北京大学研究生教育创新计划系列课程

2018

International Summer School on Polymer Characterization Techniques

北京大学
120th ANNIVERSARY OF PEKING UNIVERSITY
1898-2018

高分子表征技术暑期学校

联合主办单位

北京大学软物质科学与工程中心

北京大学化学与分子工程学院

教育部高分子物理与化学重点实验室

北京大学分析测试中心

2018年7月25日-8月3日　北京

张文彬

- *Thermal Analysis of Polymeric Materials*
- *Methods of X-Ray and Neutron Scattering in Polymer Science*
- *Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter*
- *Polymer Microscopy*
- *Structure of Materials: An Introduction to Crystallography, Diffraction and Symmetry*
- *Transmission Electron Microscopy: A Textbook for Materials Science*

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Distinguished Lectureship Award

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Dr. Cole A. DeForest is currently an Assistant Professor in the Department of Chemical Engineering at the University of Washington, where he began in 2014. He received his B.S.E. degree from Princeton University in 2006, majoring in Chemical Engineering and minoring in Material Science Engineering and Bioengineering. He obtained his Ph.D. degree under the guidance of Dr. Kristi Anseth from the University of Colorado in Chemical and Biological Engineering with an additional certificate in Molecular Biophysics. His postdoctoral research was performed with Dr. David Tirrell in the Divisions of Chemistry and Chemical Engineering at the California Institute of Technology. He has authored and co-authored >30 articles in peer-reviewed journals including Nature Materials, Nature Chemistry, Advanced Materials, and Angewandte Chemie. Dr. DeForest has received numerous research awards and honors including the NSF CAREER Award (2017), AIChE 35-Under-35 Award (2017), ACS PMSE Young Investigator Award (2017), University of Washington Presidential Distinguished Teaching Award (2016), Jaconette L. Tietze Young Scientist Award (2015), Biomedical Engineering Society Student Fellow Award (2013), DSM Polymer Technology Award (2011), ACS Excellence in Graduate Polymer Research Award (2010), MRS Graduate Student Research Gold Award (2009), Society for Biomaterials Outstanding Achievement Award (2009), Princeton University Material Science Student of the Year (2006), Princeton University Most Approachable Resident Adviser (2005), and Boulder High School Valedictorian (2002). His research has been supported through fellowships and grants from the National Science Foundation, the National Institutes of Health, and the US Department of Education.

Dr. Richard J. Spontak is an Alumni Distinguished Professor of Chemical & Biomolecular Engineering and Materials Science & Engineering at North Carolina State University in Raleigh, NC. He received his B.S. degree in Chemical Engineering from the Pennsylvania State University in 1983 and was later awarded the Ph.D. degree in Chemical Engineering from the University of California at Berkeley in 1988. He then pursued post-doctoral research in Materials Science & Metallurgy at the University of Cambridge (U.K.) and Condensed Matter Physics at the Institute for Energy Technology (Norway). In 1992, he accepted a faculty position at North Carolina State University. Since that time, Spontak has published over 275 research papers. His primary research interests relate to the phase behavior and morphology/property development of nanostructured polymers, polymer nanocomposites, electron microscopy, and stimuli-responsive media. He resides in Raleigh with his wife Josie and his two children, Danielle and Joshua.

Topic I: Small-Angle X-ray Scattering Technique

1. Course Description

This course is on structural characterization of materials by scattering techniques with a particular emphasis on characterization of soft-matter materials such as polymers, copolymers and biopolymers in solutions, gels, liquid-crystalline state and solid state. The course begins with an introduction into a general theory of scattering and then focuses on Small-Angle X-ray scattering technique. Examples of structural analysis of colloids, composite nanoparticles, functional soft-matter materials are discussed through the course. The course is equally divided into theoretical and experimental part.

2. Course Objectives

Understanding of the theory and basic principles of scattering techniques applied for structural characterization of soft matter, in particular polymers. Learn analytical and experimental approaches of scattering methods for detailed structural analysis of composite- and functional nanomaterials. Master the basic of Small-Angle X-ray scattering technique. Facilitate understanding structure-property relationship between morphology and functional properties of polymeric nanomaterials. Familiarize with modern scattering techniques in order to be able to design (and perform) scattering measurements on a wide range of soft-matter-materials such as polymers, copolymers, colloids, polymeric solutions, self-assembled nanostructures using state-of-the-art instruments.

3. Course Content

3.1 Theoretical part

Small-Angle X-ray Scattering. Introduction and General Theorems.

Lecture 1: Introduction to general theory of scattering. Elastic scattering. Rayleigh-Gans-Debye approximation. Fourier transformation and relationship between real space and reciprocal space.

