Joint DIPC, JCNS & SoftComp Workshop 2018:

Functional Polymers

19 - 21 March 2018, San Sebastian, Spain

JÜLICH
FORSCHUNGSZENTRUM

DIPC
Donostia International Physics Center

SoftComp
SOFT MATTER COMPOSITES

CFM
Materialen Fisika Zentroa
Centro de Física de Materiales
Materials Physics Center

WORKSHOP ON FUNCTIONAL POLYMERS

Joint DIPC, JCNS & SoftComp Workshop
San Sebastian 19 -21 March, 2018

Practical Information

Workshop place:

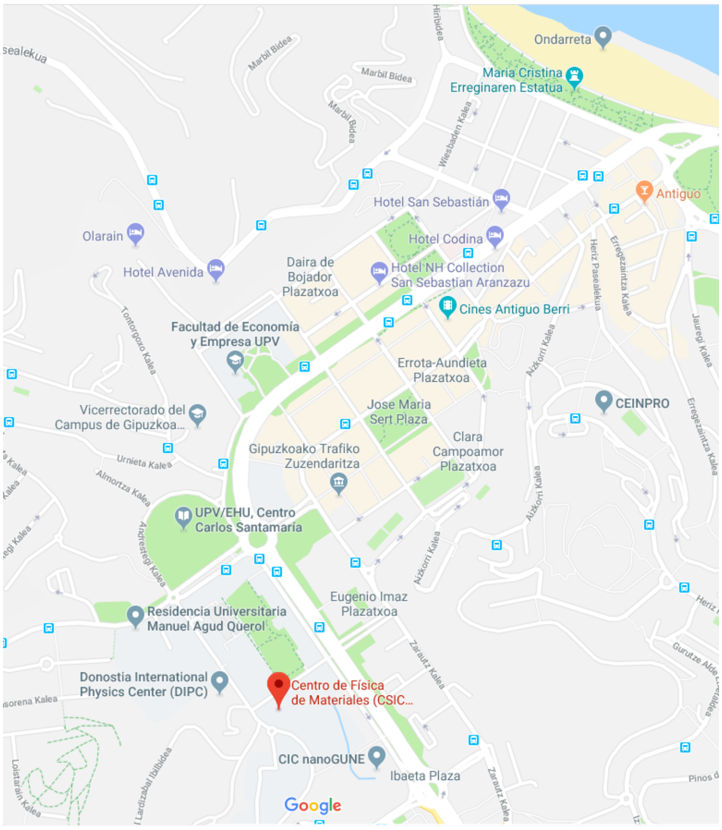
CENTRO DE FISICA DE MATERIALES (CFM) – MATERIALS PHYSICS CENTER

The CFM is a joint center of the University of the Basque Country (UPV/EHU) and the Spanish National Research Council (CSIC), located in the Campus of Gipuzkoa (San Sebastian) of the UPV/EHU (see the enclosed map)

CFM address:
Paseo Manuel de Lardizabal, 5
20018 Donostia-San Sebastian

Web-page: cfm.ehu.es

The meeting will take place in the Auditorium of the CFM (floor (-1) of the CFM building).



Workshop Dinner:

The Workshop Dinner will take place on Tuesday, March 20 at 20:30h.

Restaurant:

'La Brasserie Mari Galant'

Web page: http://www.restaurantelabrasserie.com/

Address:
Hotel de Londres y de Inglaterra
Zubieta, 2
20007 Donostia-San Sebastian

SCIENTIFIC PROGRAM

MONDAY, MARCH 19

8:30 – 9:15: Registration

9:15 - Welcome and Practical information

One Component Nano-Composites (Session-1)
Chair Person: Dieter Richter

9:30 – '*Effects of morphology on the mechanical properties of heterogeneous polymer-grafted nanoparticle networks*' (invited)
Anna C. Balazs

10:00 – '*Recovery of permittivity and depth from near-field data as a step toward infrared nanotomography'*
Lars Mester

10:20 – '*Host-induced block copolymer self-assembly into ultra-high loaded drug formulations'*
Robert Luxenhofer

10:40 – '*Structure formation in nanophase-separated comb-like polymers with lamellar morphology'*
Gaurav Gupta

11:00 – 11:30: Coffee break

One Component Nano-Composites (Session-2)
Chair Person: Michael Monkenbusch

11:30 – '*Hierarchical hybrid materials with engineered properties from ligand-driven organization of particulates'* (invited)
Michael R. Bockstaller

12:00 – *'Single-particle magnetostriction and its influence on the shear modulus of magnetorheological elastomers'*
Mikhail Shamonin

12:20 – '*Towards novel functional materials consisting of magnetic nanocomposites with supramolecular activity'*
Lisa S. Fruhner

12:40 – '*Polymer-grafted nanoparticle membranes with controllable free-volume'* (invited)
Sanat K. Kumar

13.10 – 14:30: Lunch

One Component Nano-Composites (Session-3)

Chair Person: Juan Colmenero

14:30 – ‘*Polymer chain conformation and dynamical confinement in a model one component nano-composite*’ (invited)
Dieter Richter

15:00 – ‘*Viscoelasticity and flow mechanisms of grafted nanoparticles, from star polymer melts to solvent-free colloids*’ (invited)
Dimitris Vlassopoulos

15:30 – ‘*Hyperspectral infrared nanoimaging based on nano-FTIR spectroscopy: a new dimension in chemical nanoimaging*’
Iban Amenabar

15:50 – 16:20: Coffee break

Single Chain Nanoparticles (Session-1)

Chair Person: Annette Schmidt

16:20 – ‘*Organometallic nanoparticles: how they came to be, where they are now and where will they go*’ (invited)
N. Gabriel Lemcoff

16:50 – *‘Recent advances and opportunities in SCNPs’*
José A. Pomposo

17:10 – ‘*Structure and dynamics of single-chain nanoparticles in solution*’
Marina González-Burgos

17:30 – *‘Dextran-based single-chain nanoparticles: synthesis, characterization and application in imaging’*
Raquel Gracia

17:50 – *‘Turning on fluorescence in single-chain polymer nanoparticles via aggregation-induced emission’*
Edurne Gonzalez

18:10 – *‘Soft nanoparticles as novel additives in nanocomposites: control of nanoparticle morphology and nanocomposite dynamics’* (invited)
Mark D. Dadmun

18:40 – End of presentations

TUESDAY, MARCH 20

Single Chain Nanoparticles (Session-2)

Chair Person: Sanat K. Kumar

9:00 – *'Computer simulations of single-chain polymer nanoparticles: synthesis routes and crowding effects'* (invited)
Angel J. Moreno

9:30 – *'Simulation and theory of equilibrium swelling of single chain nanoparticles'* (invited)
Jens-Uwe Sommer

10:00 – *'Properties of single-chain nanoparticles under shear flow and synthesis under crowding conditions'*
Maud Formanek

10:20 – *'Dynamics of internally functionalized dendrimers'*
Maxim Dolgushev

10:40 - *'The nano-bio world: lessons from in-silico experiments'* (invited)
Alfredo Alexander-Katz

11:10 – *'Design of patchy polymers: biomimetic self-knotting chains'*
Ivan Coluzza

11:30 – 12:00: Coffee break

Supra-Molecular Polymers (Session-1)

Chair Person: Arantxa Arbe

12:00 – *'Hydrogen bonding elastic networks and shape-memory contact printing'* (invited)
Mitchel Anthamatten

