROTRON RADIATION IN POLYMER SCIENCE

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- Early registration starts: January 15, 2018
- Abstracts due: May 15, 2018
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