SFB TRR 102

UNIVERSITÄT LEIPZIG

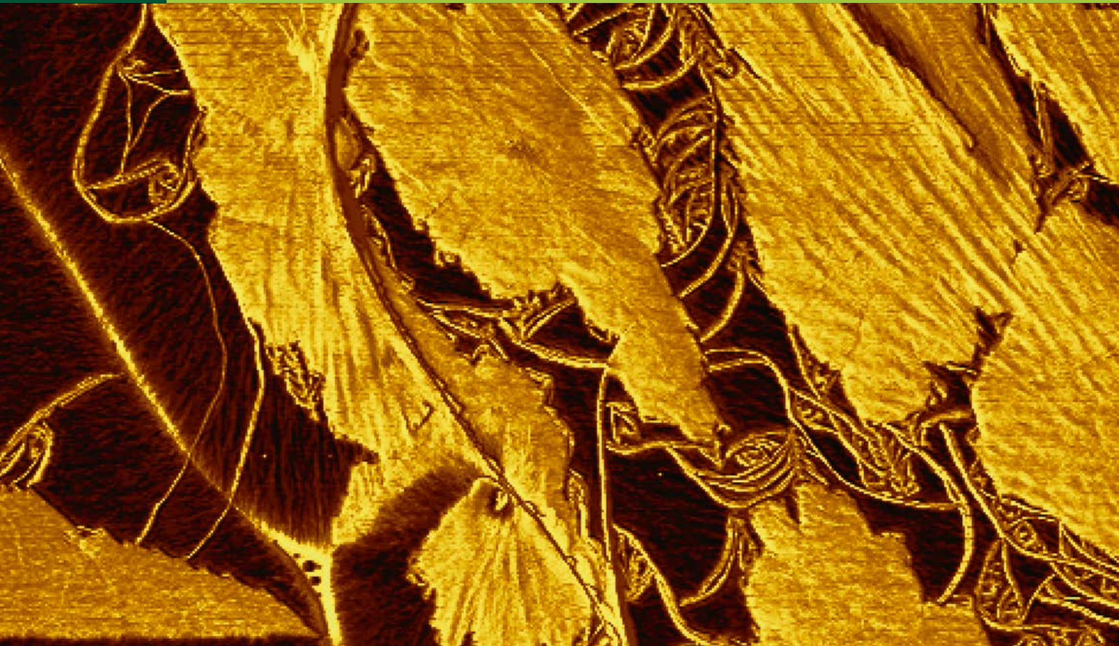
MARTIN-LUTHER-UNIVERSITÄT
HALLE-WITTENBERG

International Discussion Meeting on Polymer Crystallization 2017

From Classical Systems to Functional Materials and Biopolymers

September 17th – 20th, 2017
Wittenberg, Germany

Program & Abstracts



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Dear Colleagues and Participants of the IDMPC 2017,

On behalf of the polymer and soft matter scientists at the Martin Luther University Halle-Wittenberg and Leipzig University, we are very happy to welcome you to the *International Discussion Meeting on Polymer Crystallization 2017 – From Classical Systems to Functional Materials and Biopolymers* in Wittenberg.

This meeting continues the series of biennial meetings aiming at a deeper understanding of the mechanisms of polymer crystallization, which was initiated by Prof. Gert Strobl, University of Freiburg in 1999 in Waldau in the black forest. The last three meetings took place in Beijing 2011, Kyoto 2013, and Honolulu 2015.

Attending, but also already preparing, such a conference is an opportunity to reflect the state of the field and to consider recent developments and possible future perspectives. Although crystallization is a classical topic in polymer research, in our view our knowledge is still far from complete. This concerns fundamental scientific questions as well as our understanding of crystallization as an important step during processing of polymer materials for applications. In addition, new materials and new scientific questions come into focus. We have taken all of these aspects into account and put a special emphasis on new materials by organizing two new sessions, one on functional polymers and one on polymers of biological origin. In both of these neighboring fields, partially crystalline structures do play an important role.

We wish that the meeting will help to disseminate recent advances in these fields and to stimulate discussions about future perspectives. The conference is sponsored by our Collaborate Research Center ‘Polymers under multiple constraints’. The center also contains an IRTG (international research and training group) supporting graduate students with additional guidance and training. This meeting provides an opportunity to the members of the iRTG to present their results and to put these into relation to results from outside experts.

Concerning the conference format, we have stayed with the original format of the first meetings, i.e. to focus on invited talks and posters but tried also to create a corresponding atmosphere with plenty of time for discussion. The place of the meeting, the Leucorea, which is today a university conference center, goes back to the roots of the Martin Luther University. We hope that at the occasion of the 500th anniversary of the reformation this location provides a stimulating and interesting surrounding for your visit in Germany and Saxony-Anhalt.

Sincerely,

Thurn-Albrecht

Thomas Thurn-Albrecht Kay Saalwächter

Organizing Committee, IDMPC 2017, Martin Luther University Halle-Wittenberg

Important information

Venue

Leucorea Foundation
Collegienstrasse 62
06886 Wittenberg

Hotels

Luther-Hotel
Neustrasse 7-10
06886 Lutherstadt Wittenberg
Phone: +49 3491 4580

Acron Hotel
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Leucorea Foundation
Collegienstrasse 62
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Guide Leucorea

Audimax	Auditorium Maximum (ground floor)
Foyer	Foyer Leucorea (ground floor)
SR 1, 2, 3	Seminar room 1, 2, 3 (1st floor)
SR 4 & Cafetaria	Cafetaria (1st floor)
SR 5, 6, 7	Seminar room 5, 6, 7 (2nd floor)
Library	Library Leucorea (3rd floor)

Conference office

The conference office is located at the 1st floor.

Registration

Registration opens on Sunday, September 17, from 3:00 pm to 6:00 pm and on Monday, September 18, from 8:00 am to 9.00 am in the foyer on the ground floor of the Leucora.

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Program

International Discussion Meeting on Polymer Crystallization 2017

From Classical Systems to Functional
Materials and Biopolymers

Sunday, September 17

3:00-6:00 pm	Registration	Leucorea, foyer
6:00-6:45 pm	Evening talk: Reformation and Modern Life *Christian Senkel*	Audimax, ground floor
7:00-8:30 pm	Welcome dinner	“Brauhaus”, Market place

Monday, September 18

9:00-9:15 am	Opening *Thomas Thurn-Albrecht*	Audimax

Session 1

Audimax

Connectivity and chain architecture as constraints for polymer crystallization (Chair: G. Rutledge)

9:15-9:45 am	Avoidance of Density Anomalies as a Structural Principle for Semicrystalline Polymers *Klaus Schmidt-Rohr*	
9:45-10:15 am	The role of entanglements for polymer crystallisation *Jens-Uwe Sommer*	
10:15-10:45 am	*Coffee break*	Foyer & 1st floor
10:45-11:15 am	Chain Folding of Semicrystalline Polymers *Toshikazu Miyoshi*	
11:15-11:35 am	Crystallization in melts of semi-flexible hard polymer chains: An interplay of entropies and dimensions *Wolfgang Paul*	
11:45-1:15 pm	*Lunch break* & posters	Foyer, 1st & 2nd floor

Session 2

Audimax

Functional semicrystalline polymers (Chair: F. Kremer)

1:15-1:45 pm	Kinetics of crystallization in a model poly(thiophene) *Alberto Salleo*
1:45-2:15 pm	Model Experiments for the Crystallization of Conjugated Polymers *Günter Reiter*

2:15-2:45 pm	Highly oriented and crystalline semi-conducting and conducting polymer films prepared by high-temperature rubbing, *Martin Brinkmann*	
2:45-3:15 pm	Multi-Shape Memory Effect of Columnar Side-Chain Liquid Crystalline Polymer *Erqiang Chen*	
3:15-3:45 pm	*Coffee break*	Foyer & 1st floor

Session 3

Audimax

Crystallization under external control (flow)
(Chair: M. Beiner)

3:45–4:15 pm	The non-equilibrium phase diagrams of flow-induced crystallization and melting of polymer *Liangbin Li*
4:15-4:45 pm	Full characterization of multi-phase, multi-morphological kinetics in flow-induced crystallization of isotactic Polypropylene at elevated pressure, *Gerrit W.M. Peters*
4:45-5:15 pm	Multiplicity of Morphologies in Poly (L-lactide) Bio-resorbable Vascular Scaffolds *Julie Kornfield*

Introductory lecture

Audimax

5:15-5:45 pm	Amyloids from the origin to the end of life *Roland Riek* (Chair: J. Balbach)

Poster session & *Snack buffet*

1st & 2nd floor

6:00-8:00 pm	Presentation of posters with odd numbers.
8:00-9:30 pm	Presentation of posters with even numbers.

Tuesday, September 19

Session 4 — Audimax

Partially crystalline order in biological macromolecules
(Chair D. Huster)

8:30-9:00 am	NMR investigations of amyloid formation *Jochen Balbach*	
9:00-9:20 am	Enhanced-Sampling Simulations of Amyloids *Ulrich H.E. Hansmann*	
9:20-9:50 am	Thermal Behavior of Silk Protein *Peggy Cebe*	
9:50-10:10 am	The functional role of nanocrystals in native and artificial spider silk *Markus Anton*	
10:30-11:00 am	*Coffee break*	Foyer & 1st floor

Session 5a — Audimax

Crystallization under external control (surfaces and nucleation)
(Chair: W. Paul)

11:00-11:30 am	Effect of Solvent Affinity on Crystallization-driven Fibril Growth Kinetics in Diblock Copolymer Solutions *Wenbing Hu*	
11:30-12:00 pm	Surface Nucleation and the Design of Nucleating Agents by Molecular Simulation *Gregory Rutledge*	
12:00-1:30 pm	*Lunch break* & posters	Foyer, 1st & 2nd floor

Session 5b — Audimax

Crystallization under external control (surfaces and nucleation) (Chair: C. Schick)

1:30-2:00 pm	Crystallization Behavior of Polymer Langmuir Monolayers Observed by High-Resolution Atomic Force Microscopy *Jiro Kumaki*
2:00-2.20 pm	Interface-induced crystallization via prefreezing: A first order prewetting transition *Ann-Kristin Flieger*
2.20-2.50 pm	Oriented Recrystallization of Carbon-Coated Pre-oriented Ultrathin Polymer Films *Shouke Yan*
3:00 pm	*Coffee break* — Foyer

Excursions

3:30-6:00 pm see page 98

Dinner & discussion

6:00-7:45 pm at Luther Hotel

Poster session — 1st & 2nd floor

8:00-9:00 pm	Presentation of posters with label A.
9:00-10:00 pm	Presentation of posters with label B.

Wednesday, September 20

Session 6

Audimax

Connectivity and chain architecture as constraints for polymer crystallization (Chair: Wb. Hu)

8:30-9:00 am	Interplay between the Relaxation of the Glass of Random L/D Lactide Copolymers and Homogeneous Crystal Nucleation, *Christoph Schick*
9:00-9:20 am	The Isothermal Crystallization of Polyamide 11 Investigated from Low to High Supercooling by Simultaneous Calorimetry and Synchrotron SAXS/WAXD, *Bart Goderis*
9:20- 9:50 am	Isothermal Crystallization of Triple Crystalline Biodegradable PEO-b-PCL-b-PLLA Triblock Terpolymers, *Alejandro Müller*
10:00-10:30 am	*Coffee break* Foyer & 1st floor

Session 7

Audimax

Connectivity and chain architecture as constraints for polymer crystallization and aggregation (Chair: K. Saalwächter)

10:30-10:50 am	Crystallization of Supramolecular Polymers Linked by Multiple Hydrogen Bonds *Pengju Pan*
10:50-11:20 am	Polymorphs Selection in Random Copolymers *Yongfeng Men*
11:20-11:50 am	Nucleation Processes in Protein Aggregation *Tuomas Knowles*
11:50-12:20 pm	Rheology of self-nucleated poly(ε-caprolactone) melts, *Dario Cavallo*
12:30-12:45 pm	Closing *Kay Saalwächter*

List of posters

Poster sessions take place at the Leucorea on the 1st and 2nd floor.

Mon, Sept 18:

8:00-9:00 am	Mount of posters
6:00-8:00 pm	Presentation of posters with odd numbers.
8:00-9:30 pm	Presentation of posters with even numbers.

Tue, Sept 19:

8:00-9:00 pm	Presentation of posters with label A.
9:00-10:00 pm	Presentation of posters with label B.

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P-3B	Danke, Varun	Structure and Morphology Orientation of Comb-like Polymers with Rigid Backbones	54
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Abstracts talks

Mon, Sept 18 | 9:15 – 9:45 am | Audimax

Avoidance of Density Anomalies as a Structural Principle for Semicrystalline Polymers

Klaus Schmidt-Rohr

Chemistry Department, Brandeis University, Waltham, Massachusetts, USA

For a detailed analysis of the crystallization process, a realistic view of the chain trajectories in the lamellar semicrystalline morphology is of interest. We have come to the conclusion that the textbook models of melt-crystallized semicrystalline polymers unintentionally but inevitably contain layers with a higher density than in the crystallites.[1] Such density anomalies can be avoided by chain ends at the crystal surface and/or chain tilt in the crystallites. NMR shows that most CH^3 end groups of polyethylenes (PEs) are indeed in all-trans chains near the crystal surface. As a consequence, many chain folds cannot be tight, also in agreement with NMR data. Chain tilt in the crystallites, which decreases the density of chains emerging from the crystal, is another indispensable structural adjustment and is indeed observed ubiquitously in PE. It results in differential broadening of (*hk*0) Bragg peaks of PE, which had been mistakenly attributed to mosaicity. Published scattering patterns exhibit clear evidence of macroscopically aligned lamellar stacks with pronounced chain tilt in various oriented PE samples. Literature data furthermore show examples of increasing chain tilt angles of up to 60^o at high molecular weights, where the density reduction by chain ends is minor. Chain tilt and chain ends at the crystal surface are required to “make space” for short loops, in conjunction with noncrystalline chain segments emerging from the crystal roughly along the surface normal; these four effects together make a structure without density anomalies possible. The density problem is particularly pronounced in polymers with planar zig-zag conformations in the crystallites, such as PE. A revision of Flory’s analysis shows that for poly(ethylene oxide) and other polymers with helical crystalline conformations, larger bond tilt angles result in a higher projected density along the chain axis in the crystallites, which reduces the problem of amorphous excess density and thus the need for chain tilt in the crystallites.