12:30 – *'Progressive supramolecular polymerization of complementary subcomponents'*
Jesús del Barrio

12:50 – *'Supramolecularly-associated polymers: from structure to dynamics'* (invited)
Margarita Kruteva (replacing Wim Pyckhout-Hintzen)

13:20 – 14:45: Lunch

Supra-Molecular Polymers (Session-2)

Chair Person: Dimitris Vlassopoulus

14:45 – *'From complexation of oppositely charged polyelectrolytes to supramolecular bottlebrushes and gels'* (invited)
Michael Rubinstein

15:15 – *'Density and temperature dependence on supramolecular polymer morphology of polyethylene and polybutylene glycols with hydrogen bonding ends'*
Eunsang Lee

15:35 – *'Neutron spin-echo spectroscopy for a molecular view on supramolecular chain- and association- dynamics'*
Michael Monkenbusch

15:55 – *'Using dynamic covalent bonds to fabricate high-performance bio-inspired composites'*
Rafael Libanori

16:15 – Coffee & Posters (the list of presented posters is at the end of this program)

20:30 – Workshop Dinner

WEDNESDAY, MARCH 21

Supra-Molecular Polymers (Session-3)

Chair Person: Angel J. Moreno

9:00 – *'Strain stiffening in self-assembled biomimetic hydrogels'* (invited)
Rint P. Sijbesma

9:30 – *'Computer simulation studies of linear and nonlinear dynamics and rheology of supramolecular polymer networks formed by associating telechelic chains'* (invited)
Zuowei Wang

10:00 – *'Structure and association behavior of supramolecular linear polymer melt'*
Margarita Kruteva

10:20 – *'Single chain model for unentangled associating polymers'*
Jorge Ramirez

10:40 – *'Investigation on the local dynamics in supramolecular polymer structures using magnetic particle nanorheology'*
Melisa Hermes

11:00 – 11:30: Coffee break

Supra-Molecular Polymers (Session-4)

Chair Person: Jose A. Pomposo

11:30 – *'Influence of polymer polarity and association strength on the dynamics of supramolecular model polymers'*
Ana Bras

11:50 – *'Overcharging and reentrant condensation of thermoresponsive ionic microgels'*
Domenico Truzzolillo

12:10 – *'Nanostructured, thermoresponsive and biocompatible hydrogels based on poly(2-oxazoline)s for 3D bioprinting and biofabrication'*
Thomas Lorson

12:30 – End of the Workshop

12:45 – Lunch

List of Posters:

P1: *‘Ambient temperature non-covalent curing of waterborne polymer dispersions: polyelectrolyte interpolymer complexation’*
Maialen Argaiz

P2: ‘Unfolding luminescent polymers in flow’
Jess M. Clough

P3: *‘Incorporation of hydrogen bonding for high performance waterborne coatings’*
Nerea Jimenez

P4: *‘Studyng the role of bridging ligands in organometallic nanoparticles’*
Victoria Kobernik

P5: *‘Effect of the nanofiller topology on the dynamics of all-polymer nanocomposites’*
Paula Malo de Molina

P6: *‘Laterally-resolved properties of all-polymer composites thin films by high-resolution atomic force microscopy’*
Daniel Martínez Tong

P7*: ‘Quantification of different contributions to dissipation in various rubber nanoparticle composites’*
Shiharish M. Nagaraja

P8: *‘The new high-resolution neutron spin-echo spectrometer (J-NSE) at MLZ’*
Stefano Pasini

P9: *‘Magnetodielectric effect in compliant magnetorheological elastomers’*
Mikhail Shamonin

ABSTRACTS

Invited and oral contributions

(ordered according to the time of presentation)

MONDAY, MARCH 19

INVITED

Effects of Morphology on the Mechanical Properties of Heterogeneous Polymer-grafted Nanoparticle Networks

Tao Zhang, Badel L. Mbanga, Victor V. Yashin, and Anna C. Balazs*
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*Corresponding author; e-mail: balazs@pitt.edu

Using computer modeling, we vary the structure of networks formed from two types of polymer grafted nanoparticles (PGNs). The PGNs are interconnected by dynamic, reversible bonds that break and reform at a specified rate. The binary PGN network is arranged in a layered or random structure. Hence the design space characterizing this system involves both temporal and spatial components. Using the simulations, we probe regions of this design space to facilitate the fabrication of composites with valuable mechanical properties. In particular, we model the response of the layered and mixed structures to a tensile deformation and thus, isolate effects of molecular architecture on the mechanical behavior of the composite. We found that the layered binary PGN networks exhibit superior tensile properties (strain-at-break, toughness) and remarkable resilience in comparison with those of the random binary mixtures. The mechanical properties of the layered networks are attributed to the formation of a new, stable ordered structure when the material is deformed. Overall, our studies indicate how design approaches that explicitly consider the coupling between the temporal and spatial characteristics of the network can facilitate the creation of composites with improved materials properties.

Recovery of Permittivity and Depth from Near-Field Data as a Step toward Infrared Nanotomography

Alexander A. Govyadinov†, Stefan Mastel†, Federico Golmar†‡, Andrey Chuvilin†§, P. Scott Carney⊥, and Rainer Hillenbrand§||

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§ IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain
⊥ Department of Electrical and Computer Engineering and the Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, Illinois 61801, United States
|| CIC nanoGUNE and UPV/EHU, 20018 Donostia-San Sebastián, Spain

The increasing complexity of composite materials structured on the nanometer scale requires highly sensitive analytical tools for nanoscale chemical identification, ideally in three dimensions. While infrared near-field microscopy provides high chemical sensitivity and nanoscopic spatial resolution in two dimensions [1], the quantitative extraction of material properties of three-dimensionally structured samples is not widely used yet. Here we introduce methods to recover the thickness and permittivity of simple 3D structures (such as thin films and nanostructures) from near-field measurements, and provide their experimental demonstration [2]. This is accomplished i.e. via a novel nonlinear invertible model of the near-field interaction, taking advantage of the near-field data recorded at multiple harmonics of the oscillation frequency of the near-field probe. Our work enables quantitative nanoscale-resolved optical studies of thin films, coatings, and functionalization layers, as well as the structural analysis of multiphase materials, among others. It represents a major step toward the further goal of near-field nanotomography.

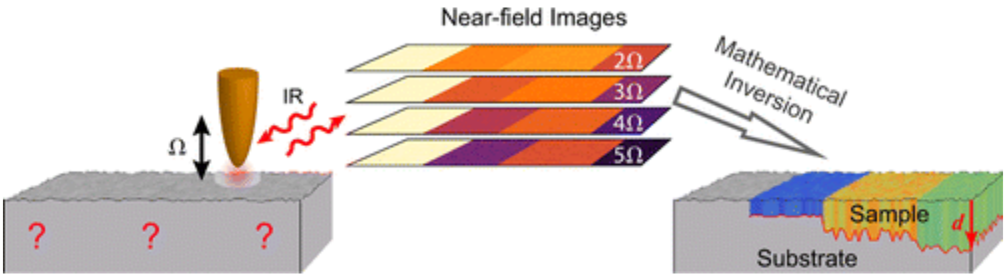

Fig. 1. Schematics of the s-SNOM experiment and the conceptual representation of the reconstruction procedure that yields the sample structure. By scanning the sample surface, a set of near-field images is recorded and normalized to the signal on a reference area with known optical properties. A mathematical inversion procedure is then applied at each pixel to recover the sample structure, i.e., thickness (represented by red curve) and dielectric permittivity (represented by fill color) of the sample layer.

