

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



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

前言

各位老师、同学们，大家好！

欢迎大家远道而来，参加我们这次暑期学校！

高分子表征技术是高分子科学和材料科学研究人员非常重要的基础。为了促进高分子表征技术的掌握和研习，作为北京大学“研究生教育创新计划”系列课程之一，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高分子科学与工程系、教育部高分子化学与物理重点实验室与北京大学分析测试中心联合推出了2018年北京大学高分子表征技术暑期学校。我们秉承“教室有届，知识无疆，有教无类，共同进步”的宗旨，希望将领域内与科学实践相关的 Knowhow 更好地和大家分享，帮助大家打好高分子表征相关技术的基础，不仅知其然，更知其所以然，从而更好地掌握如何选择正确的表征方法、实验参数、得到漂亮可信的表征结果，以及清晰地思考如何恰当地理解和诠释实验结果。本次暑期学校授课老师分别来自于美国、英国和法国。我们收到了来自于全国各地160余份学员申请。“四海之内，皆兄弟也。”我们希望暑期学校可以成为促进大家沟通、交流，甚至是合作研究的一个平台。由于课程时间和场地条件的限制，我们只能限制参加仪器实践的学员人数，深感遗憾。为了加强教学效果，特增补了若干实验专题的报告，以教授更多的实验细节。为了促进学习的效果，我们为每一个专题准备了课后作业。出勤率和课后作业将是课程评分的主要依据。请各位学员务必认真、独立完成。这是我们第一次开展的暑期学校，在组织和开展上一定会有疏忽和不周之处，还请各位学员给予理解和支持，并在课程中和课程后将意见和建议反馈给我们，以便将来改进。最后，各位学员们出门在外，请注意饮食卫生，安全第一，做到劳逸结合。北大有着一个很美的校园，无论是博雅塔下，还是未名湖畔，静园草坪，都是读书、思考和放飞自己的一个好的去处。希望大家能够喜欢而且享受在这个暑期学校短短八天的时间，带着好奇高高兴兴而来、满载知识快快乐乐而归！

预祝大家一切顺利，学有所成！



2018年7月21日

教学日程安排

- 7月25日 周三
14:00-18:00 北京大学化学学院 D 区大厅
报到及领胸卡等资料 助教：方晶、许连杰
- 7月26日 周四
08:30-09:30 北京大学理教 103
开幕式（欢迎辞、集体照、暑期学校安排介绍）
09:50-11:50 Lecture 1 Prof. Oleksandr Mykhaylyk
Small-Angle X-ray Scattering Technique-1
14:00-16:00 Lecture on Lab: Prof. Oleksandr Mykhaylyk
Practical Aspects of SAXS
（注意：需要自带笔记本电脑，学习如何使用 Igor Pro 进行数据处理等等，建议预装 30 天免费测试版 IgorPro (<https://www.wavemetrics.com/support/demos.htm>), 并使用 Irena 和 Nika macros (<https://usaxs.xray.aps.anl.gov/software/irena>).
- 7月27日 周五
08:30-10:00 北京大学理教 103
Lecture 2 Prof. Bernard Lotz
Electron microscopy and diffraction of crystalline polymers and biopolymers-1
10:20-11:50 Lecture 3 Prof. Oleksandr Mykhaylyk
Small-Angle X-ray Scattering Technique-2
- 实验部分--北京大学化学学院仪器测试中心
14:00-15:30 TEM 北京大学化学学院 B23 (TEM-A 组)
SAXS 北京大学化学学院 B604 (SAXS-A 组)
15:50-17:20 TEM 北京大学化学学院 B23 (TEM-B 组)
SAXS 北京大学化学学院 B604 (SAXS-B 组)
（注意：以上实验部分平行进行，学员分组信息见附表）
- Office Hour--北京大学化学学院 B418
14:00-17:00 Prof. Oleksandr Mykhaylyk & Prof. Bernard Lotz
（欢迎学员带具体问题来和老师讨论，请发信给张老师预约）
- 7月28日 周六
08:30-10:00 北京大学理教 103
Lecture 4 Prof. Oleksandr Mykhaylyk
Small-Angle X-ray Scattering Technique-3
10:20-11:50 Lecture 5 Prof. Bernard Lotz
Electron microscopy and diffraction of crystalline polymers and biopolymers-2
- 实验部分--北京大学化学学院仪器测试中心
14:00-15:30 TEM 北京大学化学学院 B23 (TEM-C 组)