Lecture 2: Spatial correlation function. Pair distance distribution function. Scattering length density. Form factor. Guinier's law.

Lecture 3: Porod's law. Babinet theorem. Generalized scattering models for SAXS analysis. Structure factor. Scattering invariant.

Lecture 4: Scattering from a polymer chain. Debye function. Small-Angle X-ray Diffraction and crystal structure characterization. Semi-crystalline polymers.

3.2 Experimental part

Absolute Intensity and initial SAXS data treatment. SAXS instrumentation. SAXS data collection.

Topic II: Electron microscopy and diffraction of crystalline polymers and biopolymers

Crystalline polymers have a complex, multi-dimensional structure and morphology. The length scales range from angstroms to millimeters. They include the unit-cell and crystal structure up to chain folded lamellae and the complex organization of these lamellae in spherulites.

Global techniques (X-ray diffraction, spectroscopic techniques, etc.) are valuable in analyzing these multiple aspects. The contributions of electron microscopy and electron diffraction have however been essential in reaching the present understanding of polymer structure. The most interesting aspects of electron microscopy in the investigation of crystalline polymers are (a) the combination of imaging and diffraction capabilities on the same object (b) the possibility to record diffraction information on minute amounts of material – down to 10-14 grams (c) the perfect match of these capabilities with the morphology of crystalline polymers since, given the chain-folding, the "polymer space is divided at the 10 nm scale.

Electron microscopy has limitations: the sample thickness should not exceed ≈70nm. Also, most polymers are degraded by the electron beam, which limits their "lifetime for the observation. These limitations can be overcome for the most part by appropriate preparation techniques (etching, thinning of samples) or observation techniques (low beam intensity, low magnification). Modern cameras and imaging techniques are a significant help in this respect.

This course will illustrate the interest of electron microscopy in structural investigations of polymers. In all cases, the practical, hands-on or even benchwork aspects will be privileged. The different imaging techniques will be developed (e.g. bright field, dark field). "Classical preparation techniques will be presented: shadowing, replication, etc. Several original sample preparation techniques will be introduced. They help control the morphology of the materials (e.g. by epitaxial crystallization) or reveal otherwise inaccessible structural details (e.g. via polymer decoration). The major role played by electron diffraction will be illustrated, together with the analysis of the data with the help of modeling and crystal diffraction software (e.g. Cerius2).

The course will be illustrated with examples taken mostly from our laboratory, frequently by resorting to polymer single crystals or single crystalline films generated by different means. In a more general perspective, the definition of the scientific issues, the design of the experimental approach and analysis of the data will be emphasized.

Topic III: MALDI-TOF MS Analysis of Synthetic Polymers

1. Course Goal

To develop familiarity with how to acquire and optimize mass spectral data for synthetic polymers; to critically analyze polymer mass spectra, and interpret the data in the context of polymer synthesis and functionalization.

2. Course Description

With recent advances in ionization techniques for high molecular weight analytes, mass spectrometry is rapidly becoming a critical tool for the characterization of synthetic polymers. The course will initially investigate the fundamentals of mass spectrometry and of the matrix-assisted laser-desorption ionization approach. However, the course will focus predominantly on practical aspects of polymer characterization by mass spectrometry, including sample preparation, optimization of acquisition parameters, and protocols for calibration. The lecture will also examine a number of case studies, investigating the breadth and limitations of MALDI-TOF MS for identifying end groups, characterizing block copolymers, etc. In addition to exploring the intellectual concepts behind various optimization techniques, a laboratory session will provide practical experience with sample preparation, data acquisition, and mass spectral analysis.

3. Course Content

Section 1. MS LECTURE: Mass spectrometry of synthetic polymers lecture

- 1.1. Mass spectrometry background and MALDI-TOF basics
- 1.2. Instrumental parameters: linear vs. reflector, delayed extraction, etc.
- 1.3. Precision (resolution) vs. accuracy (good calibration)
- 1.4. Practical tips: Matrices, ionization agents, sample preparation, acquisition optimization (Some case studies: determining Mn and dispersity, identifying end groups, characterizing block copolymers, analyzing azide containing polymers, and monitoring polymer degradation.)

Section 2. MS LAB

- 2.1. Instrument familiarization
- 2.2. Data acquisition of two known compounds
- 2.3. Determination of average molecular weight, dispersity, and end group identity for known compounds
- 2.4. Analysis of unknowns.

4. References

(1) Payne, M. E.; Grayson, S. M. J. Vis. Exp. 2018, (136) e57174, doi: 10.3791/57174.