[1] I. Amenabar et.al., Nature Communications, 4, 2890 (2013)

[2] B. Pollard et.al., Nature Communications, 5, 1, (2014)

Host-induced block copolymer self-assembly into ultra-high loaded drug formulations

M.M. Lübtow, M. S. Haider, R. Luxenhofer
Functional Polymer Materials, Chair for Advanced Material Synthesis, Department of Chemistry and Pharmacy, Julius-Maximilians-University Würzburg and Bavarian Polymer Institute, Röntgenring 11, 97070 Würzburg

A large portion of active pharmaceutical ingredients (API) suffer from poor water-solubility. Among many other purposes, excipients can be used to increase the apparent water solubility of insoluble compounds and thus, increase their bioavailability. In many cases, it is important to effectively suppress crystallization of drug. However, the amount of API that can be stably dispersed in an amorphous manner is often rather limited.

We have previously reported on a novel polymer platform, which is allows to formulate unparalleled amounts of the extremely water insoluble paclitaxel [1,2,3] and other APIs and API combinations [4]. More recently, we have found very pronounced effects of very small structural variations on the formulation capacity for curcumin, another highly insoluble natural compound [5].

Here, the structural variation of poly(2-oxazoline)s and poly(2-oxazine) based block copolymers will be further extended, with a focus on a weakly amphiphilic block copolymers, which does not form polymer micelles itself but only upon combination with hydrophobic small molecules. The physico-chemical characteristics of solid dispersions with a range of structurally different APIs will be discussed as well as their aqueous formulations. Ultimately, the goal is to gain a molecular understanding of the unusual capacity of this novel excipient platform for extremely water insoluble APIs.

References

[1] R. Luxenhofer, A. Schulz, C. Roques, S. Li, T. K. Bronich, E. V. Batrakova, R. Jordan, A. V. Kabanov, *Biomaterials* 2010, *31*, 4972.

[2] A. Schulz, S. Jaksch, R. Schubel, E. Wegener, Z. Di, Y. Han, A. Meister, J. Kressler, A. V. Kabanov, R. Luxenhofer, C. M. Papadakis, R. Jordan, *ACS Nano* 2014, *8*, 2686.

[3] Z. He, X. Wan, A. Schulz, H. Bludau, M. A. Dobrovolskaia, S. T. Stern, S. A. Montgomery, H. Yuan, Z. Li, D. Alakhova, M. Sokolsky, D. B. Darr, C. M. Perou, R. Jordan, R. Luxenhofer, A. V. Kabanov, *Biomaterials* 2016, *101*, 296.

[4] Y. Han, Z. He, A. Schulz, T. K. Bronich, R. Jordan, R. Luxenhofer, A. V. Kabanov, *Mol. Pharm.* 2012, *9*, 2302.

[5] M. M. Lübtow, L. Hahn, M. S. Haider, R. Luxenhofer, *J. Am. Chem. Soc* 2017, *139*, 10980.

Structure formation in nanophase-separated comb-like polymers with lamellar morphology

Gaurav Gupta,[1,2] **Varun Danke**,[2] **Mario Beiner** [1,2]
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Walter-Hülse-Straße 1, 06120 Halle, Germany
[2]Martin-Luther-Universität Halle-Wittenberg, Naturwissenschaftliche Fakultät II,
06120 Halle, Germany

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Comb-like polymers with rigid backbones and flexible alkyl side chains form an interesting class of functional materials which often exhibit nanophase separation between the main and side chain alkyl nano-domains despite of the degree of long range order. They find potential applications in organic semi-conductors light emitting diodes, electrolyte fuel cells and light weight composites. Phase separation of the domains with a layered morphology typically occurs on length scales of 1-3 nm. Here we present an insight to the structure formation, packing states of the alkyl domains and the interrelations of the side chain packing on the main chain packing in different comb-like polymers viz. alkoxylated polyesters (PPAOTs) and alkoxylated polyphenylene vinylenes (AOPPVs) with varying side chain lengths (C = 6-12) by X-ray diffractometry. Different polymorphic states are observed in both PPAOTs and DOPPVs depending on the side chain lengths and thermal treatment. The packing states of alkyl nanodomains under constraints introduced by backbones have been classified by quantifying the volume occupied per CH_2 unit (V_{CH2}) based on the crystallographic unit cell analysis. This novel approach excludes additional assumptions regarding the interdigitation or tilting of the ideally stretched side chains commonly used in structural models based on polyethylene like packing. While AOPPVs show clear indications for a densely packed, crystal- like side chain packing[1], PPAOTs show two polymorphs (A and B) with either crystalline or amorphous alkyl nano-domains depending on thermal history and side chain lengths[2]. For PPAOTs, different alkyl packing states influences the main chain packing (pi-pi stacking) which is important for tuning the functional properties. Further, the analogy of structure formation in comb-like polymers with 'defected' linear precision is discussed[3].

References:

1. T. Babur, G. Gupta and M. Beiner; About different packing states of alkyl groups in comb-like polymers with rigid backbones, *Soft Matter,* 2016, 12, 8093-8097
2. G.Gupta, V. Danke, T. Babur and M. Beiner; Interrelations between side chain and main chain packing in different crystal modifications of alkoxylated polyesters, *J. Phys. Chem. B*, 2017, 121, 4583-4591
3. V. Danke, G. Gupta, S. Reimann, W. Binder and M. Beiner; Structure formation in nanophase separate systems with lamellar morphology: Comb-like vs. Linear precision polymers (Submitted)

INVITED

Hierarchical Hybrid Materials with Engineered Properties from Ligand-Driven Organization of Particulates

Michael R. Bockstaller, Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, USA

Nanoparticle assembly structures (also called ‘particle solids’) play an important role across diverse technology areas such as solid state lighting, energy generation, or information storage. Often the functionality of nanoparticle assembly structures depends sensitively on the morphology (structural regularity, symmetry, uniformity) of the material. To control the structure and properties of particle solids, the tethering of organic ligands to the surface of particles has emerged as an effective strategy. This approach takes advantage of the possibility to tailor the interactions between particle constituents by the deliberate design of the structure and composition of organic ligands. Recent advances in surface-initiated atom transfer controlled radical polymerization (SI-ATRP) have further extended the range of possible ligand compositions to encompass polymer chains. In a first part, this presentation will discuss the role of (homo)polymer modification on the interaction between particles in assembly structures. Opportunities to harness the assembly or polymer-tethered particles as a strategy to fabricate functional hybrid materials with applications as high breakdown dielectrics and supercapacitors will be discussed. In a second part, this presentation will review recent progress in the application of SI-ATRP to design copolymer tethered particle architectures capable of organizing into non-close-packed structures that arise as a compromise from the respective structure driving forces of particle and block copolymer constituents. Polymer-ligand interactions in blends of distinct particle systems will be shown to drive the formation of hierarchical superstructures via upper or lower critical solution phase behavior. This process could ultimately facilitate the reversible formation and dissolution of microstructures in multicomponent particle solids.