References
[1] K. Fritzsching, K. Mao, K. Schmidt-Rohr, *Macromolecules* (2017)
DOI: 10.1021/acs.macromol.6b02000

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The role of Entanglements for Polymer Crystallization

J.-U. Sommer[1,2]

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[2]TU Dresden, Institut für Theoretische Physik, Zellescher Weg 17, 01069 Dresden

We use a coarse-grained polymer model to study the crystallization and melting behavior of long polymer chains in the dense state under various conditions. Our primary goal was to investigate the impact of the entanglement length on the properties of the lamellar crystal, in particular on the thickness selection, using algorithms to calculate the primitive path of the chains. In situ analysis of the local entanglement length prior to crystallization and the stem length and crystallinity at the same location reveals a direct correlation between the entanglement length and crystallization properties in the nucleation-controlled regime [1]. We have investigated various scenarios to change the apparent entanglement length in the system such as rapid cooling and cold-crystallization protocols, dilution of the melt by short chains, and the influence of solid substrates [2-4]. All studies confirm the correlation between entanglement length and thickness selection in the dense state. First results on non-concatenated ring polymer melts display a strong increase of the lamellar thickness and the degree of crystallization as compared to otherwise identical linear counterparts subject to the same thermal history [5].

References

[1] C.-F. Luo and J.-U. Sommer; Physical Review Letters **112**, 195701 (2014).
[2] C.-F. Luo, M. Kröger and J.-U. Sommer; Polymer **109**, 71 (2017)
[3] C.-F. Luo, M. Kröger and J.-U. Sommer: Macromolecules **49**, 9017 (2016)
[4] C.-F. Luo and J.-U. Sommer; ACS Macro Letters **5**, 30 (2016)
[5] H.-Y. Xiao, C.-F. Luo, D. Yan and J.-U. Sommer, manuscript (2017)

Mon, Sept 18 | 10:45 – 11:15 am | Audimax

Chain Folding of Semicrystalline Polymers

Toshikazu Miyoshi

Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

There is a long-standing controversy about chain-folding structure and mechanism of long polymer chains during crystallization. This information is a key factor to understand the crystallization mechanisms at the molecular levels. Recently, solid-state (SS) NMR combined with selectively ^{13}C isotopic labelling has been successfully utilized to determine local chain trajectory of folded polymer chains in single and bulk crystals.[1-6] In this talk, we will discuss various physical effects on chain folding and crystallization mechanisms of several polymers such as Poly(L-Lactic, Acid),[1, 2] *Isotactic*-poly(1-butene),[1, 3, 4] and *Isotactic*-Polypropylene.[1, 5, 6]

References
[1] Hong, Y.-l.; M.T.; et al, “Chain Trajectory of Semicrystalline Polymers As Revealed by Solid-State NMR Spectroscopy” *ACS Macro Lett*., 5, 355–358, **2016**.
[2] Chen W.; MT.; et al, “Molecular Structural Basis for Stereocomplex Formation of Poly(Lactide)s in Dilute Solution” *ACS Macro Lett*., 4, 1264–1267, **2015**.
[3] Hong, Y.-l.; M.T.; et al, “Three-Dimensional Conformation of Folded Polymers in Single Crystals” *Phys. Rev. Lett.,* , 115, 168301, **2015**.
[4] Hong, Y-l.; M.T.; et al, “Chain Trajectory and Crystallization Mechanism of Semicrystalline Polymer in Melt- and Solution-Grown Crystals as Studied by ^{13}C-^{13}C Double Quantum NMR” *Macromolecules 48*, 3282–3293, **2015**.
[5] Yuan, S., M.T.; et al, “Folding of Polymer Chains in the Early Stage of Crystallization” *ACS Maco Lett*., 4, 1382–1385, **2015**.
[6] Li, Z.; M.T.; et al, “Determination of Chain Folding Strcutre of Isotactic-Polypropylene Melt-Grown α Crystals by ^{13}C-^{13}C Double Quantum NMR and Selective Isotopic Labeling” *Macromolecules* 48, 5752–5760, **2015**.

Crystallization in melts of semi-flexible hard polymer chains: An interplay of entropies and dimensions

T. Shakirov, W. Paul

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Stochastic Approximation Monte Carlo simulations [1] are employed to obtain the complete thermodynamic equilibrium information for a melt of short, semi-flexible polymer chains with purely repulsive intermolecular interactions. Thermodynamics is obtained based on the density of states of our simple coarse-grained model, which varies by up to 5000 orders of magnitude. We show that our polymer melt undergoes a first-order crystallization transition upon increasing the chain stiffness at fixed density [2]. The lyotropic three-dimensional orientational ordering transition drives the crystallization and is accompanied by a two-dimensional hexagonal ordering transition in the plane perpendicular to the chains. While the three-dimensional ordering can be understood in terms of Onsager theory, the two-dimensional transition is similar to the liquid-hexatic transition of hard disks. Due to the domination of lateral two-dimensional translational entropy over the one-dimensional translational entropy connected with columnar displacements, the chains form a lamellar phase. The tilt of the chain axis with respect to the lamella surface makes this a rotator II phase.

References

[1] B. Werlich, T. Shakirov, M. P. Taylor, W. Paul, Comput. Phys. Commun. **186**, 65, (2015)
[2] T. Shakirov, W. Paul, preprint

Mon, Sept 18 | 1:15 – 1:45 pm | Audimax

Kinetics of crystallization in a model poly(thiophene)

Alberto Salleo

Materials Science and Engineering Department

Stanford University, Stanford CA 94305

Semicrystalline conjugated polymers have attracted much interest as disruptive materials for flexible, low-cost and printed electronics. Indeed, these polymers can be used as semiconductors in thin-film transistors, light-emitting diodes, solar cells and sensors. Furthermore, they have recently been made in stretchable forms. From the materials perspective, it has been known for decades that their electronic performance, as measured by carrier mobility, is very strongly dependent on the film microstructure. One of the goals of this field is to learn how to manipulate the microstructure through processing. In spite of this recognized fundamental need, very little is known about the crystallization processes in these polymers, which are crucial in microstructure formation. We used a model poly(thiophene), poly(3-hexyl-ethyl-thiophene)-(P3EHT)- to perform an in-depth, multi-technique study of crystallization kinetics and its effect on charge transport. P3EHT can be melted at temperatures below its decomposition temperature and when quenched to room-temperature it crystallizes slowly. We performed synchrotron-based x-ray diffraction, UV-Visible spectroscopy, solid-state NMR and charge transport measurements during the crystallization process. X-ray diffraction allows us to determine the structure of the unit cell and the relative degree of crystallinity of the film. I will show that transport improves with a percolation-like behavior when the distance between crystallites is approximately equal to the persistence length of the polymer. Furthermore, by combining these techniques we demonstrate that the crystallization kinetics follows a 1-D Avrami model and we extract the relevant kinetic parameters.

Model Experiments for the Crystallization of Conjugated Polymers

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M. Sommer[3]

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Much insight into crystallization of long chain polymers can be gained by studying mono-lamellar single crystals. Because of the kinetically determined lamellar thickness and the corresponding variations in melting temperature, polymer crystals allow for self-seeding, i.e., crystals can be regrown from a melt, which contains a few thermodynamically stable remnants of pre-existing crystals acting as seeds. Employing such a self-seeding approach, we demonstrated that large single crystals can be grown even from long poly(3-hexylthiophene) (P3HT) chains, with a control over the number density, size, and internal structure of these crystals exhibiting monoclinic form II with interdigitated hexyl side groups [1].

We also studied bulky substituted poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT) where weakened interchain interactions lead to a much lower melting temperature as compared to P3HT [2]. Using absorption and photoluminescence spectroscopy and a comparison with calorimetric measurements, we followed in-situ melting and recrystallization processes.

Well-ordered crystalline structures of semiconducting polymers exhibiting the same molecular conformation over many length scales represent valuable model systems for exploring relations between structure and optoelectronic properties.

References
[1] Khosrow Rahimi, et al., Angew. Chem. 124, 11293 –11297 (2012).
[2] Yingying Wang, et al., ACS MacroLett. 3, 881-885 (2014).

Highly oriented and crystalline semi-conducting and conducting polymer films prepared by high-temperature rubbing.

Martin Brinkmann[1], Amer Hamidi-Sakr[1], Laure Biniek[1], Patrick Lévêque[2], Jean-Louis Bantignies[3], David Maurin[3], Nicolas Leclerc[4].

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This contribution focuses on recent advances in growth control and oriented crystallization of semi-conducting and conducting polymers. Particular emphasis will be given to the progress made in high-temperature rubbing of such polymers. This effective large scale alignment method can orient a large palette of polymer semiconductors (PSCs) with n- or p-type character without the use of an alignment substrate. The concurrent roles of the polymer molecular weight distribution and the rubbing temperature (T_R) on the in-plane orientation have been rationalized for P3HT and PBTTT. Correlations are drawn between nanomorphology/crystallinity on one side and charge transport and optical properties on the other side.[a] It is shown that the exciton bandwidth in P3HT crystals is determined by the length of the average planarized chain segments in the crystals. The high alignment and crystallinity observed for $T_R > 200$ °C cannot translate to high hole mobilities parallel to the rubbing because of the adverse effect of amorphous interlamellar zones interrupting charge transport between crystalline lamellae. In a second part of this presentation, we show that soft doping of aligned PSCs yields highly oriented conducting polymer films with anisotropic charge conductivity and thermoelectric properties that are enhanced along the rubbing direction.[b] The unique in-plane orientation in such conducting polymer films helps rationalizing the mechanism of redox doping.

(a) A. Hamidi Sakr et al., Adv. Funct. Mat. 2016, 26, 408.
(b) A. Hamidi-Sakr, et al, Adv. Funct. Mat. 2017, 1700173

Multi-Shape Memory Effect of Columnar Side-Chain Liquid Crystalline Polymer

R. Y. Zhao, S. Yang, and E. Q. Chen

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Recently, we are interested in side-chain liquid crystalline (LC) polymers bearing the hemiphasmid side-chain that contains a rod-like mesogen linked with a half-disk end group [1-3]. We found that they could self-organize into the hexagonal and/or rectangular columnar LC phase when the size of flexible tails on the half-disk was properly chosen and the dimension of columnar lattice could approach to 10 nm easily. It is identified that the supramolecular column in the columnar phase shall contain several chains (e.g., ~5 chains) laterally associated together rather than a single chain. This “multi-chain column” provides a new type of physical crosslinking. Namely, within the confined space of the column the backbones and pendant groups of the polymer can get entangled. Using hemiphasmid side-chain LC polynorbornene as the example [4], we demonstrate that such physical crosslinks can be rather robust, giving the polymer with the typical properties of thermal plastic elastomer. Furthermore, taking the physical crosslinks to define the permanent shape and the LC formation to fix the temporary shape, we realized the side-chain polynorbornene with excellent shape memory effect. For the dual shape memory, both the shape fixity (Rf) and shape recovery (Rr) are admirably high (approaching 100%), even when a large strain of 600% was applied. Benefited from a broad LC transition, the polymer can present the high-strain multi-shape memory effect, exampled by its triple- and quadruple-shape memory with high Rf and Rr at each step.

References

[1] J. F. Zheng, X. Liu, X. F. Chen, X. K. Ren, S. Yang, E. Q. Chen, ACS Macro. Lett. 1, 641 (2012).
[2] X. Q. Liu, J. Wang, S. Yang, E. Q. Chen, ACS Macro Lett. 3, 834 (2014).
[3] Y. S. Xu, D. Shi, J. Gu, Z. Lei, H. L. Xie, T. P. Zhao, S. Yang, E. Q. Chen, Polym. Chem. 7, 462 (2016).
[4] R. Y. Zhao, T. P. Zhao, X. Q. Jiang, X. Liu, D. Shi, C. Y. Liu, S. Yang, E. Q. Chen, Adv. Mater. DOI: 10.1002/adma.201605908 (2017)

The non-equilibrium phase diagrams of flow-induced crystallization and melting of polymer

Zhen Wang, Youxin Ji, Jianzhu Ju, Xiaoliang Tang, Liangbin Li

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With a combination of extensional rheology and in-situ synchrotron ultrafast x-ray scattering measurements, we have studied the flow-induced phase behaviors of polyethylene (PE) [1], isotactic polypropylene (iPP) [2] and Poly(1-butene) (PB-1) [3] over a wide temperature and flow strength range. Non-equilibrium phase diagrams are constructed in temperature-stress space for PE, and in temperature-strain rate space for iPP and PB-1, which reflect the non-equilibrium natures of flow-induced crystallization (FIC). Applying flow is recognized to favor the formation of structure with high entropy and low conformational order. The interplay of kinetic competitions and thermodynamic stabilities between different phases leads to rich kinetic pathways for FIC and diverse final structures. The non-equilibrium flow diagrams provide a detailed roadmap for precisely processing of polymers with designed structures and properties. It demonstrates that the non-equilibrium process stimulated by flow is fundamentally different from the equilibrium phase behaviors, where a rich source of physics is still waiting for us to dig out.

References

[1] Z. Wang, J. Ju, J. Yang, Z. Ma, D. Liu, K. Cui, H. Yang, J. Chang, N. Huang, and L. Li, Scientific Reports 6, 32968 (2016).
[2] J. Ju, Z. Wang, F. Su, Y. Ji, H. Yang, J. Chang, S. Ali, X. Li, and L. Li, Macromolecular Rapid Communications 37, 1441 (2016).
[3] Z. Wang, J. Ju, L. Meng, N. Tian, J. Chang, H. Yang, Y. Ji, F. Su, L. Li, and L. Li, Soft Matter 13, 3639 (2017).

Full characterization of multi-phase, multi-morphological kinetics in flow-induced crystallization of isotactic Polypropylene at elevated pressure

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Understanding the complex crystallization behavior of isotactic polypropylene (iPP) in conditions comparable to, e.g. injection molding, where the polymer melt experiences a combination of high shear rates and elevated pressures, is key for modeling and, therefore, predicting the final structure and properties of iPP products. Coupling a unique experimental setup, capable to apply wall shear rates similar to the ones experienced during processing and carefully control the pressure before and after flow is imposed, with in-situ X-ray scattering and diffraction techniques (SAXS and WAXD) at fast acquisition rates (up to 30 Hz), a well-defined series of short-term flow experiments are carried on using 16 different combinations of wall shear rates (110 to 440 1/s) and pressures (100-400 bar) [1]. A complete overview on the kinetics of structure development during and after flow is presented. Information about shish formation and growth of α-phase parent lamellae from the shish back-bones is extracted from SAXS; the overall apparent crystallinity evolution, amounts of different phases (α, β and γ), and morphologies developing in the shear layer (parents and daughters lamellae both in α and γ phase) are fully quantified from the analysis of WAXD data. Both, flow rate and pressure were found to have a significant influence on both the nucleation and the growth process of oriented and isotropic structures. Flow affects both shish formation and the growth of α-parents, pressure acts both on relaxation times, enhancing the effect of flow, and (mainly) on the growth rate of γ-phase [2]. The high number of γ-lamellae found in the oriented layer strongly suggested the nucleation of γ directly from the shish backbone. All the observations were conceptually in agreement with the flow induced crystallization model framework [3] developed in our group, and represents a unique and valuable dataset for model validation.

