Elitenetzwerk Bayern

UNIVERSITÄT BAYREUTH

Elite Study Program - Macromolecular Science

Advanced Module M028

Self-Organized Polymer and Hybrid Structures

July, 2012
University of Bayreuth, Germany

Module Coordination:

Prof. Axel Müller, Prof. Hans-Werner Schmidt, Dr. Andreas Bernet

Guest Speakers:

Prof. Akira Hirao (Tokyo Institute of Technology, Japan)

Prof. Tatsuki Kitayama (Osaka University, Japan)

Summer term 2012

This advanced module within the Elite Study Program “Macromolecular Science” is on **"Self-Organized Polymer and Hybrid Structures**". The module covers special aspects of synthesis and applications of self-organized polymer materials and can be individually tailored adapting the interests of the students. The module consists of three elements.

I. Seminar on the scientific activities of selected conference speakers

July 18th, 2012: Lecture hall: 1.002 (Diplomandenzimmer EPIII), BGI, 12:00 - 14:00

Each participating student will select one conference speaker and will prepare a short presentation (20 minutes with discussion) including

I. Curriculum Vitae

II. University and department

III. Presentation of one recent paper

Timetable	*Student*	*Presentation about*
12:00-12:20	Haedler, Andreas	Kris Matyjaszewski
12:20-12:40	Bieligmeyer, Matthias	Bernadette Charleux
12:40-13:00	Kollath, Anna	Brigitte Voit
13:00-13:20	Burchardt, Hubertus	Holger Frey
13:20-13:40	Singer, Julia	Matthias Ballauf
13:40-14:00	Müller, Christian	Klaus Müllen

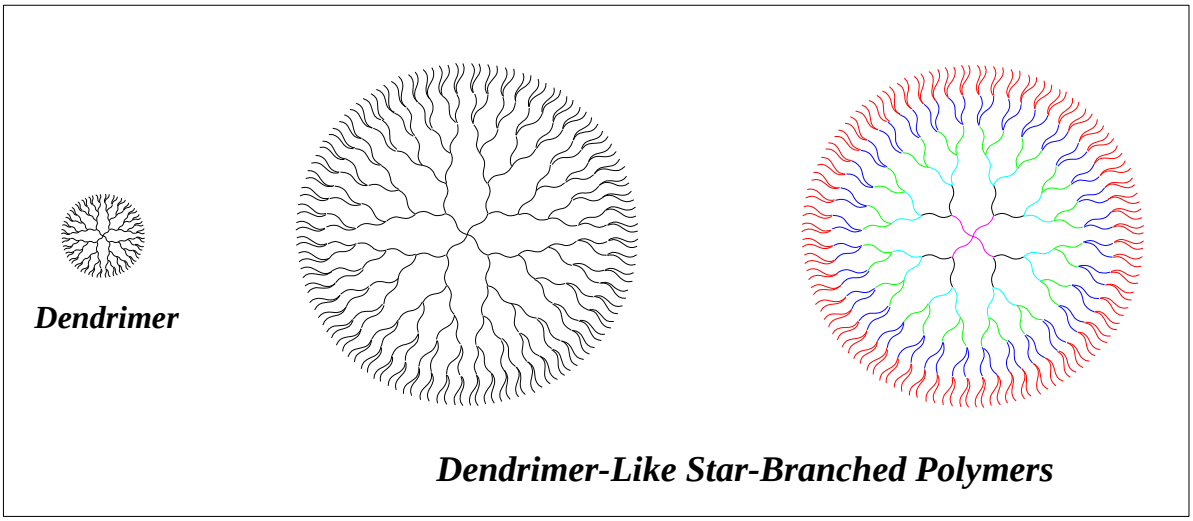
III. Series of lectures by international guest speakers and faculty members of the University of Bayreuth

July 19th, 2012: Lecture hall: Room 1.002 (Diplomandenzimmer EPIII), BGI, 10:00 - 16:00

10:00 – 11:00 Akira Hirao (Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan):

Precise Synthesis and Some Properties of Dendrimer-Like Star-Branched Polymers

It has long been studied how branching architecture influences the properties and behavior of polymers from both the theoretical and industrial viewpoints. Among various branched polymers so far synthesized, dendrimer-like star-branched polymers have emerged as a new class of well-regulated hyper branched polymers synthesized since 1995. As you can see representative examples shown in the following figure, these polymers resemble well-known dendrimers in branched architecture but are composed of dendritically branched many high-molecular-weight polymers emanating from a central core. Therefore, they are much larger in molecular size and much higher in molecular weight than dendrimers. Dendrimer-like star-branched polymers are believed as three-dimensional nano-size globular mega molecules and manifold unique and interesting characters, such as specific topological hyper branched and hierarchic layer architectures, so-called “generation”, disparate branch densities between the core and outmost layer, and many junctions and chain-ends bearing many functional groups.