Single-particle magnetostriction and its influence on the shear modulus of magnetorheological elastomers

M. Shamonin[1],V. M. Kalita[2,3], A. A. Snarskii[2,4], D. Zorinets[2]

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[2]*National Technical University of Ukraine "Kyiv Polytechnic Institute", Prosp. Peremohy 37, Kiev, 03056, Ukraine*
[3]*Institute of Physics NAS of Ukraine, Prosp. Nauky 46, Kiev, 03028, Ukraine*
[4]*Institute for Information Recording NAS of Ukraine, Shpaka St. 2, 03113, Kiev, Ukraine*

Magnetorheological elastomers (MREs) are composite materials comprised of micrometer-sized ferromagnetic particles in a non-magnetic elastomer matrix. We theoretically introduce a single-particle mechanism of magnetostriction in MREs, where the rotation of soft magnetic, mechanically rigid particle with uniaxial magnetic anisotropy in magnetic fields is implied [1]. The notion of single-particle mechanism means that the total magnetic anisotropy energy of the filling particles in the matrix is the sum over single particles. The effect of matrix deformation is clearly pronounced if the magnetic anisotropy coefficient K of particles is much larger than the shear modulus μ of the elastic matrix. An external magnetic field introduces torques on magnetic filler particles, creates mechanical stresses in the vicinity of inclusions, induces shear strain and increases the effective shear modulus of these composite materials [2]. Obtained theoretical results compare well with known experimental data. The concentration dependence of the effective shear modulus at higher filler concentrations has been estimated using the method of Padé approximants, which predicts that both the absolute and relative changes of the magnetic-field dependent effective shear modulus will significantly increase with the growing concentration of filler particles [2].

1. Kalita, V. M., Snarskii, A. A., Zorinets, D., Shamonin, M. (2016). Single-particle mechanism of magnetostriction in magnetoactive elastomers. *Physical Review E*, *93*(6), 062503.

2. Kalita, V. M., Snarskii, A. A., Shamonin, M., Zorinets, D. (2017). Effect of single-particle magnetostriction on the shear modulus of compliant magnetoactive elastomers. *Physical Review E*, *95*(3), 032503.

Towards novel functional materials consisting of magnetic nanocomposites with supramolecular activity

L. S. Fruhner[1], M. Kruteva[1], J. Allgaier[1], W. Pyckhout-Hintzen[1], S. Förster[1]

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Functional nanocomposites offer a broad application range from sensors through stretchable electronics to smart coatings for energy conversion and human health. [1] Especially, responsive materials which are able to perform self-assembly in different environments (e.g. in magnetic or electric fields, by mechanical shearing) are in the centre of interest (Fig.1). Further developments in this area would significantly benefit from deeper insights into the interactions between the nanoparticles with each other and their surrounding host matrix. Recently, we developed a synthetic procedure to obtain highly monodisperse nanoparticles consisting of a superparamagnetic iron oxide core (SPION) embedded in a polymeric shell. [2]

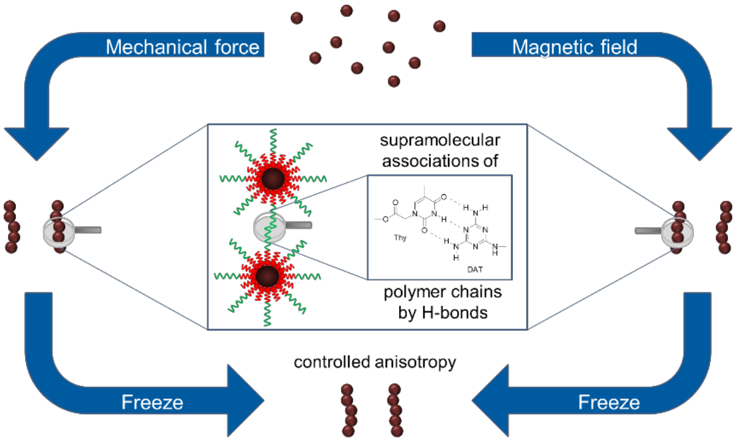
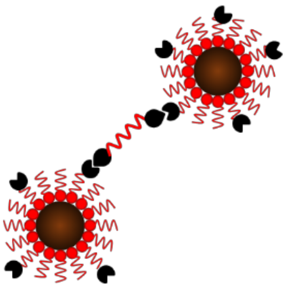


Figure 1 Design of responsive materials with controlled anisotropy and supramolecular activity

Our strategy aims at synthesising monodisperse superparamagnetic iron oxide nanoparticles (SPIONs) and coating them with α,ω-functionalised elastic polymers like polybutylene oxide (PBO). This allows us to either align the nanoparticles in a magnetic field or by mechanical force (Fig.1). The structure of the nanocomposites as well as their behaviour due to external stimuli are investigated via Small-Angle X-Ray and Neutron Scattering (SAXS/SANS).



While one end of the polymer chains carries a head group (α) to stick to the nanoparticles' surface like for example carboxylic acids, amino groups or phosphonic acids, the other end (ω) can be used to introduce supramolecular groups like thymine (Thy) which interact by H-bonding with corresponding groups like diaminotriazine (DAT) attached to the chains of the polymer matrix. By variation of the amount of Thy and/or DAT groups, the rheological properties of the system are controlled and the structures that arise from the external field or shear force can be conserved.

References

[1] P. Gómez-Romero, C. Sanchez, *in Functional Hybrid Materials*, Wiley-VCH, Weinheim, 2003.

[2] A. Feld, R. Koll, L. Fruhner, M. Krutyeva et al, *ACS Nano*, **2016**, *11*, 3767–3775.

INVITED

Polymer-Grafted Nanoparticle Membranes with Controllable Free-Volume

Sanat K. Kumar

[1]Department of Chemical Engineering, Columbia University, New York, NY.

Abstract

Polymer based membranes play a key role in several industrially important gas separation technologies, e.g., removing CO_2 from natural gas, with enormous economic and environmental impact. Baker advocates the development of novel membrane architectures since current, pure polymer membranes only offer limited systematic pathways for improvement. Here, we develop a novel hybrid membrane construct comprised entirely of nanoparticles grafted with polymers. These membranes are shown to have broadly tunable separation performance through variations in graft density and chain length. Computer simulations show that the optimal NP packing forces the grafted polymer layer to distort, yielding regions of measurably lower polymer density. Multiple experimental probes confirm that these materials have the predicted increase in "polymer free volume", which explains their improved separation performance. These polymer-grafted NP materials thus represent a new template for rationally designing membranes with desirable separation abilities, coupled with improved aging characteristics in the glassy state and enhanced mechanical behavior.

INVITED

Polymer Chain Conformation and Dynamical Confinement in a Model One Component Nano Composite

Dieter Richter[1], Christian Mark[1], Michael Monkenbusch[1], Olaf Holderer[2], Jürgen Allgaier[1], Nina Jalarvo[3], Michaela Zamponi[2], Aurel Radulescu[2]

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[2] Forschungszentrum Jülich GmbH, JCNS at Heinz Maier-Leibnitz Zentrum
Lichtenbergstraße 1, 85747 Garching, Germany
[3] Forschungszentrum Jülich GmbH, JCNS at SNS-Oak Ridge National Laboratory (ORNL),
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We report a neutron scattering investigation on the structure and dynamics of a single component nano composite (OCNC) based on SiO2 particles that were grafted with polyisoprene (PI) chains at the entanglement limit. By skillful labeling we accessed both the monomer density in the corona as well as the conformation of the grafted chains. While the corona profile follows an r^{-1} power law, the conformation of a grafted chain is identical to that of a chain in a reference melt, implying a high mutual penetration of the coronas from different particles. The brush crowding leads to topological confinement of the chain dynamics: (i) At local scales the segmental dynamics is unchanged compared to the reference melt, while (ii) at the scale of the chain the dynamics appears to be slowed down; (iii) performing a mode analysis in terms of end fixed Rouse chains the slower dynamics is tracked to topological confinement within the cone spanned by the adjacent grafts; (iv) adding 50% matrix chains the topological confinement sensed by the grafted chain is lifted partially and the apparent chain motion is accelerated: We observe a cross over from pure Rouse motion at short times to topological confined motion beyond the time, when the segmental MSD has reached the distance to the next graft.