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Mon, Sept 18 | 4:45 – 5:15 pm | Audimax

Multiplicity of Morphologies in Poly (L-lactide) Bioresorbable Vascular Scaffolds

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Poly(L-lactide), PLLA, is the structural material of the first clinically approved bioresorbable vascular scaffold (BVS), a promising alternative to permanent metal stents for treatment of coronary heart disease. BVSs are transient implants that support the occluded artery for 6 months, and are completely resorbed in 2 years. Clinical trials of BVSs report restoration of arterial vasomotion and elimination of serious complications such as Late Stent Thrombosis. It is remarkable that a scaffold made from PLLA, known as a brittle polymer, does not fracture when crimped onto a balloon catheter or during deployment in the artery. X-ray microdiffraction revealed how PLLA acquired ductile character and that the crimping process creates localized regions of extreme anisotropy; PLLA chains in the scaffold change orientation from the hoop direction to the radial direction over micron-scale distances. The multiplicity of morphologies in the crimped scaffold enable a low-stress response during deployment, which avoids fracture of the PLLA hoops and leaves them with the strength needed to support the artery. Thus, the transformations of the semicrystalline PLLA microstructure during crimping explain the unexpected strength and ductility of the current BVS and point the way to thinner resorbable scaffolds in the future.

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Amyloids from the origin to the end of life

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Protein aggregation is observed in many diseases including Alzheimer's disease. These protein aggregates are termed amyloids. Amyloids are composed of pairs of tightly interacting, many-stranded, repetitive, intermolecular beta-sheets termed the cross-beta-sheet structure. Because of this structure, amyloids can grow by recruitment of the same protein while their repeat can transform a weak activity into a potent one through cooperativity and avidity. Thus, an amyloid has the potential to replicate itself, and can be adaptive to its environment, yielding eventually cell-to-cell transmissibility, prion infectivity, and toxicity. Here, we discuss these structure-based properties within the context of Alzheimer's disease and Parkinson's disease from a structural perspective. In addition, we discuss a potential role of amyloids in the origin of life [1-3].

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Tue, Sept 19 | 8:30 – 9:00 am | Audimax

NMR investigations of amyloid formation

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Amyloids are well ordered protein aggregates involved in many functional and pathogenic processes of life. Various structural models of the molecular architecture of amyloids have been derived in the last decade mainly driven by advances in solid state NMR. This talk will summarize our NMR efforts to study not only structural features of mature fibrils but the amyloid formation mechanism. Two systems will be covered: the Alzheimer peptide Aβ(1-40) and variants as well as the human parathyroid hormone PTH(1-84). For Aβ(1-40) we show that backbone hydrogen bonds are the main driving force for fibril structure formation overwriting side chain effect and buffer conditions [1,2]. Additionally, we show that morphological properties of fibril seeds do not necessarily propagate towards the growing fibril [3]. Several molecular observations during the formation of PTH(1-84) fibrils will be presented [4] to classify them as functional amyloids and possible storage form of the hormone.

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Enhanced-Sampling Simulations of Amyloids

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The primary toxic agents in Alzheimer's disease appear to be small soluble oligomers formed either on-pathway or off-pathway to the assembly of the insoluble fibrils that are one hallmark of the illness. Hence, it is important to understand how the equilibrium between the polymorphous fibrils and oligomers is shifted by mutations, changing environmental conditions, or in the presence of prion-like amyloid strains. These processes are difficult to probe in experiments, and detailed experimental structures exist only for the amyloid fibrils. Most of these fibrils are built from $A\beta_{1-40}$ peptides that form U-shaped β-hairpins. For the more toxic $A\beta_{1-42}$ one observes in addition a S-shaped triple-β-stranded motif that cannot be formed by $A\beta_{1-40}$ peptides. We argue that the higher toxicity of this species is related to the ability of $A\beta_{1-42}$ to form this motif. In order to test this hypothesis we show that the S-shaped $A\beta_{1-42}$ peptides assemble into oligomer and fibril structures that cannot be build by U-shaped chains. Stability of these aggregates and inter-conversion between them is studied by regular and enhanced molecular dynamics techniques. These simulations allow us to propose a mechanism for formation and propagation of $A\beta_{1-42}$ amyloids.

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Tue, Sept 19 | 9:20-9:50 am | Audimax

Thermal Behavior of Silk Protein

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Silk is a naturally occurring biopolymer which has been used in textiles for over 5000 years. Silk stands as an exemplar of the class of fibrous proteins. The properties of silk protein are related to its semicrystalline nature, imparted by the secondary structures, such as the non-crystalline helices and random coils, and the crystalline beta pleated sheets. Using techniques of condensed matter polymer physics, we investigate the structure and thermal behavior of silk fibroin [1-3]. We have prepared fibroin by extracting it from the native cocoons and use this as a starting material for our investigations into the structure and properties of silk. In this presentation, I will describe our studies to quantify the amounts of the different secondary structures using X-ray diffraction, infrared spectroscopy, and high precision, high accuracy heat capacity measurements [1]. Silk degrades before melting when heated at slow rates. We used fast scanning chip-based calorimetry to heat silk at 2000 K/s, thereby minimizing thermal degradation and demonstrating the melting behavior of beta pleated sheet crystals [2, 3].

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The Functional Role of Nanocrystals in Native and Artificial Spider Silk

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Spider dragline silk exhibits remarkable characteristics such as exceptional toughness arising from high tensile strength combined with great elasticity. Its mechanical properties are based on a refined architecture on the molecular scale: Proteins with highly repetitive core motifs aggregate into nanometer-sized crystals, rich non alanine in β-sheet secondary structure, surrounded by an amorphous, glycine rich matrix. During spinning the less ordered parts are elongated, which orients both substructures and gives rise to an inherent non-equilibrium state. Thus, external stress is directly transferred to the crystallites, as demonstrated by FTIR experiments in combination with uniaxial stress [1] or hydrostatic pressure [2].

Even though the protein structure has been thoroughly studied, until recently it was not possible to artificially re-create this exceptional (morphological and functional) architecture. We show that wet spinning of a novel biomimetic protein results in fibers with a similar nanostructure as the natural template. However, only post spinning strain induces a microscopic non-equilibrium that gives rise to a similar mechanism of energy dissipation as in natural spider silk and comparable macroscopic toughness [3,4].

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Tue, Sept 19 | 11:00 – 11.30 am | Audimax

Effect of Solvent Affinity on Crystallization-driven Fibril Growth Kinetics in Diblock Copolymer Solutions

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Crystallization-driven fibril growth of one block under nano-confinement of another non-crystalline block in diblock copolymer solutions has raised the interests in two important fields. One is the self-assembly of nano-particles for hierarchical construction [1, 2]. Another is the neuro-fibrillary tangles in Alzheimer's disease [3]. The selective affinity of solvent in two blocks may influence the kinetics of the fibril growth, on processing the nano-particle assembly or hindering the disease development. We have recently performed dynamic Monte Carlo simulations of diblock copolymers in athermal solutions, with fibril crystallization of one block induced by a crystalline template but under the confinement of another amorphous block [4]. In this report, we changed the solvent affinity for two blocks and observed the variation of the fibril growth rates with the solvent selectivity. The results showed that reducing the hydrophilicity of the amorphous blocks will effectively decrease the fibril growth rates. The mechanism of solvent selectivity on the crystallization-driven fibril growth kinetics will be discussed.

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Surface Nucleation and the Design of Nucleating Agents by Molecular Simulation

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In most cases of practical interest, nucleation of polymer crystallites is believed to occur heterogeneously, through the action of additives or impurities that serve as nucleation agents, significantly reducing the activation barrier to formation of a new phase [1]. The number and activity of these nucleating agents can alter the resulting morphology of the semicrystalline polymer, for example through polymorph selection, the number and size of spherulites or the orientation of individual lamellae; the properties of the polymer can also be controlled as a consequence. The classical theories of polymer crystal growth are similarly predicated on a surface nucleation mechanism, which may proceed through one or more precursor states. We report the results of molecular simulations that examine the phenomenon of 2-dimensional nucleation on both familiar and foreign surfaces. In the first case, we obtain an atomistically detailed model for surface nucleated crystal growth that permits evaluation of some of the basic tenets of classical polymer crystal growth theories [2]. We then combine it with a continuum level model of layer-by-layer growth to create a multi-scale description of crystallization kinetics in chain molecules [3]. In the second case, we show that by systematically varying the intermolecular force field parameters that describe the foreign surface, one can rapidly screen entire classes of nucleating agents to characterize both their mechanism of action and nucleation efficiency [4]. The method is demonstrated with the crystallization of n-pentacontane, a surrogate for polyethylene, on members of the family of diamond-like materials and on those like graphene with 2D, hexagonally coordinated atomic layers. We show for the first time that, in addition to epitaxial registration and strength of adhesive interactions, the rigidity of the nucleating agent influences heterogeneous nucleation. Employing this method, high throughput computational screening of nucleating agents becomes possible.

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Tue, Sept 19 | 1:30 – 2:00 pm | Audimax

Crystallization Behavior of Polymer Langmuir Monolayers Observed by High-Resolution Atomic Force Microscopy

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Polymer monolayers spread on a water surface transform from an isolated chain to amorphous, then to a crystalline state upon compression, which can be transferred at each stage onto a substrate for observation by atomic force microcopy (AFM) [1]. Previously, we successfully observed a folded chain crystal (FCC) of an isotactic poly(methyl methacrylate) (it-PMMA) [2], its melting behavior in situ at high temperature [3], and crystallization of single isolated chains [4] at a molecular level by AFM.

In contrast to the it-PMMA, polylactide (PLA) crystallizes into an extended chain crystal (ECC) on a water surface [5]. Since the width of the crystal corresponds to the molecular weight (Mw), the chain packing in the crystal can be specifically identified. We studied the crystallization of a mixture of high and low Mw PLAs and found that the high Mw PLA first crystallized, followed by the low Mw PLA crystallization, indicating that the molecular weight recognition occurred during the crystallization process. We also studied the crystallization of a high Mw PLA monolayer highly diluted by a PLA oligomer, the Mw of which was too low to crystallize. As the crystallization of the high Mw PLA to ECC was disturbed, upon compression, FCC first formed, which then aggregated to transform into ECC; the transformation from FCC to ECC was clearly visualized. Compression of a D, L-PLA mixture forms a stereocomplex on a water surface [6]. There is a controversy whether D- and L- PLA pack in a stereocomplex in a parallel or anti-parallel arrangement. We studied the crystallization of linear and cyclic stereoblock copolymers with the parallel and anti-parallel arrangements for the D- and L-PLA block segments [7], and found that the parallel arrangement more stably formed in the sterecomplex.

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Interface-induced crystallization via prefreezing: A first order prewetting transition

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Interface-induced crystallization of a liquid on a solid substrate can either occur via heterogeneous nucleation or via prefreezing. Whereas heterogeneous nucleation takes place at finite supercooling below the melting temperature T_m, in prefreezing a crystalline layer is formed at the surface of a solid substrate already above T_m. Wetting theory predicts a jump in thickness at the formation and a divergence upon approaching coexistence. However, the thickness of the prefreezing layer has not been experimentally measured so far.

We studied ultrathin films of polycaprolactone (PCL) during the crystallization on graphite. With in-situ AFM-measurements we observe prefreezing instead of heterogeneous nucleation. The corresponding crystalline layer is formed at a temperature above the bulk melting temperature. Similar observations were already made for polyethylene on graphite [1]. In that case however, a direct measurement of the thickness of the prefreezing layer was not possible. Here, we show directly the finite thickness of the prefreezing layer for PCL. It forms with a thickness of a few nanometers which further increases during cooling. This observation demonstrates the transition is of first order, as expected for a prewetting transition.

The results prove that prefreezing can be described by common wetting theory. The studied system PCL-graphite is of importance for applications since graphitic materials are widely used as fillers for PCL.

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Tue, Sept 19 | 2:20 – 2:50 pm | Audimax

Oriented Recrystallization of Carbon-Coated Pre-oriented Ultrathin Polymer Films

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The recrystallization behavior of carbon-coated preoriented polymer thin films was studied by means of transmission electron microscopy combined with electron diffraction and spectroscopy. It was found that vacuum evaporated carbon layer can keep the molecular chain orientation of pre-oriented polymer thin films. This demonstrates the existence of strong fixing effect of vacuum evaporated carbon layers on the surface layer of the polymer films, which prevents the relaxation of surface extended macromolecular stems in the crystals or at least from a complete relaxing during high-temperature melting. The fixed surface molecular chains have in turn induced the oriented recrystallization of the thin polymer molten layer. It was further found that the crystal structures and morphologies can be well controlled through regulating the crystallization temperature. For example, the α to β transition of poly(vinylidene fluoride) has been achieved by melt recrystallization of carbon-coated highly oriented PVDF ultrathin films at atmospheric pressure. Moreover, through selective carbon-coating with the help of a mask and subsequent recrystallization of the pre-oriented polymer thin film lead to patterned structure control in the coated domains of a polymer thin film. A fully structure control can be fulfilled through a combination of surface carbon-coating at desired domains and recrystallization on an oriented substrate with heteroepitaxy.

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Interplay between the Relaxation of the Glass of Random L/D Lactide Copolymers and Homogeneous Crystal Nucleation: Evidence for Segregation of Chain Defects

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Random L isomer rich copolymers of poly(lactic acid) containing up to 4% D isomer co units have been cooled from the molten state to obtain glasses free of crystals and homogeneous crystal nuclei. The kinetics of enthalpy relaxation and the formation of homogeneous crystal nuclei have then been analyzed using fast scanning chip calorimetry [1]. It has been found that the relaxation of the glass toward the structure/enthalpy of the supercooled liquid state is independent of the presence of D isomer co units in the chain. Formation of homogeneous crystal nuclei in the glassy state requires the completion of the relaxation of the glass [1,2]. However, nucleation is increasingly delayed in the random copolymers with increasing D isomer chain defect concentration. The data show that the slower formation of homogeneous crystal nuclei in random L/D lactide copolymers, compared to the homopolymer, is not caused by different chain segment mobility in the glassy state but by the segregation of chain defects in this early stage of the crystallization process [3].