15:50-17:20 SAXS 北京大学化学学院 B604 (SAXS-C 组)
TEM 北京大学化学学院 B23 (TEM-D 组)
SAXS 北京大学化学学院 B604 (SAXS-D 组)
(注意: 以上实验部分平行进行, 学员分组信息见附表; Lotz 教授将参与 TEM-C、TEM-D 组的实验;)

Office Hour--北京大学化学学院 B101

14:00-17:00 Prof. Oleksandr Mykhaylyk
(欢迎学员带具体问题来和老师讨论)

7月29日 周日 北京大学理教 103
08:30-10:00 Lecture 6 (视频授课) Prof. Scott Grayson
MALDI-TOF MS Analysis of Synthetic Polymers
10:20-11:50 Lecture 7 Prof. Bernard Lotz
Electron microscopy and diffraction of crystalline polymers and biopolymers-3

实验部分--北京大学化学学院仪器测试中心

14:00-15:30 MALDI-TOF MS 北京大学化学学院 A111 (MS-A 组)
15:50-17:20 MALDI-TOF MS 北京大学化学学院 A111 (MS-B 组)

7月30日 周一 北京大学理教 103
08:30-10:00 Lecture 8 Prof. Oleksandr Mykhaylyk
Small-Angle X-ray Scattering Technique-4
10:20-11:50 Lecture 9 Prof. Bernard Lotz
Electron microscopy and diffraction of crystalline polymers and biopolymers-4
14:00-15:30 Lecture 10 Prof. Richard Spontak
3D TEM Techniques in Polymer Science-1
(提交 SAXS, TEM, MS 作业截止于 30 日 16:00)

7月31日 周二 北京大学理教 103
研究报告—高分子表征技术在科研中的实践 (具体摘要附后)
08:30-09:20 Lecture 11A Prof. Oleksandr Mykhaylyk
SAXS characterization of core-shell nanoparticles
09:20-10:10 Lecture 11B Prof. Bernard Lotz
Analysis of experimental data in structural analysis of polymers: Missed opportunities and successes
10:20-11:10 Lecture 12A Prof. Cole DeForest
User-Programmable Hydrogel Biomaterials to Probe and Direct 4D Stem Cell Fate
11:10-12:00 Lecture 12B Prof. Richard Spontak
Solvent Templating and Solvent-Vapor Annealing of Charged Thermoplastic Elastomers

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| 14:00-15:30 | Lecture 13 | Prof. Richard Spontak |
| | 3D TEM Techniques in Polymer Science-2 | |
| 15:50-17:20 | Lecture 14 | Prof. Cole DeForest |
| | Introduction to Radical Photopolymerization and Photolithographic Patterning | |
| 8月1日 周三 | 北京大学理教 103 | |
| 08:30-10:00 | Lecture on Lab | Prof. Cole DeForest |
| | Practical Aspects of Photolithography | |
| 10:20-11:50 | Lecture 15 | Prof. Richard Spontak |
| | 3D TEM Techniques in Polymer Science-3 | |
| 14:00-15:30 | Lecture 16 | Prof. Wen-Bin Zhang |
| | 要点回顾, 案例分析 | |
| | (提交 3D TEM, 光刻作业截止于 1 日 16:00) | |
| 8月2日 周三 | 北京大学理教 103 | |
| 08:30-10:00 | Lecture on Lab | Prof. Richard Spontak |
| | Practical Aspects of 3D TEM | |
| 10:20-11:50 | 闭幕式 | |
| | (结语、颁发结业证书、颁发优秀营员奖) | |