INVITED

Viscoelasticity and flow mechanisms of grafted nanoparticles, from star polymer melts to solvent-free colloids

Dimitris Vlassopoulos
FORTH, Institute of Electronic Structue & Laser and
University of Crete, Department of Materials Science & Technology
Heraklion 70013, Crete, Greece

Using a wide range of well-characterized polymers, single chain nanoparticles and polymer-grafted nanoparticles, we systematically investigate their dynamics for different number of entanglements, grafting densities and core fractions, and focus in particular on the coupling of polymeric and colloidal responses. To this end, we start with star polymers of different functionalities, investigated two decades ago, and bridge to self-suspended nanoparticles. We the aid of dynamic rheological measurements at various temperatures, appropriately complemented by creep tests, we obtain the complete linear viscoelastic spectrum. We show how to quantify the typically observed two relaxation modes, a faster polymeric and a slower colloidal. Where appropriate, scattering data are obtained and used to support that assignment and quantify the slow modes. In this regard, we discuss the analogies with polymer (entangled or Rouse-like) dynamics and colloidal glass transition. Finally, we present selective nonlinear shear data from measurements of stress start-up and relaxation upon flow cessation. We compare against respective data obtained with linear or star polymers and discuss the specific role of nanoparticles. Dynamic diagrams of viscosity or relaxation time versus molecular size or core fraction provide the basic ingredients for tailoring flow properties and obtaining a universal description of the behavior of grafted nanoparticles in the melt.

Work in collaboration with D. Parisi and F. Snijkers (Crete), E. Buenning and S. K. Kumar (New York), G. Sakellariou (Athens) and M. Bockstaller (Pittsburgh).

Hyperspectral infrared nanoimaging based on nano-FTIR spectroscopy: a new dimension in chemical nanoimaging

I. Amenabar[1], S. Poly[1], M. Goikoetxea[1], W. Nuansing[1], P. Lasch[2], and R. Hillenbrand[1,3]

[1]CIC nanoGUNE Consolider, 20018 Donostia - San Sebastián, Spain
[2]Proteomics and Spectroscopy (ZBS 6), Robert-Koch-Institut, Berlin, Germany
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An ultimate goal in polymer science is the non-invasive compositional mapping of materials with nanometer-scale spatial resolution. The emerging development of Fourier transform infrared nanospectroscopy (nano-FTIR [1]) enables a plethora of novel possibilities for nanoscale-resolved chemical and structural analysis [2,3]. Nano-FTIR is based on performing FTIR spectroscopy of the infrared light scattered by a metallized atomic force microscope tip probing the sample surface (see Fig. 1a). Here we demonstrate that nano-FTIR spectra of organic materials (i.e. polymers), can be acquired in less than 2 seconds. Furthermore, we discuss the novel technical improvements that together with the fast nano-FTIR spectra acquisition enable the recording of reliable nanoscale-resolved two-dimensional broadband spectroscopic maps (hyperspectral data cubes). Such hyperspectral data cubes (see Fig. 1b) can be recorded within time scales of very few hours, allowing for the analysis of real-world applications.

We apply hyperspectral IR nanoimaging for studying a three-component polymer blend film (see Fig. 1b) and we demonstrate that in combination with multivariate data analysis, it provides spatially resolved chemical information. Particularly, we demonstrate that unique information about the spatial distribution of individual polymers can be obtained with a spatial resolution of about 30 nm [4]. Among others, we identify and spatially map nanoscale-size areas where chemical interactions between different polymer components occur. We foresee wide application potential of hyperspectral infrared nanoimaging for unprecedented chemical materials characterization and quality control in various field ranging from materials sciences to biomedicine.

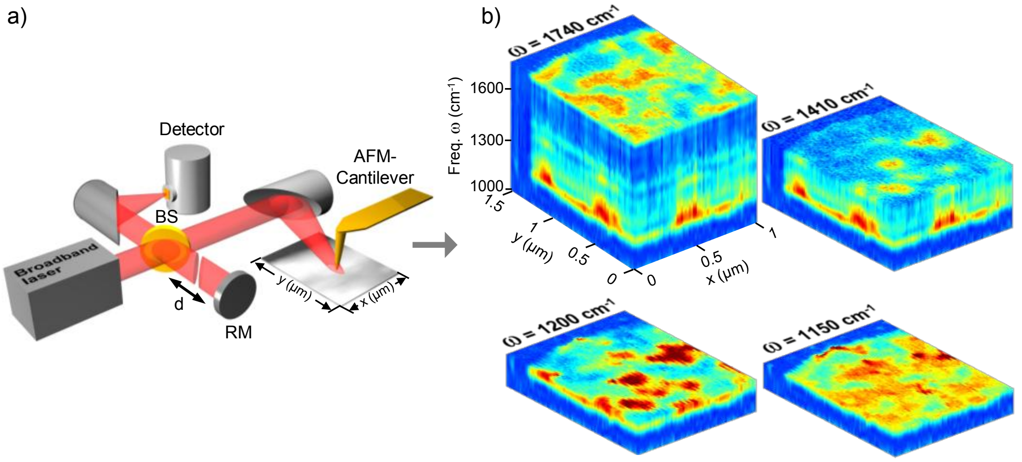

Fig. 1. (a) Nano-FTIR setup. (b) Hyperspectral data cubes cut at different frequencies ω, showing infrared absorption.

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INVITED

“Organometallic Nanoparticles: How They Came to Be, Where They Are Now and Where Will They Go”

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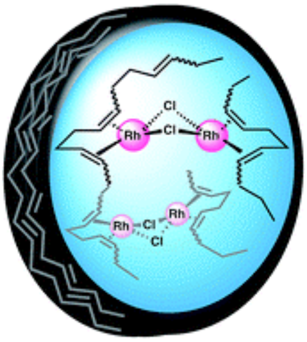
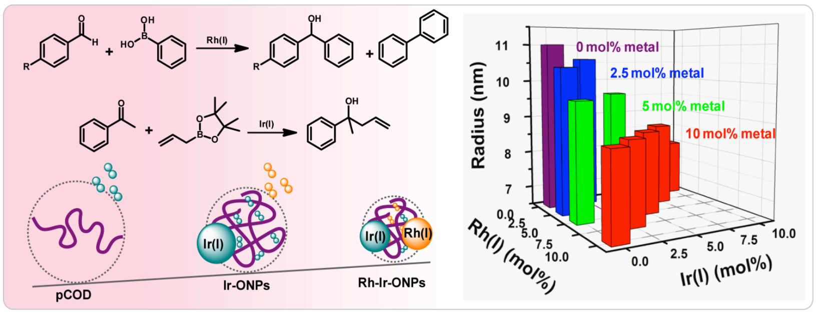
My talk will summarize recent developments in our group dealing with the synthesis of organometallic nanoparticles (OMNPs) and how they came to be by a serendipitous finding (as usually recurrent in chemical research). The OMNPs are based on the affinity of 1,5-hexadiene units in ROMP derived polycyclooctadiene, or even simple polybutadiene, to chelate various transition metals. I will detail the synthesis, characterization and some of the properties of these materials, including the effect of the polymer microstructure on the binding kinetics. Applications in catalysis will also be presented.