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Wed, Sept 20 | 9:00 – 9:20 am | Audimax

The Isothermal Crystallization of Polyamide 11 Investigated from Low to High Supercooling by Simultaneous Fast Scanning (Chip) Calorimetry (FSC) and Synchrotron SAXS/WAXD

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An in-situ FSC-SAXS/WAXD approach was used to study the isothermal crystallization of polyamide 11 (PA11) at different degrees of supercooling in order to elucidate its bimodal crystallization rate behavior with temperature [1]. Time resolved WAXD analyses over the complete range of supercoolings revealed that mesomorphic material was produced in less than a second at high supercooling, whereas at very low supercooling crystals were obtained [2]. The crystalline to mesomorphic ratio was found to increase gradually with increasing crystallization temperature. Analysis of the SAXS data supported the existence of a crystallization temperature dependent semicrystalline morphology composed of alternating solid and liquid-like layers with the solid layers made from crystalline, mesomorphic and rigid amorphous patches. Moreover, the crystalline or mesomorphic patches alternate with rigid amorphous patches in neighboring solid layers. The relation between details of this peculiar morphology and the crystallization rate as a function of the crystallization temperature will be discussed.

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Isothermal Crystallization of Triple Crystalline Bio-degradable PEO-b-PCL-b-PLLA Triblock Terpolymers

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PEO-b-PCL-b-PLLA triblock terpolymers are fascinating materials, as they can develop three different crystalline phases[1]. Adjusting the block composition and crystallization conditions, each block is able to crystallize sequentially and separately from a homogeneous melt. Thus, crystallization drives superstructure formation into mixed spherulites that include lamellae of PLLA, PCL and PEO. The PLLA block crystallizes first at higher temperatures upon cooling from the melt (and templates the morphology), then the PCL block, and finally the PEO block[2]. In this work, a three-stage crystallization protocol was applied to study the isothermal crystallization kinetics of each block. The crystallization was studied by WAXS, SAXS, DSC and AFM. At the PLLA crystallization temperatures, both PCL and PEO molten chains caused a strong diluent effect on PLLA crystallization. The overall crystallization rate of PLLA block in the terpolymers was faster than that of analogous diblock copolymers. In the second stage, the PCL crystallization was followed after PLLA was fully crystallized, and a nucleating effect (increased crystallization rate and decreased supercooling) induced by the previously formed PLLA crystals was observed. In the third stage, the PEO crystallization rate greatly decreased due confinement effects of PLLA and PCL crystals. Understanding the complexity of the crystallization behaviour of triple crystalline triblock terpolymers is at the very early stage of current research in crystallization of block copolymers[3].

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Wed, Sept 20 | 10:30 – 11:00 am | Audimax

Nucleation Processes in Protein Aggregation

Tuomas P. J. Knowles

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Filamentous protein aggregation underlies a number of functional and pathological processes in nature. This talk focuses on the formation of amyloid fibrils, a class of beta-sheet rich protein filament. Such structures were initially discovered in the context of disease states where their uncontrolled formation impedes normal cellular function, but are now known to also possess numerous beneficial roles in organisms ranging from bacteria to humans. The formation of these structures commonly occurs through supra-molecular polymerisation following an initial primary nucleation step. In recent years it has become apparent that in addition to primary nucleation, secondary nucleation events which are catalysed in the presence of existing aggregates can play a significant role in the dynamics of such systems. This talk describes our efforts to understand the nature of the nucleation processes in protein aggregation as well as the dynamics of such systems and how these features connect to the biological roles that these structures can have in both health and disease.

Crystallization of Supramolecular Polymers Linked by Multiple Hydrogen Bonds

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Supramolecular polymers (SMPs) have different crystallization behavior from conventional polymers. Crystallization of SMPs occurs in a “confined” and “dynamic” manner. Because of the reversible and stimuli-responsive natures of non-covalent bonds in SMPs, crystalline structure and crystallization kinetics of SMPs depend strongly on crystallization conditions (e.g., crystallization temperature, T_c). This offers a feasible way to tune the physical properties and functions of SMPs in processing. We first selected the 2-ureido-4[1H]-pyrimidione (UPy)-bonded poly(L-lactic acid) (PLLA) as a model SMP and investigated the crystallization kinetics, polymorphic crystalline structure, and phase transition of supramolecular PLLAs (SM-PLLAs). Crystallization rate and crystallinity of SM-PLLAs were strongly depressed as compared to the non-functionalized PLLA precursors. Crystalline structure of SM-PLLAs was sensitive to T_c. A low T_c (80~100 °C) facilitated the formation of metastable β crystals of PLLA in SM-PLLAs. The β crystals formed in SM-PLLAs transformed into the more stable α crystals in the following heating process. We further studied the stereocomplex crystallization between UPy-functionalized PLLA and poly(D-lactic acid) (PDLA). It was found that the stereocomplexation ability of PLLA and PDLA was highly improved after UPy end functionalization; this was ascribed to the enhanced interchain interaction.

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Wed, Sept 20 | 11:20 – 11:50 am | Audimax

Polymorphs Selection in Random Copolymers

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Many polymers exhibit different polymorphous structure depending on crystallization condition. In random copolymers, the melt state is often structured having segregations of crystallizable chain segments originating from the melting of previous crystals when the system has not been treated at temperature high enough (much higher than the equilibrium melting temperature of the corresponding crystals). Clearly, when being annealed at different melt temperatures, the size of such segregations can be varied so that the followed crystallization can be affected under different confinements. We report in this work a peculiar observation of polymorph selection during crystallization of a butane-1/ethylene random copolymer of 10 mol% ethylene co-units. Depending on previous crystalline size, melt temperature and crystallization temperature, the system showed a systematic variation in polymorphs. It turns out that such polymorphs selection depends on the interplay between the domain size of segregated long crystallizable sequences and the size and energy barrier of the critical nucleus of the respective crystalline forms. Our results provide a clear understanding of the polymorphs selection during crystallization of a random copolymer as well as homo-polymers under confinement.

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Rheology of self-nucleated poly(ε-caprolactone) melts

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Contrary to low molar mass molecules, semicrystalline polymers exhibit a strong influence of the melt-annealing conditions on the re-crystallization. An enhanced concentration of nuclei is found after a mild melting treatment, in comparison to annealing at high temperatures and long times. [1,2] The intimate nature of these “self-nuclei” is still under debate, since they are elusive to the most commonly adopted characterization techniques. [2,3]
In this work, the self-nucleation process is studied by probing the effect of self-nuclei on the rheological properties of the non-equilibrium melt. Three poly(ε-caprolactone)s with different molar mass were investigated by shear rheometry. The viscoelastic functions of the melt were determined at the same temperatures, reached either from the solid state or from the melt, i.e., with or without the presence of self-nuclei. Differences in the rheological behavior of these melts are striking. The Newtonian viscosity, plateau modulus and flow activation energy show a drastic increase with respect to the isotropic melt. The results indicate the existence of an attractive intermolecular interaction between chain segments within the self-nuclei, which is able to provide “extra” physical entanglements, different from the topological ones. As such, the flow behavior of self-nucleated melts display analogies with that of “associative” polymers possessing specific inter-chain interactions, e.g., hydrogen or ionic bonds.

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Abstracts Posters

Dissection of elastomeric performances of ethylene based semicrystalline multi-block copolymers.

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The crystallization properties, morphology and elastomeric behavior of some ethylene/1-octene multi-block copolymers produced by chain shuttling technology [1] are analyzed. We evidence that the samples consist of a reactor blend of chains characterized by alternation of crystalline (hard) blocks with low octene content and amorphous (soft) blocks with high octene content, having different length and different number of blocks. The sample show similar degree of crystallinity and melting temperature, and good elastomeric properties at 25°C. Differences occur for the crystallization temperature, morphology and elastomeric properties at 60°C. These differences reflect differences in segregation strength. For samples containing a high fraction of chains with hard-blocks of short length, and long soft-blocks, the segregation strength is high, and the hard domains are well separated at high correlation distances. For samples containing a high fraction of chains characterized by long hard-blocks and short soft-blocks some kind of interpenetration of the hard segments in the soft domains occurs, with consequent decrease of segregation strength and inter-domain distance. Since the long hard-segments can also connect different hard-domains, a well interpenetrated network is formed. Therefore, the samples forming an interpenetrating network crystallize at lower temperatures (more slowly), show high mechanical strength and ductility, and good elastomeric properties even at high temperatures. The samples with no inter-woven structure with short hard-blocks, instead, form a more heterogeneous morphology, show low mechanical strength and lose elastomeric properties already at 60°C.

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NMR investigations of dynamics in the different phases of semicrystalline polymers

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The melt-crystallized morphology of semicrystalline polymers strongly depends on the diverse dynamics in the amorphous and crystalline region. The connections between structure formation and dynamics of polymer chains are investigated with SAXS and NMR spectroscopy, respectively, comparing polymers with and without intracrystalline dynamics (crystal-mobile and crystal-fixed). Proton time-domain techniques enable the analysis of the phase components, the intracrystalline and the amorphous phase dynamics. The intracrystalline motion displays only a weak dependence on morphology [1]. SAXS results show, that the morphology of the crystal-fixed polymer, poly-ε-caprolactone (PCL), and the crystal-mobile polymer, polyethylene oxide (PEO), are qualitatively different [2]. The crystal thicknesses in PCL are well-defined, whereas in PEO a crystal reorganization process caused by the intracrystalline dynamics leads to a uniform amorphous region [2].

To investigate the impact of the crystalline growth and reorganization process on the morphology separately, polymers with slower intracrystalline mobility, e.g. polyoxymehtylene (POM), will be investigated. Further investigations address the relationship between morphology and entangled dynamics in the amorphous phase.

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Structure and Morphology Orientation of Comb-like Polymers with Rigid Backbones

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Comb-like polymers with rigid backbones and flexible side chains are an important class of functional materials with applications in various fields like organic semiconductors and light weight components in high performance composite materials. A common feature of such polymers is the formation of layered structures with typical spacing in the 1-3 nm range wherein the side chains (long methylene sequences) aggregate to form alkyl nanodomains [1]. Crystallographic analysis in poly (1,4-phenylene-2,5-n-didecyloxy terephthalate) (PPDOT) and poly (2,5-didecyloxy-1,4-phenylene vinylene) (DOPPV) each having 10 alkyl carbons per side chain shows that PPDOT exhibits an orthorhombic unit cell, whereas the DOPPV is characterized by a monoclinic unit cell. The interplay between backbone and side chain packing within the alkyl nanodomain leading to different crystallographic states is discussed. Investigations on molecular orientation in extruded fibers of poly (1,4-phenylene-2,5-n-dialkyloxy terephthalate)s (PPAOT) and poly (2,5-dialkyloxy-1,4-phenylene vinylene)s (AOPPV) show that the backbones in case of PPAOT align along the shear direction whereas in AOPPV they align preferentially perpendicular to the shear direction [2]. Potential reasons for the differences in the preferred orientations for PPAOT and AOPPV are considered.

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The Decisive Role of Intra-Crystalline Chain Dynamics for the Morphology of Semicrystalline Polymers

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A special feature of some semicrystalline polymers is the existence of the so-called α_c-relaxation, caused by a translational motion of the chains in the crystal. Although it was recognized already early on that these crystal-mobile polymers generally have a higher crystallinity than crystal-fixed polymers [1], differences in the semicrystalline morphology have not been analyzed in detail and the relaxation process has not been taken into account in most crystallization models. Using an extended method for quantitative analysis of small angle x-ray scattering data [2] we here compare the structural characteristics for two model polymers, namely PEO (crystal-mobile) and PCL (crystal-fixed). PCL follows the expectations of classical crystallization theories. The crystal thickness is well defined and determined by the crystallization temperature T_c. In contrast, for PEO the amorphous thickness is better defined. We hypothesize that due to the α_c-relaxation, the crystalline lamellae thicken directly behind the growth front until the amorphous regions reach a minimal thickness. This assumption is consistent with NMR experiments, which give the time scale of intra-crystalline dynamics [3] and which show that crystal reorganization takes place on the same time scale as crystal growth itself. In keeping with this model, crystal-mobile and crystal-fixed polymers exhibit a different melting behavior during heating. The crystallization of PCL leads to the formation of marginally stable crystallites which constantly reorganize during heating, while in PEO due to the presence of the α_c-relaxation, much more stable (thickened) lamellar crystals form, which melt only at much higher temperatures.

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SAXS Study on Density Fluctuations in Crystallization Process of Poly(trimethylene terephthtalate)

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Polymer crystallization mechanism especially at large supercooling has not been fully understood yet. Kaji et al. found that the density fluctuations occur in the early stage of crystallization in poly(ethylene terephthalate).[1] Research on such a fluctuations have been done from both theoretical [2] and experimental [3] aspects. But an interpretation for the fluctuations has not been fully obtained. Recently the strong density fluctuations are reported in the early stage of glass-crystallization process for poly(trimethylene terephthalate) (PTT)[4]. In order to clarify the density fluctuations in PTT, we have studied the crystallization processes of PTT from the glass and the melt by small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD).

The density fluctuations of several hundred Å have been obtained in the SAXS results in the early stage of crystallization process both from the glass and the melt. The fluctuations appear simultaneously with the generation of the nodular crystals of several tens Å. From the results we conclude that the fluctuations is due to the nodular crystals heterogeneously aggregated in space.

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Transition from Ring- to Chain-Dominated Phases in Supramolecular Polymer Networks

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Rheological properties of supramolecular polymers depend on their structures including the size, the number, and the topology of aggregates. A linear polymer with hydrogen bonding units at both ends is one of widely used precursors to build the supramolecular polymer networks. Due to complex interplay between chain stiffness, hydrogen bonding interaction, and polymer conformational entropy it is difficult to theoretically predict the structure of the supramolecular polymer. In this work, we investigate structures of supramolecular polyethylene glycol and polybutylene glycols whose ends are capable of the hydrogen bond using a coarse-grained (CG) model via stochastic approximation Monte Carlo simulation (SAMC) method. Our CG force field is constructed by Boltzmann inversion of the probability distributions of all-atom polymer conformations. SAMC provides all the thermodynamic information of the system, which allows one to investigate supramolecular structures in a wide temperature range. This work especially focuses on the transition from ring- to chain-dominated phases since the contaminant of rings in a melt is known to significantly influence its rheology. In a limit of dilute concentration, the transition temperature (T^*) shows non-monotonous behavior as molecular weight of the precursor increases due to competition between chain stiffness and hydrogen bonding. We also investigate the polymer concentration (c) dependence on T^* to construct a c-T phase diagram.

Small polyethylene systems: On the ground state of single chains and few chain aggregates

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The phase behavior of polyethylene has been under investigation for the last six decades. Investigation of single-chain crystallization in solution is a technically difficult problem, because in molecular dynamics simulations as well as in experiments, it is not so easy to distinguish kinetic and thermodynamic effects on chain folding. The general picture, however, is, that single polyethylene chains in solution fold into lamellar crystals. We present results of a Stochastic Approximation Monte Carlo (SAMC) simulation, which gives a possibility to analyze thermodynamical equilibrium properties of a system. Our simulation study of relatively short polyethylene chains is based on a chemically realistic united atom model [1]. Simulational results for low-energy states of single chains of different lengths demonstrate a set of various ground-state configurations: from stretched and hairpin-like configurations of short chains to a helix-like structure reeled round one of the chain's ends. Aggregates of a few short polyethylene chains exhibit another set of ground states, depending on chain length and number of aggregated chains. However, with increasing chain length, single chain and aggregate morphologies become more similar.