(2) Hanton, S.D.; Owens, K. G. Polymer MALDI sample preparation in Mass Spectrometry on Polymer Chemistry Barner-Kowollik, C. et al., eds. Wiley-Interscience: New Jersey, 2012. https://doi.org/10.1002/9783527641826.ch5

(3) Weidner, S. W.; Trimpin, S. Mass spectrometry of synthetic polymer, Anal. Chem.; 2008, 80, 4349-4361.

Topic IV: Introduction to Radical Photopolymerization and Photolithographic Patterning

1. Course Description

Photopolymerization enables the rapid creation of linear polymers and 3D materials following directed light exposure over a wide range of temperatures and in the absence of solvent, permitting diverse applications in additive manufacturing, electronics, adhesives, and coatings. This course will guide students through the fundamentals of radical photopolymerization, starting with a mechanistic evaluation and kinetic analysis of reaction steps (i.e., initiation, propagation, chain transfer, termination) and a discussion of monomer and initiator selection, while focusing on its relative advantages and limitations compared with other schema. Turning our attention to one of the central benefits of photopolymerization, we will examine several lithographic strategies (e.g., mask-based, mask-less, multi-photon) to regulate material formation in both time and space based on select irradiation. Laboratory demos (both physical and virtual) will supplement lecture discussions, providing opportunities to examine lithographic processes firsthand while emphasizing practical tips to achieve maximum photopatterning fidelity.

2. References

(1) Chen, M., Zhong, M. & Johnson, J.A. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chemical Reviews, 116, 10167-10211 (2016).

(2) Odian, G. Principles of Polymerization, 4th Edition, John Wiley & Sons, 2004.

Delivery and 4D Cell Culture.

Topic V: Transmission Electron Microtomography (TEMT or 3D TEM)

1. Course Objectives

1) Students will extend their knowledge of TEM to include 3D imaging.
2) Students will learn the operational principles and potential of TEMT.
3) Students will appreciate the challenges associated with beam damage.
4) Students will learn various methods by which to perform reconstructions.
5) Students will be able to use TEMT as an analytical characterization tool.

2. Course Content

Lecture 1:

- Introduction to the subject
- Examples and motivation
- Fiducial markers
- Specimen damage
- Data acquisition

Lecture 2:

- Alignment algorithms
- Resolution considerations
- Denoising and segmentation
- Motif searching

Lecture 3:

- Materials applications
- Global quantitation
- Mesoscale crystallography
- Local quantitation

Lecture 4:

- Practical exercise of performing TEMT from start to finish.

Lecture 11A

SAXS characterization of core-shell nanoparticles

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Soft Matter AnalyticaL Laboratory (SMALL)
Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

Abstract
Small-angle X-ray scattering is a non-destructive methods conveniently designed for structural characterization of soft matter materials from nano- to micron scales. Recent developments of X-ray optic components, synchrotron radiation sources and laboratory SAXS instruments, complimented by a further progress in modelling and analysis, made SAXS technique one of the most reliable (and popular) for structural characterization of nanoparticles and colloids. In this respect, spherical core-shell particles represent a very wide group of structural organizations taking place in nature: homogeneous spheres, vesicles, multilamellar vesicles, liposome, polymersomes, micelles, core-shell particles with a single shell and onion-like core-multi-shell formations. Density fluctuations and phase-separation taking place in the core and/or the shell may complicate the structure causing both formation of substructure or irregularities within the particle components. An application of reciprocal space models and real space models together with contrast variation techniques for structural characterization of core-shell particle formations will be demonstrated in the talk. In particular, a step-by-step process of SAXS model development for structural characterisation of both block copolymer spherical micelles (using reciprocal space) and core-shell polymer nanoparticles (using real space) will be presented.

Lecture 11B

Analysis of experimental data in structural analysis of polymers: Missed opportunities and successes.

Bernard Lotz

Institut Charles Sadron (CNRS and Universté de Strasbourg), Strasbourg, France

Abstract
Papers submitted for publication end up all too frequently with sentences of the type: "Further experiments are needed to answer the questions raised by the present observations . Such statements are frequently an easy way out of difficulties. The presentation will illustrate different (mostly structural) problems for which the published data were sufficient to reach the correct interpretation. In many cases what was required

was not more experimental data but more time and effort spent on their analysis in order to reach the correct model. Several classical but also some personal experiences will be presented – both successes and failures. In most cases, the structural problems were known and the data were available in the literature - sometimes for decades. In some cases, the structural model existed, but its more general validity was not perceived. There are of course exceptions, but these examples suggest that a significant part of our research time should be devoted to "sit and think rather than to collect yet more experimental data.