教学大纲

一、课程目的与要求

针对高分子表征技术中若干专题，分别详细介绍其原理、仪器和表征技术；为科研中涉及的表征技术和实验方案提供最为相关的直接介绍和具体指导。

二、课程简介

高分子表征技术暑期学校是高分子专业高年级本科生和研究生的一门专业基础选修课，针对具有一定高分子科学基础和实践经验的研究生进行讲授。每期暑期学校课程的内容主要针对若干具体的高分子表征技术，详细介绍其原理、仪器和实验，致力于提供与科研中涉及的表征技术和实验方案最为相关的直接介绍和具体指导。这些具体的表征技术包括聚合物热分析、高分子质谱、光化学与光刻技术、散射与衍射技术、高分子电镜结构解析与高分子电镜形貌三维重建等几个部分。课程取材上力求既包括高分子化学与物理的基础实验表征技术，又希望能教授本学科发展用到的最新表征手段。目的在于为学生对如何选择正确的表征方法、实验参数、并得到一个好的表征结果提供一个基本的了解和掌握，并就如何恰当地理解和诠释实验结果有一个清晰的思路和方法，为其日常的科研工作打下坚实的基础。本课程以课堂教授为主，适当结合上机实践，使学生对所学的知识具像化，获得实践体验。

三、教学内容（每个专题的英文课程大纲见后）

1. 绪论与高分子科学基础
2. 高分子散射与衍射技术
3. 高分子电镜衍射与结构解析
4. 高分子质谱表征技术
5. 高分子光化学及光刻技术
6. 高分子电镜形貌与三维重建

三、评分标准

1. 符合以下条件的可获得结业证书：
 - (a) 截止至8月1日16:00的出勤率>80%（所有报告部分）；
 - (b) 截止至8月1日16:00之前完成并提交各个部分的作业，且得分不低于60分。
2. 从获得结业证书的学员中，根据截止至8月1日16:00之前完成并提交各个部分的作业得分总分的高低，取前10%，评为“优秀学员”，并颁发奖状。

四、主要参考书

- B. Wunderlich, *Thermal Analysis of Polymeric Materials*, Springer, 2005.
- R.-J. Roe, *Methods of X-Ray and Neutron Scattering in Polymer Science*, Oxford University Press, 2000.
- P. Lindner, T. Zemb, *Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter*, Elsevier, 2002.
- L. C. Sawyer, D. T. Grubb, G. F. Meyers, *Polymer Microscopy*, 3rd Ed., Springer, 2008.
- M. D. Graef, M. E. McHenry, *Structure of Materials: An Introduction to Crystallography, Diffraction and Symmetry*, 2nd Ed., Cambridge University Press, 2012
- D. B. Williams, C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*, Springer, 1996.

主持教师简介

张文彬，特聘研究员，生于 1981 年 11 月。2000 年进入北京大学化学与分子工程学院，2004 年毕业获得有机化学学士学位。

2006 年 1 月赴美国阿克伦大学，师从程正迪院士和 R. P. Quirk 教授，研究高分子化学和物理，2010 年 5 月获得高分子科学博士学位。之后，他先在阿克伦大学跟随程正迪院士进行一年的博士后研究，进而于 2011 年 9 月赴加州理工学院跟随 D.A.



Tirrell 院士进行蛋白质生物材料方向的第二站博士后研究。2013 年 8 月进入北京大学化学与分子工程学院工作。张老师长期致力于结合合成高分子和生物高分子的独特基元和设计理念，发展具有不寻常结构和性质的精密结构大分子。至今为止，已有 105 篇文章在 *Science*, *Proc. Natl. Acad. Sci.*, *J. Am. Chem. Soc.*, *Adv. Mater.*, *Angew. Chem.*, *Adv. Funct. Mater.*, *Macromolecules* 等国际著名学术期刊上发表。此外，还撰写 ACS Symposium Series 生物材料专著章节一章，*Adv. Polym. Sci.* 专著一章；授权美国专利 2 项，申请中国发明专利 2 项，在国际学术会议上 15 次作邀请报告。2014 年 3 月，入选中组部青年千人计划。2015 年 1 月，得到科技部 863 青年科学家专题支持。2017 年 3 月，获日本化学会“2017 The Distinguished Lectureship Award”。