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Morphology – Density Relations in Polyamide 12

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A two-phase model consisting of alternating amorphous and crystalline layers is often used to describe the morphology of semi-crystalline polymers. However, this simple model – at least in the case of polyamide 12 (PA12) - does not allow rationalizing the outcome of different techniques which are sensitive to particular features of the semicrystalline morphology. Therefore, several authors argued for the existence of a third phase [1], [2]. This third phase is the rigid amorphous fraction (RAF) and is in fact a phase with a higher density and lower mobility than the amorphous fraction but without the order of the crystalline. Although the existence of this RAF seems beyond dispute, there clearly is no consensus on its topology. Based on a combination of temperature dependent WAXD, SAXS, solid state NMR, and density measurements a new morphological model is proposed for PA12, which consists of alternating solid and mobile (liquid) amorphous layers. The solid layers are in turn composed of crystalline and rigid amorphous patches with the density of the latter being intermediate between that of mobile amorphous and crystalline matter. This morphology, which includes a clear picture of the RAF topology, leads to a similarity in the WAXD and SAXS based crystallinity as well as to matching SAXS based dense and NMR based rigid fractions. The model adequately describes the SAXS patterns and produces overall densities that are identical to experimentally observed ones.

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Chain Tilt in the Crystalline Lamellae of Poly(ethylene oxide) Investigated by Mid-Chain Defects

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While many traditional schematic models show the crystalline polymer chains aligned parallel to the lamella thickness L_c recent sophisticated studies on poly(ethylene) show that the crystalline polymer chains are tilted at an angle ϕ to the lamella thickness [1].

Here, we investigate the chain tilt of poly(ethylene oxide) (PEO) by the means of mid-chain defects using wide-angle X-ray scattering and solid state ^{13}C MAS cross polarization NMR spectroscopy. At low temperatures, one polymer chain of PEO$_9$-meta-PEO$_9$ and PEO$_{11}$-TR-PEO$_{11}$ [2-4] containing a 1,3-disubstituted benzene and a 1,4-disubstituted 1,2,3-triazole defect in central position of the polymer chain, respectively, form crystals and the other PEO chain as well as the defect remain amorphous. The aromatic defects of these two polymers can be incorporated into the crystalline lamellae upon heating below T_m and the corresponding structure models confirm that the amorphous PEO chains exit the tilted lamellae at a preordained angle. Thus, the chain tilt angle ϕ can directly be calculated from the bent angle ξ between the amorphous and crystalline PEO chains, which is given by the substitution patterns of the aromatic mid-chain units and a tilt angle range between $36° \leq \phi \leq 60°$ is determined. Furthermore, our studies on PEO$_9$-para-PEO$_9$ containing a 1,4-disubstituted benzene mid-chain defect confirm that also linear unbent PEO chains form tilted lamellae.

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Synthesis, aggregation and crystallization of precision polymers with repetitive folding elements

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The investigation of ordering phenomena in biological and synthetic macromolecules still presents an interesting and promising field of research. Biological macromolecules form stable secondary or higher structures via inter- and intramolecular ordering processes, which are based on the interaction of their precisely placed amino-acids and the rotational constraints resulting from the peptide bonds. [1] Especially the understanding of the secondary structure formation from polypeptides is essential as it depends strongly on their (bio)chemical environment.

We investigate the aggregation and crystallization behavior of different precision polymers, which are characterized by repeating sequences of synthetic polyolefins and different biomimetic structure-elements. Constraints like 2,6-diaminopyridine and urea induce a conformational restriction while poly(amino acids) like poly-L-glutamic acid, poly-L-aspartic acid, poly-L-lysine and poly-L-leucine display a large conformational variability and dynamic α-helical-to-coil-transition. [2] All included moieties additionally interact with each other via supramolecular interactions influencing the crystallization behavior of the polyethylene chain. Therefore, acyclic diene metathesis (ADMET) polymerization was used to achieve a periodic incorporation of the constraint into the polymer backbone, resulting in precision polymers, which were analyzed via DSC and WAXS measurements. [3]

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Crystallization and Tensile Deformation Mechanism of Propylene/Ethylene Copolymers in α and γ Polymorphs

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Isotactic polypropylene (iPP) is a widely used commercial polymer with various polymorphs. γ-form, which can only crystallize at high pressure for isotactic polypropylene, is a usual polymorph for propylene copolymers. The subsequent crystallization behavior during cooling for copolymer initially in pure α-form and γ-form processed at different melt temperature has been studied [1]. Specifically, sample initially in α-form led to higher fraction of γ-form (f_γ) and onset crystallization temperature (T_{onset}) than that of sample in γ-form under low melted temperature, which was caused by the difference between morphology of samples previously in α-form and γ-form.

Tensile deformation properties of the propylene/ethylene copolymers were also studied [2, 3]. The influence of stretching temperature and content of co-unit in transition behavior from γ-form to α-form during stretching was investigated. The critical stress for the polymorph transition was obtained which depends strongly on the stretching temperature and content of co-unit. The critical stress was higher for sample with lower co-unit content with less partitioning of ethylene co-unit in propylene crystalline lattices.

This work is supported by NSFC (21134006, 51525305) and ExxonMobil.

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Tailoring Properties of Polypropylene through CrystalliZAtion in the Presence of Polymeric Nucleating Agents

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In this communication, we present a strategy for the addition of polymeric nucleating agents for the crystallization of isotactic polypropylene (iPP) that guarantees a perfect fine dispersion of nucleating particles within the entire mass of the polymer, with consequent their high efficiency even at very low concentrations. The Ziegler-Natta catalyst particles are coated by a thin skin of poly(trimethylallylsilane) (PTMAS) or poly(vinylcyclohexane) (PVCH) that will act as nucleating agents, by prepolymerization of the corresponding monomers. PVCH shows higher nucleation efficiency than PTMAS with greater increase of crystallization temperature by standard cooling from the melt. Both polymeric nucleating agents affect the crystal morphology greatly reducing the size of shperulites. This in turn affects the mechanical properties improving ductility and flexibility. The presence of the nucleating agent accelerates the crystallization of iPP and affords crystallization of the α form even upon fast crystallization by quenching the melt, condition that generally produces crystallization of the mesomorphic form of iPP (1). Crystals of α form so obtained show a nodular morphology and absence of spherulitic superstructure. This novel iPP material is characterized by outstanding and unexpected properties of high mechanical strength and modulus and contemporarily high ductility, flexibility and good transparency due to the nodular morphology of α form (2).

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The Crystallization Transition and Microstructure Evolution of Long Chain Aliphatic Polyamide

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Deformation-induced microstructure evolution of a long chain aliphatic polyamide, with an emphasis on lamella development, polymorphism transition and molecular orientation, is investigated in this work. When the materials was deformed above T_g of polyamide1012, a series of complex SAXS patterns are continuously identified at intermediate strain including four points, a figure-eight and an X-shaped pattern, accompanied with two-bars pattern on the meridian, which corresponds to the transient microstructure. Such particular structure is resulted from the approach of tilted lamellae along the drawing direction, the insertion and the orientation of new lamellae. To investigate the temperature dependence, the microstructure developments at different temperature, which was below, above, or close to T_g, are compared. Based on the comprehensive results, the correlation between microstructure and mechanical response has been successfully established, which is featured by the synchronous occurrence of transient structure with slight strain hardening.

The authors thank the financial support from NSFC (21574140).

Deformation and nano-void formation of β-phase isotactic polypropylene during uniaxial stretching

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Pseudo-hexagonal β-form is known to transform into thermodynamically stable monoclinic α-form during elongation. It is also reported that the nano-sized void is formed during deformation. Since the crystal deformation/void formation mechanism of β-iPP is not fully understood, we aim in this study to clarify the deformation behavior of β-iPP in both terms of crystal transformation (angstrom scale) and the void formation (nanometer scale). The film of β-iPP was prepared by melt crystallization of PP with 0.2% DCNDCA as a nucleating agent ($k_\beta = 0.94$). The samples were drawn uniaxially at 100ºC with fixed strain rate of 0.66 min^{-1}. Synchrotron radiation WAXD/SAXS measurements were performed at BL40B2 in SPring-8, Japan. Deformation of β-iPP proceeded as follows; (i) at the yielding point of $\varepsilon = 0.1$ β-form started to decrease followed by increase in amorphous fraction. (ii) at $\varepsilon = 0.4$, α -form crystal with the chain orientation parallel to the stretching direction was formed. Importantly, as soon as α-form crystallized, formation of nano-sized void was initiated. Above findings strongly suggest that the β-form transforms to amorphous and/or mesomorphic state before recrystallization into α -form crystal. A detailed analysis on void structure by means of SAXS streak scattering is also to be discussed based on lamellar deformation during elongation.

Acknowledgement
This work was supported by the Impulsing Paradigm Change through Disruptive Technologies (ImPACT) program.

Bi-axial nano oriented crystals (NOCs) of Polyamide 66

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We found that polyamide 66 (PA66) crystallizes into novel “bi-axial nano-oriented crystals (bi-NOCs)”, when the supercooled melt was elongated above a critical elongational strain rate.

We used PA66 (M_w=87×10^3, M_w/M_n=2.31). We used roll system to generate strain rate. We observed the structure and morphology of NOCs by means of polarizing optical microscope and small/wide angle X-ray scattering from three directions, through, edge and end. Polarizing optical micrographs suggested the formation of NOCs. SAXS patterns showed typical two-point pattern, which indicates the formation of NOCs. The two-point pattern showed orientation along machine direction (MD) for through and edge view, while along normal direction (ND) for end view. Size of a nano crystal (NC) was 11nm along MD and ND. WAXS patterns showed chain orientation along MD for through and edge views, while along ND for end view. From these observed facts, we concluded that the arrangement of NCs and chains showed bi-orientation along MD and ND.

The bi-orientation of NCs and chains suggests the important role of hydrogen bond planes (HBPs) in formation of NOCs. As the crystals of PA66 includes “rigid” HBPs[1], the HBPs should change into hydrogen bond clusters (HBCs) after melting. The HBCs should become nuclei. Under large strain rate, the HBCs would be parallelly oriented to the roll surface due to hydrodynamic effect, which should be the reason of the formation of bi-NOCs.

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Relations between morphology and crystallization behavior of poly (l-lactide) / poly (butylene succinate) bioblend nano-composites with graphene oxide nano-sheets

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Bio-based blend nanocomposites of poly(L-lactic acid) (PLA) and poly(butylene succinate) (PBS) [1] with different concentration (from 0.1 wt% to 0.5 wt%) of Graphene Oxide nano-sheets (GOs) were prepared by melt blending. The resulting morphology is investigated with scanning and transmission electron microscopy (FE-SEM and TEM). FE-SEM of fracture surfaces revealed that the addition of GO to the bio-based PBS/PLA blend improves the adhesion between the two polymers, indicating that GOs nanosheets locate at the interface.[2] TEM analysis showed that the nanofillers are preferentially found in the PBS phase (minority component). The grapheme oxide nanosheets act as nucleting agents for both semi-crystalline polymers. The nucleating effect of the added particle is compared to the one of own self-nuclei for each polymer, to define a convenient nucleating efficiency (NE) scale. A value of around 80% is determined for GO towards PBS, among the highest nucleating efficiencies ever reported for this polymer. On the other hand, the efficiency in nucleating PLA is equal to a modest 15%, due to the uneven distribution of the filler in the two polymers. A close relationship between the nanocompostie complex morphology and crystallization behavior of the two different polymers is thus established.

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Temperature dependent IR-Transition Moment Orientational Analysis applied to thin supported films of Poly-ε-Caprolactone

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We present a technique to obtain Infrared (IR)-spectra in dependence of temperature (*T*) and atmospheric composition, but also in dependence on polarization and inclination of the incident light. Based on the obtained spectra the three dimensional molecular order parameter tensors of IR-active transition dipole moments in 7 μm-thin films of Poly-ε-Caprolcatone (PCL) are monitored in dry nitrogen for 35°C < *T* < 59°C. Crystallinity and macroscopic order of the crystallites remain largely unaltered up to *T* ≈ 50°C, above which both quantities decline. These reductions are interpreted as the melting of a thermodynamically less stable, surface induced layer of flat on lamellae,[1] which formed at highest temperatures, in the beginning of the non-isothermal crystallization process. The results illustrate the fertility of temperature dependent, IR-Transition Moment Orientational Analysis (IR-TMOA)[2] to understand kinetic and thermodynamic factors in the evolution of ordered, complex structures.

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Crystallization of Isotactic Poly(methacrylic acid) at the Air-Water Interface and in Thin Films

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Perfect isotactic poly(methacrylic acid) (i-PMAA) was synthesized and characterized by NMR spectroscopy. Langmuir isotherms of i-PMAA were measured and compared with atactic PMAA. The crystallization of i-PMAA on the water surface strongly depends on the pH-value of the subphase. We found that i-PMAA solutions can immediately form crystalline nanoparticles upon spreading at the air-water interface at neutral pH value. They have diameters of approximately 14 nm to 40 nm and their size can be increased 60 nm to 100 nm without aggregation upon compression on the Langmuir trough. Helical structures are observed when i-PMAA is spread on water having pH value of 10. The morphology of i-PMAA was studied after transfer in LB films by AFM. i-PMAA can also be crystallized in thin films after treatment for several weeks with water. Wide-angle X-ray diffraction (WAXD) studies of these films show a new Bragg reflection at $2\theta = 7^{\circ}$ (d = 1.20 nm) indicating the crystallization of i-PMAA which might correspond to the helical pitch distance as known for isotactic poly(methyl methacrylate) (i-PMMA) [1-3]. The crystallization is also observed by polarized optical microscopy and AFM.

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New insights into crystalline transition in nylon 46

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Nylon 46 (PA46) is an important engineering plastic. Two crystal structures, monoclinic and triclinic, have been proposed for the α form of PA46. To distinguish which one is more suitable for the melt crystallized PA46, we prepared double oriented samples of PA46 by mechanical rolling at 180 °C followed by annealing at 260 °C. The samples showed the typical α phase diffractions. Combining the two-dimensional (2D) wide-angle X-ray diffraction (WAXD) patterns obtained with the X-ray beam perpendicular and parallel to the chain axis, we concluded that PA46 adopted the monoclinic structure that was determined by Atkins based on the electron diffraction of single crystals grown from solution [1]. On heating, the room temperature α phase firstly transformed into high temperature α phase, and then changed into γ phase which is pseudo-hexagonal [2]. We observed that directly cooling down the sample after high temperature rolling could result in the γ phase retained at room temperature, which was evidenced by 2D WAXD. This room temperature γ phase was a new observation. It was relatively stable and would transform to high temperature γ upon heating. For comparison, we also studied the thermal transition of the melt quenched samples. The obtained amorphous PA46 crystallized in γ phase during heating. The non-oriented γ phase would change into α phase during cooling, showing the typical Brill transition.