Lecture 12A

User-Programmable Hydrogel Biomaterials to Probe and Direct 4D Stem Cell Fate

Cole A. DeForest

Department of Chemical Engineering, Department of Bioengineering, Institute for Stem Cell and Regenerative Medicine, Molecular Engineering & Sciences Institute, University of Washington, Seattle, WA

Abstract

The extracellular matrix directs stem cell function through a complex choreography of biomacromolecular interactions in a tissue-dependent manner. Far from static, this hierarchical milieu of biochemical and biophysical cues presented within the native cellular niche is both spatially complex and ever changing. As these pericellular reconfigurations are vital for tissue morphogenesis, disease regulation, and healing, in vitro culture platforms that recapitulate such dynamic environmental phenomena would be invaluable for fundamental studies in stem cell biology, as well as in the eventual engineering of functional human tissue. In this talk, I will discuss some of our group's recent success in reversibly modifying both the chemical and physical aspects of synthetic cell culture platforms with user-defined spatiotemporal control. Results will highlight our ability to modulate intricate cellular behavior including stem cell differentiation, protein secretion, and cell-cell interactions in 4D.

Lecture 12B

Solvent Templating and Solvent-Vapor Annealing of Charged Thermoplastic Elastomers

Richard J. Spontak

Departments of Chemical & Biomolecular Engineering and Materials Science & Engineering, North Carolina State University, Raleigh NC 27695

Abstract

Block copolymers continue to capture the attention of the academic and industrial worlds due largely to their fascinating ability to spontaneously self-assemble into a wide variety of "soft" nanostructures that are ideally suited for a broad range of diverse nanotechnologies. The development of thermoplastic elastomers (TPEs), such as triblock copolymers with glassy endblocks and a rubbery midblock, also endows these materials with elastic network-forming characteristics, and selective solvation of the rubbery midblock results in thermoplastic elastomer gels (TPEGs) with remarkable mechanical properties for stimuli-responsive materials such as dielectric and shape-memory elastomers, which will be discussed. While most block copolymers are inherently nonpolar, targeted functionalization of block copolymers can permit these materials to be used in polar environments. Sulfonation of block copolymers, for example, yields materials that possess amphiphilic properties for new applications such as separation membranes and fuel cells. Combination of TPEs with a sulfonated midblock produces a unique TPEG that is capable of forming a physical hydrogel. We have recently demonstrated that these materials are competitive candidates for electroactive media, selective membranes and soft photovoltaics. Controlled use of solvency during dissolution and casting yields nonequilibrium materials with templated morphologies. Unfortunately, the inherently high incompatibilities and glass transition temperatures of such block ionomers effectively prevent the use of thermal annealing, routinely employed to refine the morphologies of nonionic block copolymers. An alternative approach is therefore required to control morphological development in block ionomers. This presentation likewise explores the morphological characteristics of midblock-sulfonated block ionomers differing in their degree of sulfonation and cast from solvents varying in polarity, followed by solvent-vapor annealing (SVA). Electron microscopy and synchrotron scattering confirm that films deposited from different solvent systems form nonequilibrium morphologies due to solvent-templated self-assembly and drying. A series of SVA tests reveals that exposing cast films to the vapor of a polar solvent constitutes the most effective SVA protocol, yielding the equilibrium morphology anticipated from simulations, as well as unexpected in-plane ordering.

Basic 1D SAXS
1. See the real instrument;
2. Demo experiments.

Basic 1D SAXS
1. See the real instrument;
2. Demo experiments.

Advanced Experiment
1. See the real instrument;
2. Demo experiments with selected samples from students.

Project 1:
Take two polystyrenen samples one with hydroxyl end groups, one with something else. Then, acquire spectra, optimize, calibrate, and confirm which has which end groups, as well as determine Mn and dispersity (usually the software does this).

Project 2:
Take some unknown polymer and acquire a spectra, determine the polymer based on the repeat unit mass, and guess the end groups based on the distribution offset. It can also be performed on or selected samples from students.


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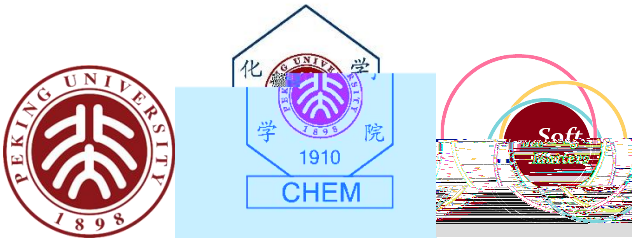
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