课程顾问



马玉国，博士，北京大学化学与分子工程学院教授，博士生导师，学术课题组长。现任北京大学化学与分子工程学院党委书记，北京大学分析测试中心主任，软物质科学与工程中心副主任。1994年7月和1997年7月于北京大学化学学院分别获得学士学位（北京地区高等学校优秀毕业生）和硕士学位，师从周其凤院士，研究方向为液晶高分子。2002年12月于美国依利诺伊大学化学系获得博士学位，师从 Steven C. Zimmerman 教授，研究方向为有机、高分子及材料化学的交叉领域。

2003年1月至2005年8月在美国康奈尔大学化学与化学生物学系 Geoffrey W. Coates 教授的实验室进行博士后研究，方向为金属有机催化化学。2005年9月起回国任北京大学化学与分子工程学院高分子系副教授，从事有机/高分子光电性能材料、结构材料的制备和性质研究。至今已在 J. Am. Chem. Soc., Angew. Chem. Int. Ed., Chem. Commun., Org. Lett., Chem. Soc. Rev. 等国际重要学术期刊上发表了相关论文 80 余篇。申请中国专利 8 项，已获授权 6 项。受邀撰写英文专著一章、中文两章。2007年5月起任博士生导师，2011年8月晋升为教授。2015年12月至2016年12月挂职任内蒙古大学校长助理（中组部、团中央“博士服务团”）。2000年获 Pacifichem 2000 Outstanding Presentation Award；2002年获美国依利诺伊大学化学系 R. C. Fuson Memorial Travel Award；2008年入选“教育部新世纪优秀人才支持计划”；所开设的本科生主干基础课《有机化学》（英语教学）于2013年入选教育部“来华留学英语授课品牌课程”；2013年获北京大学“青年教师教学基本功比赛”一等奖、优秀教案奖。

课程顾问



李子臣 博士，教授，博士生导师，1968年3月25日出生。1987.7 在山东大学化学系获理学学士学位。1990年8月在中科院化学研究所获硕士学位。1990年9月考入北京大学攻读博士学位，其中1993.8-1994.7在日本早稻田大学联合培养一年，1995年1月在北京大学获博士学位。1995.1-1996.12在北京大学化学学院从事博士后研究，其中1996.3-1996.5，1996.7-1996.12，作为日本学术振兴会 (JSPS) 特别研究员赴早稻田大学合作研究。1997年1月起在北京大学化学学院工作，任讲师；1997.8 晋升为副教授；2002.8 晋升为教授。曾任北京大学化学学院副院长（2004-2008），现任北京大学化学学院高分子科学与工程系主任。主要从事高分子合成化学研究，包括新型聚合反应，多组分聚合反应，可控自由基聚合反应；精密结构高分子的合成方法学；高分子绿色合成、可控降解与回收利用；刺激响应性高分子的设计合成及其在生物医学领域应用等。已发表学术论文 180 余篇。2002 年获教育部首批高校优秀骨干教师荣誉称号；2003 年度获中国化学会高分子科学创新论文奖，2003 年获中国化学会青年化学奖。2004 年入选教育部“新世纪优秀人才支持计划”，2004 年获北京市教育教学成果（高等教育）一等奖（第 5 完成人）；2005 年获国家教学成果二等奖（第 5 完成人），2009 年获“北京市优秀教师”荣誉称号，2010 年获 Feng Xinde Polymer Prize for “The best paper from China” published in the journal of “Polymer” during 2009。2012 年获得国家杰出青年基金；2014 年获国家教学成果二等奖（第 3 完成人）。现为《Chin. J. Polym. Sci. 》副主编（2014~）；《高分子学报》，《高分子通报》，《高等学校化学学报》，《功能高分子学报》，《Chem. J. Chin. Univ. 》编委；<Macromolecules>，<ACS Macro Lett.>，<Polymer>，<J. Mater. Chem. B>，<Polymer International> 顾问编委。亚洲高分子学会联合会（FAPS）理事（2008~），中国化学会高分子学科委员会委员、秘书长（2010-2018）、副主任（2018.4~）。