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Effects Of Phase Separation and Crystallization on Morphology of Poly(propylene carbonate)/Poly(3-Hydroxybutyrate) Blend Thin Films

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For partially miscible crystalline/amorphous polymer blends, the combined effects of phase separation and crystallization can result in multiple morphology. In this study, the effects of composition and melting time on the morphology and structures of poly(propylene carbonate)/poly(3-hydroxybutyrate) blend thin films was investigated. A low PPC content in the film resulted in compact PHB spherulites, filling the whole space, whereas the amorphous PPC spherical microdomains scatter in the PHB region. With increasing PPC component and melting time, a large amount of PPC aggregates to the surface to form a network uplayer, whereas the PHB thick domains connected by its thin layer form a continuous PHB region, leading to a superimposed bilayer structure. If PPC content reached 70 wt%, a PPC-top and microporous PHB-bottom bilayer structure can be developed. We suggested that phase separation can take place mainly along the normal direction of the film surface at 190 ºC, attributed to the different surface energies of the two components. After cooling, the crystallization occurred, leading to further segregation and solidification along film planes. This superimposed bilayer by interplay between phase separation and crystallization may provide availability to tailor the final structure and properties of crystalline/amorphous polymer films.

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Mechano-optical rheology of semi-crystalline polymers.

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Since polymeric liquids subjected to an external field (flow) often respond with a related anisotropy of their refractive index and stress, flow birefringence is commonly used for structural characterization of these materials. In this respect, rotational geometries are well suited for visual observations of the flow and, consequently, mechano-optical rheology of polymeric liquids. New applications of a rheo-optical method based on a combination of rotational rheology and a recently developed optical technique – shear-induced polarized light imaging (SIPLI) are presented [1]. Simultaneous rheo-optical studies using rheo-SIPLI have already been successfully used for characterization of self-assembled copolymers and liquid crystals [1, 2]. The proposed rheo-optical method is also effective for studying flow-induced crystallization of semi-crystalline polymers (FIC) [3]. Simultaneous optical measurements and mechanical rheology are performed during FIC. These experiments enable a relationship between the shish formation, detected by SIPLI, and the viscosity upturn, measured by the rheometer at the same time, to be established. The results are compared with small-angle x-ray scattering. It is also shown that SIPLI setup can be used for birefringence measurements. The normal stress difference calculated from the birefringence of a sheared polymer melt (polyethylene) correlate well with both the total normal force measured by the rheometer transducer during the same experiment and the first normal stress differences measured independently on the same polymer using cone-and-plate geometry.

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Polythiophene Adsorption and Restructuring on Gold Surfaces

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Scanning tunneling microscopy is used to study the complex adsorption behavior of poly-3-hexyl-thiophene (P3HT) on Au(001) [1] and Au(011). Upon electrospray deposition under ultrahigh vacuum conditions, weakly adsorbed polymer chains are found on Au(001), which exhibit a truly 2D random-coil-like chain backbone structure. Their end-to-end distance and their radius of gyration are reported as function of the polymer length. Additionally, a fraction of the P3HT molecules is constraint into a fully stretched configuration along the high-symmetry [110] crystal direction, indicating a stronger molecule-substrate interaction. This adsorption is accompanied by local lifting of the Au(001) surface reconstruction [2] underneath the polymer chains [3].

For the more open Au(011) surface that exhibits a missing-row (2x1) reconstruction, we find a stronger interaction between P3HT and the gold surface. Polymer chains align predominantly along the missing rows by changing their conformation into an all-trans state. The presence of the polymer is inducing a local reorganization process changing the surface reconstruction from 2x1 to a 3x1 reconstruction. These results will be compared with similar findings for smaller thiophene oligomers (sexithiophene, 6T) on both substrates [4,5].

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Novel three-dimensional nano-oriented crystals of polyesters

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We crystallized the supercooled melt of polyesters by the melt-elongation. We used three kinds of polyesters, such as poly(ethylene terephthalate); PET, poly(ethylene-2,6-naphthalene dicarboxylate); PEN and poly(butylene terephthalate); PBT. We found that the novel three-dimensional (3D) morphology of "nano-oriented crystals (NOCs)" was formed, while in the case of isotactic polypropylene, one-dimensional morphology of NOCs was formed [1,2]. We observed the structure and morphology of NOCs by means of polarizing optical microscope, small/wide angle X-ray scattering. The nano crystals of 10 nm in order showed single crystal like monoclinic arrangement. The molecular chains were mainly oriented along the elongational direction. We clarified the mechanism of formation of 3D-NOCs of polyesters and an important role of the Benzene plane. In the elongational flow, the Benzene planes will be arranged by the effect of hydrodynamics [3] and packed locally in parallel. The parallel-packed Benzene planes should become a precursor of a nucleus, which would result in homogeneous nucleation [4] and formation of 3D-NOCs.

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Influence of Propylene-based Elastomer on Stress-whitening for Impact copolymer

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Two pure impact copolymer polypropylenes (ICP), one pure homo-polypropylene (HPP) and their compounds with different type and fraction of Vistamaxx^{TM} propylene-based elastomer (“Vistamaxx”) were used to investigate the stress whitening activated in the impact processes via ultra-small angle X-ray scattering technique. A characteristic macroscopic whitening of deformed materials was showed due to the formation of voids or cavities with a typical size up to the wavelength of visible light, that is, some hundreds of nanometers. The stress whitening presented in ICP is confirmed to be caused by the interfaces existed between ethylene-propylene (EP) rubber and polypropylene (PP) matrix, such kind stress whitening is apparently unlike the one initiated in the crystal phase of HPP. In this study, Vistamaxx with high crystallinity can adjust the compatibility of EP rubber and PP matrix which results in a reduction of interfaces, thus, a phenomenon of reduced stress whitening can be observed in blends of ICP with Vistamaxx. However, the enhancement of stress whitening can be found in blends of ICP with Vistamaxx which occupied low crystallinity. Such behaviors can be assigned to the poor compatibility between Vistamaxx and PP matrix.

Crystallinity and Stress induced Crystallization in Ethylene-Propylene Rubbers

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In this communication we report a study of the influence of the presence of crystallinity in the undeformed state and of the occurrence of stress-induced crystallization (SIC) on the mechanical properties and elastic behavior of ethylene-propylene-diene (EPD) random terpolymers, which are the basic material of many commercial rubbers. EPD terpolymers with ethylene concentration in the range 44-78 wt% have been analyzed. EPD samples with high ethylene content of 78wt% are crystalline in the undeformed state and crystallize from the melt in the pseudohexagonal form of polyethylene. Samples with 71-64 wt% of ethylene show broad diffraction profiles typical of amorphous copolymers but show endothermic peaks in the DSC heating curves and well-defined correlation peaks in the small angle X-ray diffraction (SAXS) patterns. This indicates that presence of a certain amount of crystals that are not visible by wide angle diffraction. Further crystallization of the pseudohexagonal form of PE occurs during deformation (SIC). These results indicates that in EPD terpolymers, even when the concentrations of propene units is high in the range 30-40 wt%, ethylene sequences are long enough to crystallize, due to partial inclusion of propene units in the crystals (1). The crystallinity present in the undeformed state and its improvement during deformation are keys for understanding the remarkable mechanical performances of these rubbers.

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Fiber surface-induced nucleation of polylactide

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Fiber-reinforced semicrystalline polymer composites are largely employed for their improved strength with respect to the pure polymer matrix. The adhesion between the polymer and the fiber is known to play a key role in determining the overall mechanical behavior. When semicrystalline polymers are employed, the heterogeneous nucleation on the surface of the solid fiber is an efficient way to improve the adhesion and speeding up the composite production rate. However, fiber induced nucleation studies are still scarce and mainly limited to polyolefins, despite the increasing importance of bio-based polymers and composites.

In the work, the nucleation process of polylactide (PLA) on several fibers was studied in-situ by means of hot-stage polarized optical microscope. Several commercially available fibers (i.e., PET, Kevlar and glass fibers) are employed and compared to stereocomplex enantiomeric PLA blend and annealed homochiral PLA fibers. The nucleating efficiency of the various heterogeneous substrates is quantitatively compared on the basis of the derived free energy barrier for critical nucleus formation, ΔG^*.

It results clear that the PLA stereocomplex fibers has higher nucleating ability, due to the identical surface chemistry between the substrate and PLA homocrystal, although the crystalline structure of stereocomplex and homochiral crystals is not the same. On the other hand, the nucleation kinetics of PLA homocrystal on fibers of the very same crystal is even more efficient, and simply follows the secondary nucleation process: the induction times for the birth of the nucleus display the same temperature dependence of crystal growth.

Epitaxial Crystallization of Polyethylene via Prefreezing: Effect of Strength of Substrate Interaction

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The process of crystallization is most often initiated at an interface to a solid surface due to a decreased nucleation barrier. A solid surface can induce crystallization either by heterogeneous nucleation [1] or by prefreezing [2], where these two processes are very different from each other from a thermodynamics point of view. Previously we observed prefreezing occurring in polyethylene on the surface of graphite [2]. In this system a thin crystalline layer is first formed at the solid interface at a temperature 16 K higher than bulk melting temperature and the thickness of this prefreezing layer increases upon approaching melt-solid coexistence. Here we present another case where polyethylene crystallizes via prefreezing on a molybdenum disulfide substrate which has a stronger effect on the crystallization of polyethylene. Using in-situ high temperature AFM measurements we show that the prefreezing layer is stable in a temperature range up to about 47 K above the bulk melting temperature.

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Bond-orientational Order Assisted Crystal Nucleation in Polyethylene

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Flexibility and connectivity are the most prominent characteristics of polymer, how does flexible chain transform into rigid conformational ordered segments may be the key step for crystallization [1]. We investigate the nucleation process of polyethylene with full-atom molecular dynamic simulation, during which the structural evolution is analyzed with three order parameters, including conformational order, modified bond-orientational order [2] and density. Coupling between conformational and bond-orientational orderings results in the formation of hexagonal clusters first, which is dynamic in nature and absence of density order. Whilst nucleation of orthorhombic clusters occurs inside hexagonal clusters later, which involves all three order parameters and proceeds via the coalescence of neighboring hexagonal clusters rather than standard stepwise growth process. This demonstrates that nucleation of PE crystal is a two-step process with the assistance of bond-orientational order, which is different from early models for polymer crystallization but in line with that proposed for spherical “atoms” like colloid and metal.

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The confined crystallization of polymer in Anodized aluminum oxide template

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The one dimensional (1D) polymer nanostructures with controlled morphologies and properties can be easily achieved from Anodized aluminum oxide (AAO) template. In AAO template, confinement effect and interface effect determine the crystallization and dynamical behavior.[1-4] Some aspects of questions are worthwhile for deeper understanding: (1) discrimination between the interfacial and confinement effect on the dynamics of multiscale chain-motions; (2) discrimination between segmental dynamics and chain dynamics on the crystallization of polymer. Moreover, the studies on the comparison of confinement effect between 1D polymer nanostructures and two dimensional (2D) polymer thin film by employing the same polymer is also less explored. In the present study, poly(3-hydroxybutyrate) (PHB) was selected as a model to explore the above aspects. Interfacial effect slows down the dynamics of PHB segmental mobility and shows strong dependence on pore size. Spatial confinement accelerates the dynamics of segmental mobility. Both effects slow down the chain mobility which consequently slow down the crystallization kinetics of PHB. The inhibited crystallization of PHB in AAO nanopores can be attributed to both segmental and chain mobility. By contrast, only chain mobility plays the role on the crystallization of thin film. Segmental mobility does not change with film thickness.

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A new microscopic kinetics model for nucleation of polymer crystallization

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Nucleation is a fundamental step of polymer crystallization and the mechanism is not fully understood yet [1]. Classical nucleation theory based on the capillary approximation has achieved success in the field of polymer crystallization; however, there are still some open questions remained: (1) Which pathway is chosen for nuclei formation of polymer lamellar crystals, stem by stem or cluster by cluster? (2) How to describe the many intermediate states during nucleation? In this work, we propose a microscopic kinetics model without the prerequisite thermodynamics parameters. In our new model, crystal nucleation is considered as a series of elementary processes: attaching and detaching of units. Correlation factors were introduced to describe the variation of the rate constants to attach and detach a unit with the cluster size. Via the microscopic kinetics, we can determine the equivalent thermodynamics parameters and simulate the time evolution of cluster size distribution [2]. Application of the new model to some polymers will be given. The critical size of nuclei in poly(butylene succinate) during crystallization and melting will be estimated. The model describes nucleation of small molecules and polymer chains in a unified view, which we believe can be applied to other kinetic processes far from equilibrium.

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Effects of Melt Structure on Shear-induced Crystallization of Isotactic Polypropylene

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Based on a control of the melt structure at temperatures near but below the equilibrium melting point we investigated the role of shear stress imposed by the wall of the capillary die on crystal morphology of isotactic polypropylene (iPP). Bundles of partially ordered nanoscale chain segments within the quiescent melt at temperatures between the nominal melting temperature and the equilibrium melting point allowed for the possibility of shear-induced or shear-assisted formation of crystalline cylindrites which were investigated by means of polarized optical microscopy and small/wide-angle X-ray scattering.[1-4] The SAXS patterns of near melting point structured melt monitored at 180 °C can be fitted by using a form factor for polydisperse cylinders. It was found that the average radius and height of the bundles of partially ordered chain segments were about 17 nm and 40 nm, respectively. For a given structured melt, the number of cylindrites increased with shear stress. Concomitantly, the nucleation density of α-iPP within a single cylindrite structure increased with shear stress at the expense of β-iPP nucleation density.

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Crystallization-Driven Reversible Actuation in Cross-Linked Poly(ε-caprolactone)

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Crystallization of the pre-deformed polymer network under constant load can result in a non-trivial macroscopic elongation accompanied by network stiffening, which is reversible upon melting. Such actuation, known as the reversible shape-memory effect (rSME), is in focus due to fundamental interest of underlying molecular mechanisms and numerous potential applications. The rSME was studied in cross-linked linear poly(ε-caprolactone) (PCL) under various constant loads [1]. A striking rSME under stress-free conditions was found in PCL with the highest obtained cross-link density. The viscoelastic and thermal properties of the material as well as size and orientation of the crystals formed in PCL networks under and without load were investigated. As concluded, the directed growth of crystals is the origin of the reversible actuation in both loaded and free-standing PCL. The mean field approach was employed to calculate the free energy change during non-isothermal crystallization of PCL networks under load, whereby the possible morphology and orientation of crystals were analyzed. The analytical results on the nanocrystalline structure along with fitting curves of the temperature dependent strain, which were obtained by modeling the SME in PCL under load, are in good accordance with experimental findings.