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Recent advances and opportunities in SCNPs

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Linear polymer chains can be folded to individual SCNPs, *i.e.* single-chain nanoparticles, by means of different intra-chain cross-linking procedures.[1] SCNP formation is reminiscent to protein folding into functional bioentities, although current synthetic methods lack the perfection of protein folding to highly-efficient and selective enzymes. Two limiting SCNP molecular architectures can be obtained depending on the synthesis route and the amphiphilic nature of the SCNP precursor employed: *Type I* or sparse morphology, resembling the morphology of intrinsically disordered proteins[2] and *Type II* or globular morphology, mimicking the typical 3D conformation of enzymes.[3]

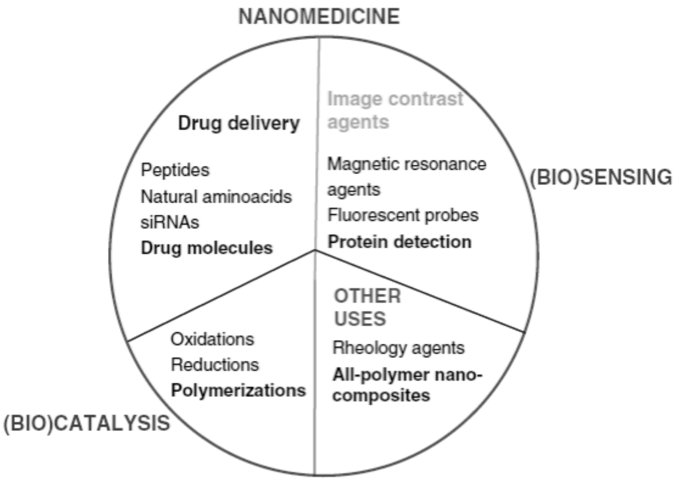

Figure 1. Main applications of single-chain polymer nanoparticles.[4]

Type I-SCNPs show the presence of multiple locally compact, but accessible, sites / cavities / zones, so-called "local pockets", whereas *Type II*-SCNPs display, on average, a single pocket of larger size. The possibility to anchor, either temporally or permanently, active species like drugs or catalysts onto these local pockets paves the way to the use of SCNPs in a variety of nanomedicine and catalysis applications, among other several uses[4] (see Figure 1).

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Structure and Dynamics of Single-Chain Nano-Particles in Solution

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Single Chain Nano-Particles (SCNPs) are polymeric soft nano-objects consisting of uni-macromolecular chains collapsed to a certain degree by means of intramolecular bonding. The usual techniques for SCNP formation result in sparse, non-globular morphologies in solution [1] that are very similar to those displayed by bio-macromolecules, in particular by intrinsically disordered proteins (IDPs) [2]. IDPs and SCNPs are intrinsically polydisperse both in size and topology [3]. The similarities between SCNPs and IDPs suggest using SCNPs as model to mimic bio-macromolecules in different environments and situations. The ultimate goal of biomolecular studies is to understand the behavior of these entities in realistic situations (cellular environment), where macromolecular solutions are highly concentrated. The effective nano-confinement induced by crowders can dramatically modify biological function, through changes in the conformation and dynamics of the macromolecules respect to diluted in vitro conditions [4]. We could thus exploit the analogies found between SCNPs and IDPs to address the essential question of the change of the properties of biomacromolecules in increasingly crowded environments.

We present an investigation, by combining small-angle neutron scattering (SANS) and coarse-grained molecular dynamics (MD) simulations, on the conformational properties of single-chain nano-particles (SCNPs) in crowded macromolecular solutions. By using linear chains as crowders, SANS shows a crossover from almost unperturbed SCNP conformations in dilute conditions toward a continuous collapse of the macromolecule with increasing crowding. This collapse starts when the total concentration of the solution reaches the value of the overlap concentration of the pure SCNP solutions. MD-simulations prove the generalizability of these experimental findings and extend them to the case when the SCNPs themselves are used as crowders -a situation which in real systems leads to unavoidable formation of aggregates, as shown here by SANS and DLS. In addition, we have investigated the dynamics of SCNPs in dilute solution by means of Neutron Spin Echo. The dynamic structure factor reveals a large impact of internal crosslink on the macromolecular mobility manifested as a high internal friction [5]. This is another striking resemblance with intrinsically disordered proteins [6].

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Dextran-based single-chain nanoparticles: synthesis, characterization and application in imaging

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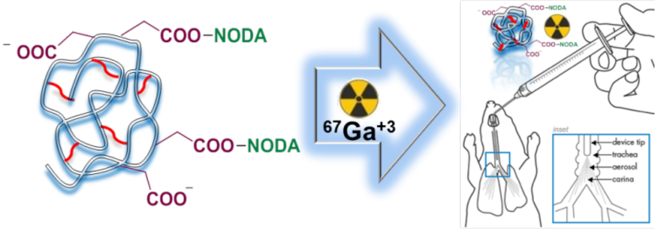
The development of synthetic strategies for the controlled compaction of single polymer coils into unimolecular single-chain polymer nanoparticles (SCPNs) is the object of intense research.[1] New mimetics of biomacromolecules, such as proteins, can be obtained and applied in different fields including nanomedicine.[2-5] Our group has developed an environmentally-friendly strategy to easily obtain water-dispersible SCPN.[3,5] In addition, our synthetic approach allows further functionalization to be easily achieved, offering the possibility to anchor active species for applications in nanomedicine. The aim of the present work is to present the design, synthesis and characterization of novel DXT-SCPNs and their functionalization in order to incorporate radioactive elements for nuclear imaging.

Dextran-based single-chain nanoparticles (DXT-SCPNs) smaller than 20 nm were prepared by controlled addition of a dithiol cross-linker to the methacrylate-functionalized dextran precursor polymer (poly DXT-MA) in aqueous media and mild conditions (r.t., no catalysts, air atmosphere).[5] The size of DXT-SCPNs obtained was studied using traditional nanoparticle characterization techniques (DLS, TEM and GPC-SEC). More interestingly, the effect of the amount of cross-linker on the intramolecular compaction of the precursor polymer into SCPNs and the resulting morphology of the final SCPNs were demonstrated using Taylor dispersion analysis (diffusion coefficient, ViscosizerTD) and SEC-AF4 techniques.

Incorporation of carboxylic acids on the surface of the DXT-SCPNs was easily achieved in aqueous buffer. Further functionalization of the DXT-SCPNs with the well-known chelating agent NODA was achieved by amidic coupling and the gamma emitter ^{67}Ga was thus incorporated by chelation. The acquisition of single-photon emission computed tomography (SPECT) images immediately after aerosol administration of the radiolabelled DXT-SCPNs to healthy rats allowed the *in vivo* assessment of the regional lung deposition of our SCPNs.



In summary these SCPNs may find use as modular nanoplatforms integrating soft nanoparticles and active imaging agents for imaging-based diagnostics.

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Acknowledgements

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 604434.