课程顾问

陈尔强，男，1966年7月生，1988年、1991年于复旦大学获学士、硕士学位；1998年于美国Akron大学获博士学位。1994至1998年于复旦大学材料科学系任教；1998至2000年于美国Akron大学及美国标准与技术研究院（NIST）从事博士后研究。2000年加入北京大学，2001年起任教授、博士生导师。现任北京大学高分子化学与物理教育部重点实验室主任、Polymer编辑、中国科学院大学兼职教授、DSM Ahead B.V.（荷兰）科学顾问。曾获2000年度国家杰出青年科学基金、2000年度ICTAC-Perkin Elmer青年科学家奖（国际热分析与量热学联合会）、2007年度首届Polymer冯新德奖、2016年度北京大学教学优秀奖。主要从事高分子结晶、液晶、自组装行为及高分子结构与性能关系的研究工作。



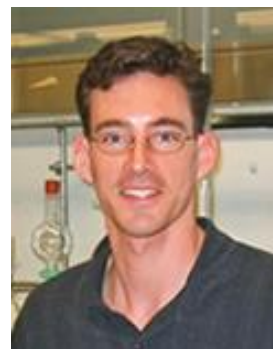
授课教师简介

Dr. Sasha Mykhaylyk obtained his MSc in Physics (optics and spectroscopy) from Taras Shevchenko Kiev State University in 1991 (Diploma with distinction was awarded on graduation). After obtaining a PhD in solid state physics and crystallography from the Institute for Problems of Materials Science (the Ukrainian Academy of Sciences) in 1996, he became a Research Scientist at the same institute where he was later promoted to a Senior Scientist. After holding Royal Society/NATO Fellowship at the University of Cambridge in 2000-2001 he joined the University of Leeds in 2002 as a Research Associate. He moved to the University of Sheffield in 2004 where he was promoted to a Research Fellow in 2011 and Senior Research Fellow in 2017.



Bernard Lotz was born in Alsace, France, where he has spent most of his research career at the Centre de Recherches sur les Macromolécules, which became later the Institut Charles Sadron (ICS), a laboratory owned and run by the French Centre National de la Recherche Scientifique (CNRS). He is currently Emeritus Directeur de Recherche at CNRS. He has held various positions as visiting scientist and visiting professor at several American and Japanese Universities and Research Institutes. His research interests include the phase transitions, structure and morphology of crystalline polymers and biopolymers, and block copolymers. He has authored or coauthored over 300 research papers, reviews, and book chapters.

Scott was born in St. Louis, MO, and graduated from Chaminade College Preparatory. He came to Tulane for the first time to carry out Bachelor's degrees in Chemistry, Mathematics, and History in 1996, and then moved to the University of Bradford where he completed a master's degree in Archaeological Chemistry under the direction of Professor Carl P. Heron in 1998. He completed his doctoral studies in Chemistry in 2002 at the University of California, Berkeley, with Professor Jean Fréchet, developing new dendritic architectures for biological applications. He continued his training as a post-doctoral researcher in the labs of C. Grant Willson, at the University of Texas at Austin, developing new polymer materials for photolithography and biosensing, and has been an Assistant Professor at Tulane University since 2005. He is now full professor in Tulane University.





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.



专题课程大纲

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 ≈ 70 nm. 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 M_n 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.
- (3) Ruskowitz, E.R. & DeForest, C.A. Photoresponsive Biomaterials for Targeted Drug Delivery and 4D Cell Culture. *Nature Reviews Materials*, 3, 17087 (2018) DOI: 10.1038/natrevmats.2017.87.

Topic V: Transmission Electron Microtomography (TEM 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 TEM.
- 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 TEM 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
- Denosing and segmentation
- Motif searching

Lecture 3:

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

Lecture 4:

- Practical exercise of performing TEM from start to finish.

研究报告摘要

Lecture 11A

SAXS characterization of core-shell nanoparticles

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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

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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.

实验部分内容

1、高分子散射与衍射技术

Basic 1D SAXS

1. See the real instrument;
2. Demo experiments.

2、高分子电镜衍射与结构解析

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.

3、高分子质谱表征技术

Project 1:

Take two polystyrene 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 M_n 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.

附录：相关信息

1、报到及实验和讨论地点



北京大学化学与分子工程学院
(出地铁 4 号线北京大学东门站 C 口即是)

2、上课地点



北京大学理科教学楼 103
(出地铁 4 号线北京大学东门站 B 口，进北大东门，直走，在第二个岔路口左转，理教即为左手边第一幢楼。)

致谢

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