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Spatial Orientation and Order of Molecular Subunits in Films of Organic Semiconductors

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Conjugated donor/acceptor copolymers have obtained significant attention due to their soft matter properties combined with semiconducting characteristics, which allows for their operation in organic field effect transistors or solar cells, for instance [1]. Because the devices' macroscopic properties arise from the materials' molecular organization, a detailed understanding of the microscopic structure is essential for targeted developments. In order to shed light on the spatial orientation and order in thin films of *P(NDI2OD-T2)* the technique of *Infrared Transition Moment Orientational Analysis* (IR-TMOA) is employed. Therefore, the absorbance of structure-specific bands depending on the inclination of the sample *and* on the polarization of the IR light is evaluated [2, 3]. This enables to determine the *tensor of absorption* separately for the respective molecular moieties as well as to deduce the orientation of atomistic planes defined through the polymer subunits, relative to the substrate and hence relative to each other. We found that the solvent used for spin coating (chlorobenzene or a chloronaphthalene:xylene mixture) determines the alignment of the T2 part (either face on or edge on), whereas the NDI unit is not affected. On the other hand, the inclination of the NDI plane is well retained for diverse sample thicknesses in between nano- and micrometers.

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Large area three-dimensional polarization control in P(VDF-TrFE) polymer films on graphite

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Ferroelectric polymers are attractive candidates for functional layers in electronic devices like non-volatile memories, piezo- and magnetoelectric sensors, and capacitor-based high speed energy storage devices. Unfortunately, such thin films often reveal low di- and piezoelectric responses due to reduced crystalline and electrical dipole order, leading to compensation effects and low effective electric performance. One of the best characterized and often applied ferroelectric polymers is poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)). We will present results on micron-sized domains with three dimensional ferroelectric polarization alignment in P(VDF-TrFE) films on graphite. The ferroelectric domains have been achieved by a combined procedure of electrical poling and mechanical annealing with an atomic force microscopy tip. They show strongly increased lateral and vertical piezoresponse compared to the as-prepared film and can be deliberately written and switched.

Development of improved materials from poly(lactic acid) with the aid of plasticizers and crystallization-promoting gelators

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Polylactic acid (PLA) is a bio-based polymer which might become an alternative for petroleum-based plastics such as polypropylene and polystyrene. However, at present, the properties of PLA do not meet the requirements for a number of applications. The challenge to be addressed is to develop transparent PLA with an increased heat distortion temperature, balanced stiffness and toughness and increased barrier properties. The method explored to reach this multi-dimensional goal is to blend PLA with combinations of plasticizers (for reducing the brittleness) and crystallization-promoting gelators (to increase the crystallinity). Upon cooling, the gelator forms a fine fibrillary network, which nucleates the PLA crystallization. The resulting, small-sized crystal aggregates limit the scattering of visible light and enhance transparency, which is desired for packaging purposes. An increased crystallinity is required to enhance the barrier properties and increase the heat distortion temperature.

The semicrystalline morphology and efficiency of the gelator fibrillary network depends on the cooling conditions and the addition of plasticizers. Both aspects are addressed using Differential Scanning Calorimetry, optical microscopy and time-resolved synchrotron SAXS/WAXD.

Serine substitution in Amyloid-β – a possible link between β-Methylamino-L-alanine and Alzheimer's disease?

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β-Methylamino-L-alanine (BMAA) was found as a possible reason for increased ALS-PDC (amyotrophic lateral sclerosis–parkinsonism/dementia complex) [1]. It is a non- proteinogenic amino acid produced by cyanobacteria that can be enriched via the food chain in plants, seafood, higher animals, and humans [2]. This is a critical factor because cyanobacteria are known for their excessive blooms not only in marine ecosystems but also in lakes that are used as fresh water source for millions of people supplying BMAA to human nutrition [3].

Although BMAA is known as a neurotoxin for several decades, its mode of action is still topic of controversial discussions. One of the more commonly accepted pathologic pathways is its function as a neurotransmitter mimetic where it can overstimulate glutamate receptors, deplete glutathione, increase free radical concentration and subsequently leads to neuronal damage [4]. Besides this, BMAA can also be misincorporated in proteins. Recent findings showed that serine tRNA synthetase accepts BMAA as substrate which may finally lead to a serine-BMAA substitution [5].

Assuming that BMAA can substitute Ser8 or Ser26 of Amyloid-β, the question arises if this may alter Amyloid-β fibrillation and structure leading to a higher risk for neurodegenerative pathogenesis.

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Structure formation of peptides in the PRIME20 model

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The relation between conformations of a polypeptide is governed by local minima in the free energy function. Coarse-grained models tend to simplify the free energy in such a way that these local minima are ignored. To circumvent this problem, the level of coarse graining needs to be chosen appropriately. PRIME20[1] provides reasonable detail by mapping each amino acid to four beads, but keeps parameter space simple with the set of interactions reduced to 19 energy parameters.

Poly-Glutamines (polyQ) are associated with Huntington's disease due to their ability to aggregate into an amyloid state. Single polyQ chains have been found to form a beta hairpin as a precursor to these aggregates. We will discuss the temperature dependent end-to-end distance of the chains in relation to TTET and FRET experiments performed on polyQ chains.
We perform thermodynamic simulations of single PRIME20 chains using the "SAMC"[2] variation of Wang-Landau Monte Carlo sampling which provides insight in different statistical ensembles at the expense of dynamic information. The aforementioned polyQ are compared to poly-Alanines with a lower tendency to form beta structure motifs.

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Effects of thermal denaturation and UV-B irradiation on eye lens crystallin proteins

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Crystallins are the major vision-related (i.e. refractive) proteins found in the eye lens. The mammalian lens consist of three classes of proteins, α-, β- and γ-crystallins, the former also acts as chaperone [1]. Commonly, proteins are subject to a continuous degradation and replacement process, but the eye lens proteins have no turnover and hence have to remain stable and soluble for a lifetime. So far, most studies have focused on single eye lens proteins and their interactions at low concentrations [2]. Here we combine NMR and other biophysical techniques to monitor stress induced aggregation and changes of the interactions of crystallins at various concentrations [3]. This allows us to investigate molecular effects which might lead to cataract in a highly concentrated eye lens surrounding.

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Dynamic and Structural Properties of Polyglutamine

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More than ten diseases are known that are based on the expansion of polyglutamine sequences within the disease-related proteins, which leads to the formation of amyloids. We tested, whether the propensity to form amyloids is due to distinct structural and/or dynamic properties of the monomeric state of polyglutamine (polyQ) chains. Using triplet-triplet energy transfer (TTET) and time-resolved fluorescence resonance energy transfer (trFRET) we were able to characterize the structure (end-to-end distribution) and the intrachain dynamics of monomeric polyQ chains of different length. The results were compared to the properties of the previously characterized model chains poly-(glycine-serine) and poly-serine [1-4] and of fragments from IDPs, which do not form amyloids. The results show that intrachain dynamics in polyQ chains are slower than the dynamics of all other investigated chains and that longer polyQ chains contain a fraction of pre-formed loop structures in the conformational ensemble, which may explain their tendency to form oligomers of β-hairpins.

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Effects of Hofmeister Ion Series on Stability of a Salt Bridge

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Salt bridges are important components of protein structure stability. They can be defined as an interaction of two aminoacid side chains of opposite charge [1]. Such Coulomb attraction interaction is sensitive to presence of other charged species in the vicinity. Concentration of charged species – free ions can be significant in a crowded environment of a living cell. Additionally Hofmeister ion series have been shown to have a significant impact on structure and dynamics of water and solvated proteins [2, 3].

We have investigated effects of Hofmeister ion series on an arginine – aspartic acid salt bridge by means of computer simulations [4]. Changes in thermodynamic properties of a salt bridge and dynamic properties of their solvation shells will be discussed in a poster.

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Amyloid Protein Aggregation in the Presence of Temperture-Sensitive Polymers

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The formation of amyloid fibrils is considered to be one of the main causes for many neurodegenerative diseases, such as Alzheimer's, Parkinson's or Huntington's disease [1, 2]. Current knowledge suggests that amyloid-aggregation represents a nucleation-dependent aggregation process *in vitro*, where a sigmoidal growth phase follows an induction period. Here, we studied the fibrillation of amyloid β 1-40 ($A\beta_{40}$) and Parathyroid hormone (PTH) in the presence of thermoresponsive polymers, expected to alter their fibrillation kinetics due to their specific hydrophobic and hydrophilic interactions with proteins [3]. Mixtures in varying concentrations and the conjugates of PTH or $A\beta_{40}$ with poly(ethylene glycol) methyl ether acrylate were studied *via* time-dependent measurements of the thioflavin T (ThT) fluorescence and transition electron microscopy (TEM). The studies revealed that amyloid fibrillation was altered, accompanied by either reduction or elongation of the lag phase of PTH or $A\beta_{40}$ fibrillation in the presence of studied polymers [4].

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Early oligomers and the process of oligomerization of the amyloid peptides Aβ40 and Aβ42

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Similar to synthetic polymers like polyamides, amyloidogenic proteins as well as short peptide sequences display the inherent ability to form long and very stable fibers called fibrils. Along the pathway from a single peptide to the mature fibrils, various transient and long-lived intermediate states are formed spanning the whole range between small and mostly unstructured oligomers to well-ordered, β-sheet rich protofibrils. As early oligomeric states were found to be neurotoxic, they are a presumptive key to understand the development of neurodegenerative diseases [1].

In order to reveal the leading mechanisms of amyloid aggregation, we studied the appearance and development of early oligomeric states of the Aβ40- and the Aβ42-peptides using a combined approach of single-molecule fluorescence spectroscopy and imaging techniques, such as TEM and AFM. Additionally, thermodynamic stabilities of the detected amyloid aggregates were studied by the use of ultrafast-scanning calorimetry.

We could reveal and characterize soluble oligomers of the Aβ40- and the Aβ42-peptide and found distinct differences in terms of size distribution as well as the process of oligomerization. While the fibrillation of Aβ42-peptides includes small and large oligomers, the assembly of Aβ40-peptide display only small oligomers and an overall slower kinetic of fibril formation. We will discuss our results by the use of thermodynamic models of self-assembly.

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Amyloid peptide aggregation near interfaces

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Amyloid peptides aggregate into characteristic fibrils with cross-β-sheet structure, also known as amyloid plaque. They are associated with several diseases such as Alzheimer's disease or type II diabetes. However, there is evidence that indicates the soluble transient oligomers, instead of mature fibrils, as the toxic species. Amyloid-forming peptides are natively soluble and only aggregate under certain circumstances. Comprehensive knowledge on the aggregation mechanism and a detailed characterisation of the transient species is essential to understand the physiological role of these peptides [1].

Interfaces, such as nanoparticles, can act to accelerate or inhibit peptide aggregation. Experimental studies and molecular dynamics simulations (MD) presented an accelerated fibril formation in the presence of citrate-stabilised gold nanoparticles [2,3]. The role of gold surfaces in oligomer formation and peptide aggregation is discussed in this study. Moreover, possible mechanisms for the observed acceleration of the peptide aggregation by a reduction of the conformational space that is sampled are presented.

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Characterization of Chimaeras of a Thermoresponsive Polymer and the Parathyroid Hormone

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The parathyroid hormone (PTH) is an 84 residue peptide from the parathyroid glands which controls the calcium and phosphate level in human blood. The peptide adopts an α-helical conformation at the *N*-terminus and is intrinsically disordered at the *C*-terminus. Amyloidogenic properties of PTH have been reported [1]. Here we show the *in vitro* formation of amyloid fibrils of PTH 1-84 and of the pharmaceutically relevant *N*-terminal fragment PTH 1-34 under physiological conditions. To get further insights into the mechanism of amyloid fibrillation we investigated the effect of thermoresponsive polymers [2] on PTH. We covalently attached polyacrylate based polymers to ^{15}N isotope labelled PTH 1-84 and used two dimensional NMR techniques for the characterization of the resulting chimaeras. This allows the observation of amino acid sequence specific changes of the cross peaks corresponding to the peptide backbone according to the polymer state. The studies revealed strong dependencies of chemical shifts on the temperature, the peptide attachment site and the polymer molecular weight.

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Characterization of the Self-Assembly Process of Hydrophobin SC3 at Interfaces and in Solution

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Hydrophobins are small amphiphilic proteins (~ 7-10 kDa) produced by filamentous fungi that self-assemble at interfaces. They are divided into two classes based on hydropathy plots and solubility. By forming extremely stable amphipathic membranes, foams and emulsions hydrophobins are thought to fulfill a great variety of tasks during the fungal lifecycle such as coating of airborne spores and facilitating contact between fungus and host during infection. [1] Their ability to modify surfaces is of great interest in many fields such as medicine, material science and cosmetics. [2] To harness this ability to its full potential the exact mechanisms of the self-assembly process at interfaces and in solution must be better understood on a molecular level.

Class I hydrophobins are characterized as highly insoluble and known to form stable amyloid fibrils called rodlets at the air-water-interface. We investigated the self-assembled structures of class I hydrophobin SC3 at the air-water-interface using a Langmuir-filmbalance coupled with a fluorescence microscope. The use of two dyes of different hydropathy showed the potential to force the protein into different superstructures of several micrometers in dimension upon compression. To our knowledge, this difference in self-assembled superstructure has not been visualized before. Future investigations using Atomic Force Microscopy (AFM) are planned to investigate their underlying structures on a scale of several nanometers. Furthermore, we attempted to covalently attach 3-Maleimido-PROXYL to the N-terminus of SC3. This stable radical can be investigated using electron paramagnetic resonance (EPR) spectroscopy in order to examine the self-assembly of the protein in solution. Again, to the best of our knowledge, no such experiments have been reported before. We are hoping to get a coherent picture of the aggregation that can then be compared to that of class II hydrophobins, which generally differ in their dominant

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Applying Principal-Components Analysis to Single DNA Molecules in a Thermophoretic Trap

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We report on single DNA molecules in liquids trapped over several minutes applying a feedback-driven dynamic temperature field. The thermophoretically induced drift velocities, which make the trapping of single nano-objects possible, are generated by spatially and temporally varying the temperature at a plasmonic nano-structure. The randomization of the positions and conformations by Brownian motion is prevented with the help of feedback-controlled switching of local temperature fields. A model-free statistical tool called principal-components analysis as introduced by Cohen & Moerner [1] is employed to assess the distortion of the DNA's conformation and conformation dynamics.