Architectural similar dendrimer-like star-branched block copolymers consisting of different polymer segments introduced at each layer have also been synthesized. As compared to linear block copolymers, they are considered to be unprecedented block copolymers having hierarchic layer-based architectures. Because of their special and unique architectures, different polymer segments are expected to be phase-separated at the molecular level, followed by self-organizing, to form quite interesting and characteristically shaped microdomains and supramolecular assemblies ordered in nanoscale, which should be different from those formed by linear block copolymers and even asymmetric star-branched polymers. Thus, dendrimer-like star-branched polymers and their block copolymers are promising next-generation functional materials with many potential applications in the fields of nanoscience and nanotechnology such as nanoreactors having catalysts and enzymes, multicompartment micelles, carriers of drugs and genetic materials, sharp-persistent electronic and photo nano-devices, etc.[1-4]

In this presentation, we would like to describe the precise synthesis of such interesting and characteristic hyper branched polymers by means of living anionic polymerization, some solution properties, and shapes observed by GIXS and AFM measurements.[5-8]

References

(1) A. Hirao et al., *J. Polym. Sci., Part A: Polym. Chem. Ed*. (Feature Article), **2006**, *44*, 6659-6687.

(2) Y. Gnanou et al., *New J. Chem*., **2007**, *31*, 1097-1110.

(3) A. Hirao, A Precise Synthesis of Dendrimer-Like Star-Branched Polymers: In *Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly*, John Wiley & Sons, 2011. Chapter 5, pp133-167.

(4) M. J. Monteiro et al., *Macromolecules* **2011**, *44*, 7067-7087.

(5) A. Hirao et al., *Macromolecules* **2005**, *38*, 8701-8711.

(6) A. Hirao, A. Deffieux, *J. Am. Chem. Soc*., **2008**, *130*, 5670-5672.

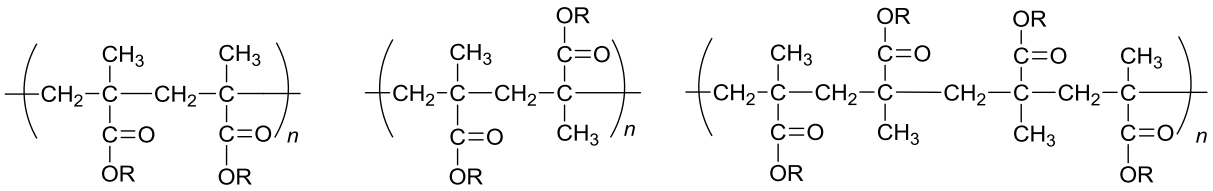
(7) A. Hirao, A. Deffieux, M. Ree et al., *Macromolecules* **2009**, *42*, 4558-4570.

(8) A. Hirao et al., *Macromolecules* **2012**, *45*, 100-112.

11:00 – 14:00 Lunch Break

14:00 – 15:30 Prof. Tatsuki Kitayama (Department of Chemistry, Graduate School of Engineering Science, Osaka University, Japan):

Stereospecific living polymerization of methacrylates — A polymerization chemistry from polymer structures



[Isotactic] [Syndiotactic] [Heterotactic]

Properties of vinyl polymers are often affected by the difference in their stereochemical structures, i.e., stereoregularity or tacticity, in addition to other principal structural parameters such as molar mass and its distribution (MMD). Stereospecific living polymerization is one of advanced methods for precise polymer syntheses, which allows us simultaneous control of molar mass and stereoregularity. Anionic polymerization of carbonyl-containing polar vinyl monomers (acrylates and methacrylates) has often been challenged by side reactions involving the carbonyl group, which deteriorate the control of the polymerization processes. Proper selection of initiators as well as additives has been proved effective to suppress such difficulties. We have developed a series of stereospecific living polymerizations of methacrylates that utilize additives such as trialkylaluminums for syndiotactic [1], aluminum bisphenoxides for heterotactic [2], and lithium silanolates for isotactic [3] living polymerizations. In this lecture, importance of detailed structural analyses of the polymers will be emphasized in view of polymerization chemistry.

(1) Kitayama T, et al., *Makromol.Chem.Suppl.* 1989, **15**, 167.

(2) Kitayama T, et al, *Tetrahedron,* 1997, **53**, 15263; Hirano T, et al., *Polym. J.*, 1998, **30**, 767.

(3) Kitaura, T., Kitayama, T. *Macromol*. *Rapid Commun*., 2007, **28**, 1889.

15:30 – 16:00 Coffee Break

17:00 – 18:00 Lecture hall: H14, NW I Axel H. E. Müller (Bayreuth University):

Farewell Lecture: "Wie wir Indien suchten und Amerika entdeckten"

18:00 Chemistry Department Summer Party: NWI Building, Main entrance

III. Participation „Self-Organized Polymer and Hybrid Structures"

July 20, 2012: Lecture hall: H 17, NW II, 08:45 - 18:30