Turning on Fluorescence in Single-Chain Polymer Nanoparticles *via* Aggregation-Induced Emission

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Aggregation-induced emission (AIE) dyes are special type of molecules that emit strong fluorescence only when they are immobilized or aggregated. Recently, AIE-based fluorescent nanomaterials have drawn considerable attention due to their potential use in biological imaging, especially in cell imaging. Even if during the last years several types of AIE-based nanomaterials have been developed[1], to date, AIE dyes have never been immobilized within single-chain polymer nanoparticles (SCNPs). In this work we have combined the possibilities offered by AIE molecules with the huge potential of SCNPs to construct innovative fluorescent soft nanoparticles. We have defined a methodology to encapsulate hexaphenylsilacyclopentadiene (HPS) dye molecules into water-soluble poly(oligo(ethylene glycol) methyl ether methacrylate-*co*-2-acetoacetoxy ethyl methacrylate)) (P(OEGMA-*co*-AEMA)) SCNPs in order to obtain water-based fluorescent nanoparticles. In addition, we have studied the effect of different parameters, such as the molecular weight of the polymer precursor or the amount of HPS, on the final size and fluorescence properties of the nanoparticles. Finally, HPS dye was also encapsulated into micelles formed by P(OEGMA-*b*-AEMA) block copolymers and results were compared with the ones obtained with the fluorescent SCNPs.

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INVITED

Soft Nanoparticles as Novel Additives in Nanocomposites: Control of Nanoparticle Morphology and Nanocomposite Dynamics

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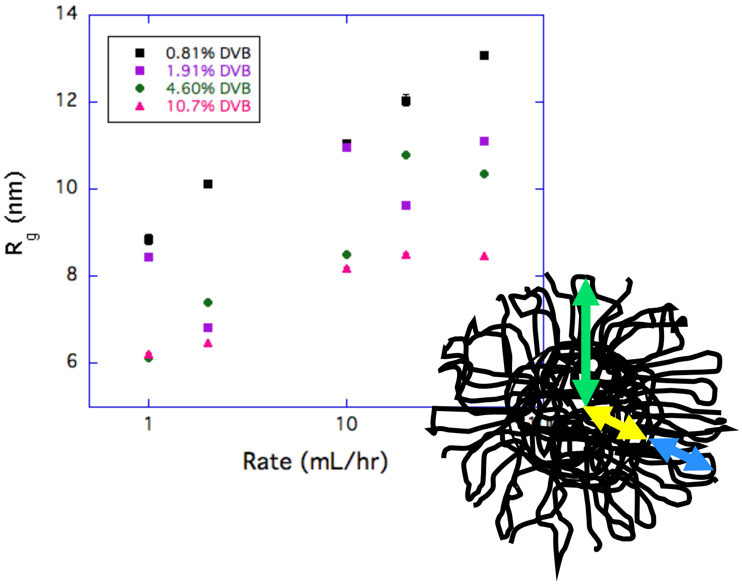
Interest in single chain, soft nanoparticles has increased significantly due to their use as model self-assembling macromolecules, and as novel additives in polymer nanocomposite. Our group and others have shown that the addition of soft single chain nanoparticles can dramatically influence the dynamics of neighboring polymer chains and that the motion of these soft nanoparticles mimics the diffusive behavior of nanogels, where the transport of the nanoparticle relies on the cooperative motion of neighboring linear chains. In this talk, we will report small angle neutron scattering results that correlate synthetic conditions of the soft nanoparticle to their internal morphology. This analysis provides characterization of the individual nanoparticle molecular weight, the radius of the crosslinked core, the thickness of the fuzzy interfacial layer, and provides insight into methods to control the overall topography of the soft nanoparticle. The dynamics of both the polymer chain and these soft nanoparticles themselves in a polymer nanocomposite has also been studied and correlated to the morphological characteristics of the nanoparticle. These



results provide fascinating insights that can be utilized to more accurately predict the impact of soft nanoparticles on the ultimate properties of their mixtures with polymer matrices.

TUESDAY, MARCH 20

INVITED

Computer simulations of single-chain polymer nanoparticles: synthesis routes and crowding effects

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By means of computer simulations, we design and investigate different protocols leading to polymeric single-chain nanoparticles (SCNPs) with specific structures and different properties in solution. On one hand the analysis of the conformations of SCNPs synthesized in good solvent reveals that they share basic ingredients with intrinsically disordered proteins (IDPs), as topological polydispersity, sparse conformations, and compact local domains [1]. Unlike in the case of linear macromolecules, crowding leads to collapsed conformations of SCNPs resembling those of crumpled globules, at volume fractions (about 30%) that are characteristic of crowding in cellular environments. Our results for SCNPs - a model system free of specific interactions - propose a general scenario for the effect of steric crowding on IDPs.

On the other hand, dense solutions of globular SCNPs obtained via, e.g., solvent-assisted routes, exhibit soft caging, reentrant diffusivity and weak dynamic heterogeneity. This constitutes a realization, in a real macromolecular solution, of the static and dynamic anomalies predicted by models of purely repulsive ultrasoft particles. Quantitative differences depend on the specific SCNP degree of compressibility, i.e. on the specific synthesis route adopted, as well as on the intrinsic topological polydispersity [2]. This new class of soft colloids opens up the possibility of getting insight into the mechanisms of diffusion in crowded environments, as well as to draw new strategies for tailoring rheological properties of polymer based nanomaterials.

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INVITE
D

Simulation and theory of equilibrium swelling of single chain nanoparticles.

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Cross-linking a single polymer chain with itself can lead to soft nanoparticles with well-defined properties. We study such single-chain nanoparticles (SCNP) obtained by cross-linking of flexible chains in good and in poor solvents using Monte Carlo simulations. We also derive a theoretical framework which describes consistently the behavior of single-chain nanoparticles, and which relates the cross-link topology with the structure and the swelling behavior of the nano-particles. We show that SCNP obtained by cross-linking in poor solvents preserve their shape during swelling in good solvents only if a critical cross-linking probability per monomer is reached. In this case the Flory−Rehner model describes the swelling of SCNP. Otherwise SCNPs swell into non-compact structures. Cross-linking in good solvent leads to non-compact structures up to the highest degree of polymerization we have considered in our simulations. For the case of non-compact swelling, or unfolding of the structure during swelling, we obtain a good theoretical description using a mean-field model by taking into account the cross-linking topology by means of the connectivity matrix of the cross-linked chain. The crossover between the two regimes can consistently be described using a scaling argument. In particular we show that the cross-over from the a compact network-like particle to a fluffy chain-like structure scales with a characteristic crosslink probability per monomer $f_c \sim N^{-2/3}$, where N denotes the number of Kuhn segment in the precursor chain.

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Swelling Behavior of Single-Chain Polymer Nanoparticles: Theory and Simulation
Macromolecules **50**, 7410 (2017)

Properties of Single-Chain Nanoparticles under Shear Flow and Synthesis under Crowding Conditions

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Single-chain nanoparticles (SCNPs) are an emergent class of soft nano-objects of molecular size of 5-20 nm, resulting from the purely intramolecular cross-linking of the reactional functional groups of single polymer precursors. A growing interest is being devoted in recent years to develop a SCNP-based technology with multiple applications in catalysis, nanomedicine, or rheology, amongst others. To this end, we need good control over the size and shape of SCNPs, as well as a deeper understanding of their behaviour under non-equilibrium situations, such as shear flow.