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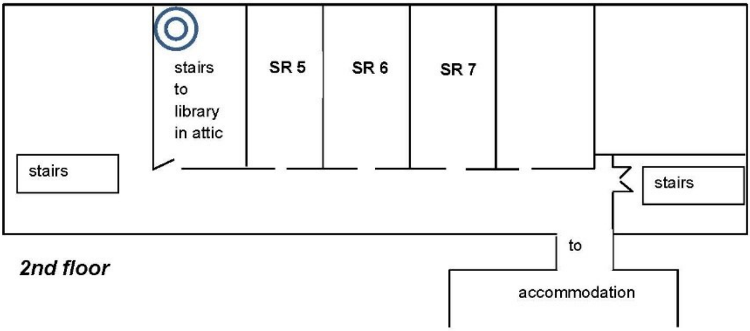
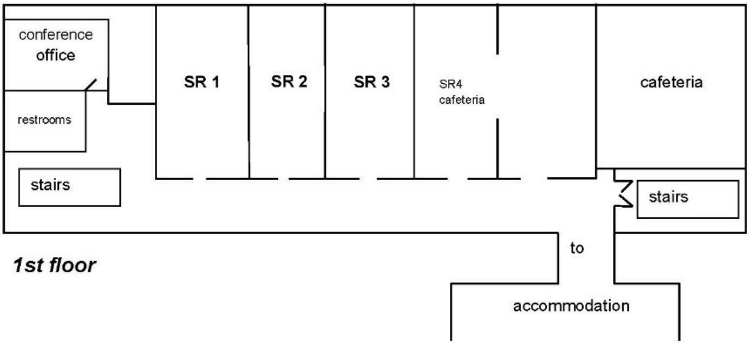
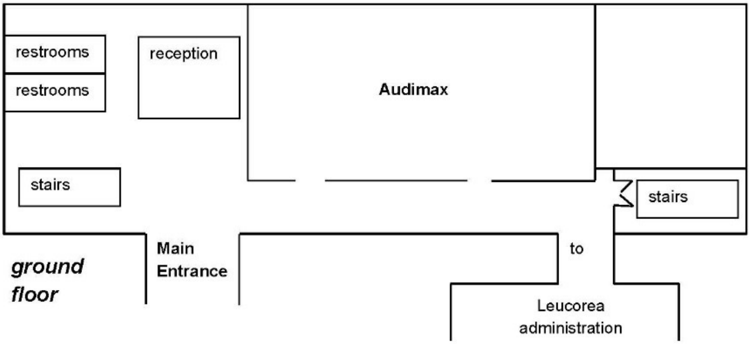
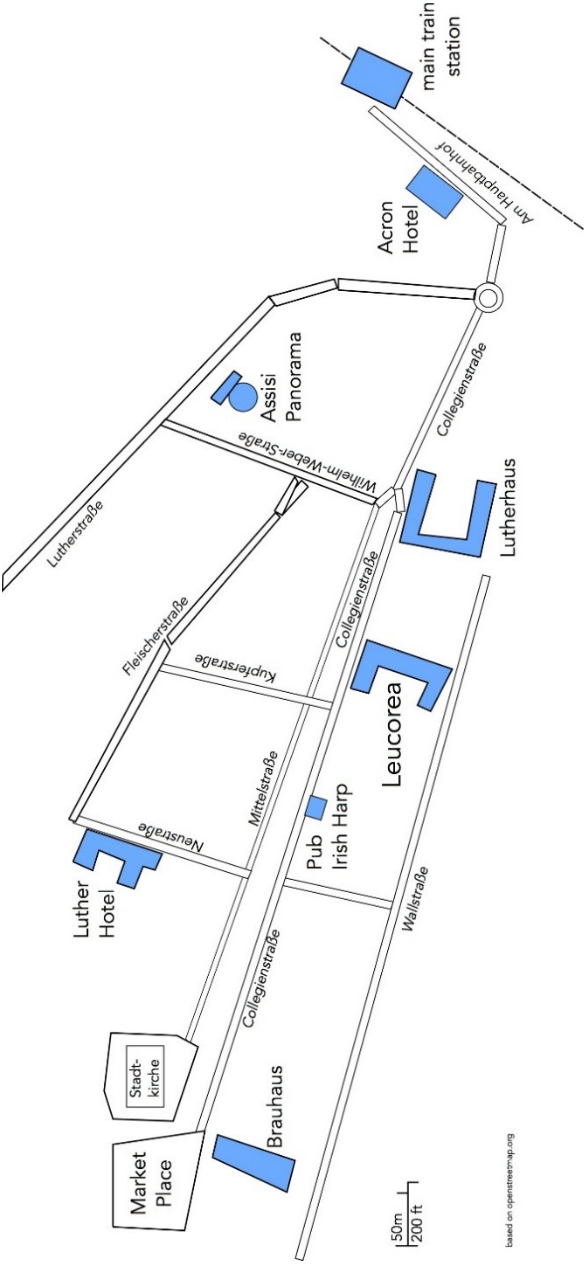
Map of Leucorea







Map of Wittenberg



based on openstreetmap.org

Excursions

There are different options for you to get to know Wittenberg, the place where the reformation started 500 years ago.
Should you be interested in tranquility and nature you may choose to go on a hiking tour and explore the surrounding forests.
Please choose between the different offers. You may of course take part in several activities. As all tours a limited please come to the **reception desk** to collect your **voucher** for the selected tour(s) at any of the following times:

➢ Sun, Sept 17	3:00 pm – 6:00 pm
➢ Mon, Sept 18	8:00 am – 9:00 am 12:00 pm– 1:00 pm
➢ Tue, Sept 19	8:00 am– 9:00 am

Sunday, September 17

Classical guided tour

4:30 – 5:30 pm | Meeting place: Leucorea Courtyard

The tour will lead you through the historic district of Wittenberg between Castle Church and Luther House. You will find all important sights such as the houses of Luther and Melanchthon, the Town Church of St. Mary's, the historic market square, the homes of Lucas Cranach and the Castle Church with ist famous „theses door", where the reformation startet in October 1517.

Guided city tour by night

8:30 – 9:30 pm | Meeting place: In front of "Brauhaus"

On that tour Martin Luthers wife Katharina von Bora and the wife of painter Lucas Cranach Barbara Cranach will lead you through Wittenberg and will tell you about the age of reformation from the perspective of women of that time. This walk will be supplemented by humorous and interesting stories from the 16th century.

Tuesday, September 19

Visit to the Luther House

4:00 – 5:00 pm | Luther House, Collegienstrasse 54

You may have a look at the home of Martin Luther, the place where he had his theological breakthrough, where he offered lectures to students from all over Europe, and where he wrote his treatises that changed the world.

The house originally built as an Augustinian monastery served as his home for 35 years accommodating also his wife Katharina and their growing family.

Luther 1517 – Yadegar Asisi 360° Panorama

3:30 – 5:30 pm | Lutherstrasse 42

Discover Wittenberg 500 years ago at the time of Martin Luther, Frederick the Wise and Lucas Cranach. The artist Yadegar Asisi has dedicated a huge cyclorama to the time when the monk and scholar Martin Luther published his 95 thesis on church reform in Wittenberg.

You should schedule about 30 minutes for visiting the panorama.

Classical guided tour

3:45 – 4:45 pm | Meeting place: Courtyard Leucorea

4:30 – 5:30 pm | Meeting place: Courtyard Leucorea

The tour will lead you through the historic district of Wittenberg between Castle Church and Luther House. You will find all important sights such as the houses of Luther and Melanchthon, the Town Church of St. Mary’s, the historic market square, the homes of Lucas Cranach and the Castle Church with ist famous „theses door“, where the reformation startet in October 1517.

Guided hiking tour through the Forest Bad Dübener Heide

3:30 – 5:30 pm | Meeting place: Courtyard of the Leucorea

The tour leads you through an area of former cole mines which were flooded to create a unique ecosystem. You will walk though a quaint forrest passing small idyllic lakes.

About …

… Wittenberg

Wittenberg is home to numerous historical sites, such as All Saints' Church (Schlosskirche), where Luther is said to have nailed his 95 theses, St. Mary's Church (Stadtkirche), the parish church in which Luther often preached and the museums Luther's Home and Melanchthon's Home. Many of Wittenbergs sites were added to the UNESCO world heritage list in 1996. Also portraits and other paintings by Lucas Cranach the Elder and Younger can be seen or modern architecture by Friedensreich Hundertwasser can be admired.

… Foundation Leucorea

The LEUCOREA Foundation was established in 1994, with the aim of reanimating academic life in Wittenberg, the place where one of the most renowned universities in Germany was inaugurated 500 years ago.

Keeping this tradition in mind, the LEUCOREA serves as an umbrella organization, enriching the research landscape through a spectrum of academic projects, as well as through the work of various partners and university institutions. The LEUCOREA has also established a conference centre with good facilities and links to the cultural and touristic opportunities that the city of Wittenberg has to offer.

… Martin Luther University Halle-Wittenberg

Education and research with a 500-year-old tradition: Martin Luther University Halle-Wittenberg (MLU) offers a wide range of academic subjects in the areas of humanities, social sciences, natural sciences and medicine. The oldest and largest university in Saxony-Anhalt was created in 1817 when the University of Wittenberg (founded in 1502) merged with Friedrichs University Halle (founded in 1694). Today the university has around 20,000 students and 340 professors.

MLU's academic profile in the field of the humanities is shaped by the core research areas "Enlightenment – Religion – Knowledge" and "Society and Culture in Motion. Diffusion - Experiment - Institution". The university's core scientific research is in "Materials Science – Nanostructured Materials" and "Biosciences – Structures and Mechanisms of Biological Information Processing". The Faculty of Medicine focuses on epidemiology, nursing research and research on signal transmission.As a member of the Central German University Alliance Halle-Jena-Leipzig, MLU cooperates closely with other universities, and with external research institutes and industries. This is visible at a local level on the Weinberg Campus, the second largest technology park in Eastern Germany. All of the university's natural science institutes are concentrated here. They work in partnership with companies and major German research institutes, such as the Max Planck Society and the Fraunhofer-Gesellschaft.

… Leipzig University

Leipzig University was founded in 1409 making it one of the oldest universities in Germany. It is an interdisciplinary, international comprehensive university and among the top 15 in Germany in the fourth consecutive year (by the Shanghai Ranking).

The University consists of 14 faculties with 128 institutes. 35,000 persons research, teach and study at the university and more than 4,300 persons are employed at the University Hospital of Leipzig. The university offered 136 courses of study in the 2009/10 winter semester. 5,686 doctoral candidates are registered at the UL (2,439 in medicines), 631 of whom are enrolled in 20 structured graduate training programmes (as per the end of 2009). The research potential in Leipzig is fortified by 20 non-university research institutions and five other universities.

As a university steeped in tradition, Leipzig University has always become stronger when emerging from difficult transitions. The phase after the Berlin Wall fell in 1989 was dominated by a virtually complete restructuring of the humanities and social sciences while the life sciences and natural sciences were adapted to new accents in research and teaching. The fundamental reformation of its structures and courses of study was also combined with the opportunity to promote interdisciplinary collaboration from the onset and take advantage of arising synergies.

… SFB/TRR 102

The SFB/TRR 102 is a Collaborate Research Center (CRC) at the Universities of Halle and Leipzig. Our focus is lying on open problems of polymer research which are characterized by the occurrence of strong correlations between local structure and global conformation of the chain. We investigate processes of structure formation and self-assembly of synthetic and biological chain molecules, for which the formation of molecular structures and the molecular dynamics are strongly affected by constraints like specific internal interactions, external forces, geometrical confinement, crowding or topological restrictions. Two prominent examples for such processes and central topics of the CRC are crystallization in the area of synthetic polymers and the formation of amyloids in the area of biopolymers.

The Fraunhofer Institute for Microstructure of Materials and Systems (Halle) and the Leibniz Institute for Surface Modification (Leipzig) also participate in the SFB/TRR 102.

Further information about our activities including the Integrated Research Training Group ‘Polymers: random coils and beyond’ can be found at: www.natfak2.uni-halle.de/sfbtrr102.

Imprint

International Discussion Meeting
on Polymer Crystallization 2017
– From Classical Systems to Functional
Materials and Biopolymers

Publisher: Collaborative Research Centre
SFB/TRR 102 „Polymers under multiple constraints:
restricted and controlled molecular order and mobility“
http://www.natfak2.uni-halle.de/forschung/verbund/sfbtrr102/

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Cover image: Martha Schulz; AFM image showing
semicrystalline Poly-ε-caprolacton (PCL) with
2D spherulitic structure on silicon substrate

Layout/Design cover: unicom Werbeagentur GmbH, Berlin

Layout texts: Beate Horn

Print: Impress Druckerei, Halle

Circulation: 200 copies

Program Overview

Time	Sunday (September 17, 2017)	Monday (September 18, 2017)	Tuesday (September 19, 2017)	Wednesday (September 20, 2017)
8:00 am		**8:00 am Registration/ mount of posters**		
			8:30 am Session 4 (Chair: D. Huster) J. Balbach U. H. E. Hansmann P. Cebe M. Anton	**8:30 am Session 6** (Chair: Wb. Hu) C. Schick B. Goderis A. J. Müller
9:00 am		**9:00 am Opening**		
		9:15 am Session 1 (Chair: G.C. Rutledge) K. Schmidt-Rohr J. - U. Sommer T. Miyoshi W. Paul		
10:00 am				Coffee break
			Coffee break	**10:30 am Session 7** (Chair: K. Saal-wächter) T. Knowles P. Pan Y. Men D. Cavallo
11:00 am			**11:00 am Session 5a** (Chair: W. Paul) Wb. Hu G.C. Rutledge	
		Lunch break and posters		
12:00 pm			Lunch break and posters	
				12:30 pm Closing
1:00 pm				
		1:15 pm Session 2 (Chair: F. Kremer) A. Salleo G. Reiter M. Brinkmann E. Chen		
			1:30 pm Session 5b (Chair: Ch. Schick) J. Kumaki A-K. Flieger S. Yan	
2:00 pm				
3:00 pm	**3:00 pm Registration/ mount of posters**		Coffee break	
		Coffee break		
			3:30 pm Excursions or free time	
		3:45 pm Session 3 (Chair: M. Beiner) L. Li G. W. M. Peters J. Kornfield		
4:00 pm				
	4:30 pm Guided city tour			
5:00 pm				
		5:15 pm Introductory lecture R. Riek		
6:00 pm	**6:00 pm Start of conference** Evening talk C. Senkel	**6:00 pm Poster session** and snack buffet	**6:00 pm Dinner and discussion** at Luther-Hotel	
7:00 pm	**7:00 pm Welcome dinner** at Brauhaus			
8:00 pm			**8:00 pm Poster session**	
	8:30 pm Guided city tour			
9:00 pm				

🟩 Partially crystalline order in biological macromolecules

🟪 Functional semicrystalline polymers

🟨 Crystallization under external control (flow, surfaces, nucleation, confinement)

🟦 Connectivity and chain architecture as constraints for polymer crystallization