SCNPs are generally synthesized at high dilution (~ 1 mg/mL) to avoid intermolecular cross-linking and aggregation. The stochastic nature of the cross-linking process leads to a large topological polydispersity of the resulting SCNPs. However, due to the self-avoiding character of the precursor chains, their distribution is dominated by sparse topologies. It has been shown recently [1] that indeed the size R of SCNPs scales with the polymerization degree N as $R \sim N^{\nu}$, with an average exponent of $\nu \approx 0.5$, which is rather different from the limit of globular spherical objects ($\nu = 1/3$).

Inspired by previous work that found a collapse of SCNPs to crumpled globular conformations under crowding conditions [2], we propose that employing crowding conditions directly at synthesis will lead to more compact conformations of the resulting SCNPs. By means of molecular dynamics simulations, we investigate the formation of SCNPs in the presence of purely steric crowders of equal topology as the precursors. Apart from probing the effect of increasing crowding density on the shape and size of the resulting SCNPs, we also look at the effect of different topologies (linear chains and rings). We find that in the case of linear precursors, the structure of the resulting SCNPs is weakly affected by the density at which the synthesis is performed. However, crowding has significant effects if ring precursors are used: Higher concentrations lead to the formation of SCNPs with more compact and spherical morphologies. Such SCNPs retain in the swollen state (high dilution) the crumpled globular conformations adopted by the ring precursors in the crowded solutions [3].

Furthermore, we investigate the behavior of single SCNPs – synthesized under dilute conditions - in the presence of homogeneous shear flow by employing a multiscale simulation approach, that combines multi-particle collision dynamics for the solvent with standard molecular dynamics for the monomers. We study how the topology of each individual SCNP affects its change in shape as well as its dynamic response to increasing shear rates. Although we find different responses, none of the topologies approach the limits of tumbling or tank-treading found previously for, e.g., linear chains or vesicles, respectively.

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Dynamics of Internally Functionalized Dendrimers

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Dendrimers, being hyperbranched polymers of very high symmetry, are promising materials in fields of chemistry, biology, and medicine.[1] Recently, new types of such symmetric macromolecules have been synthesized;[2] among them the internally functionalized dendrimers are of a particular interest. We analyze the dynamics of such functionalized dendrimers that have additional functional units, which do not branch out further.

The dendrimers are modeled in the framework of semiflexible treelike polymers,[3] where their architecture is described through beads connected by springs (bonds) and semiflexibility is taken into account by constraining the bonds' orientations. The dynamics of the structures is modeled by a set of Langevin equations.

We show that the additional functional beads clearly leave their fingerprints in the relaxation spectrum of the structures. We find a group of relaxation times which does not exist for homogeneous dendrimers.[4] In particular, this part of the spectrum leads to an additional process in the intermediate frequency region of the imaginary part of the complex dielectric susceptibility. Thus, the presence of functional beads is clearly manifested in the local dynamics of the non-functionalized segments on intermediate frequencies.[4]

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INVITED

The Nano-Bio World: Lessons from In-Silico Experiments

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NanoBio interactions lie at the core of biological function and their understanding promises to bring major advances in different areas such as healthcare and the environment. It is also strongly believed that such an understanding will allow the design of new synthetic platforms able to reproduce or interface with biological systems in a seamless way. In this talk I will present our work on the interaction of nanoparticles with biological membranes. Emphasis will be placed on the important discoveries that we have come across from performing multiscale simulations of such nanomaterials. In particular, I will present our work on understanding how nano particles interact with lipid bilayers, and how a recently discovered class of nano particles is able to translocate across bilayers without disrupting the membrane. Such nanoparticles essentially behave as “nano chamaleons” altering on-the-fly their surface chemistry to mimic that of the membrane and fuse with it. The origins of such behavior, as well as the fusion pathway by which such nanoparticles enter cells will be presented. Of particular interest along this fusion process is the discovery of a new pathway to translocate charge across the membrane in a timescale of seconds, not hours. Furthermore, we have also discovered that these nanoparticles can mimic several different functions performed by membrane proteins such as fusion proteins and signaling proteins, opening new possibilities in delivering drugs, as well as serving as “artificial membrane proteins” themselves. To finalize I will give a perspective on exciting new avenues of research in this area.

Title : Design of patchy polymers: biomimetic self-knotting chains

Authors: Ivan Coluzza, Francesca Nerattini, Chiara Cardelli, Luca Tubiana, Valentino Bianco, Peter van Oostrum, Barbara Capone, Erik Reimhult, Christoph Dellago

Abstract:

We present a novel theoretical framework within which we are able to design new experimentally realisable materials with tuneable self-assembling properties.

Our work takes inspiration from the results obtained with our recently developed protein coarse graining procedure, namely the “Caterpillar” model [1,2]. Based on these results we postulated the “maximum valence principle" (MVP). According to the MVP in order for a generalised bead-spring system to be designable and foldable, it is sufficient for the chain to have a sequence of different isotropic interactions combined with directional interactions that further constrain the configurational space. Based on this principle we introduced an optimal set of modular sub-units, and the definition of a design procedure necessary to choose a string of the units that once bonded into a chain will spontaneously fold to a specific target structure [3-6].
We show that such structures can be highly non-symmetrical and posses interesting topological properties fully controllable by the sequence of beads along the chain.

Biomimetic patchy polymers represent a considerable step forward in the synthesis of novel materials, because they are based on a limited alphabet of particles that can be reused and assembled, practically, in an infinite number of combinations. Artificial modular self assembling systems such as this one are not available at the moment and the one we propose is the first of this kind.

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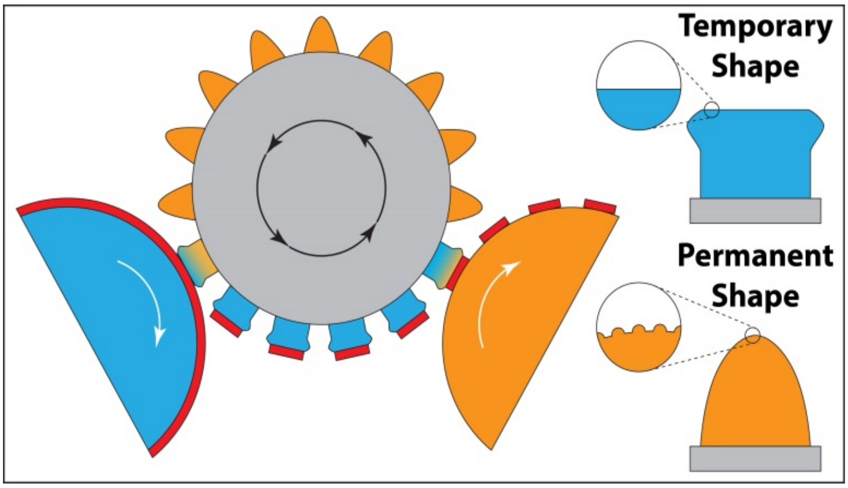
INVITED

Hydrogen Bonding Elastic Networks and Shape-Memory Contact Printing

Mitchell Anthamatten, University of Rochester

An overview of our efforts to understand the relevance of H-bonding within condensed polymer melts and elastomers will be presented. Reversible association of hydrogen-bonding side-groups of linear polymers and crosslinked elastomers sharply influences dynamic mechanical behavior, giving rise to valuable viscoelastic, shape-memory and self-healing properties. However, association of side-groups is often unpredictable owing to the presence of polymer backbones, chain entanglements, and to nanophase segregation between of molecular parts. We will describe how H-bond strength, density, and type affect glass formation and viscoelastic behavior. A series of poly(butyl acrylate) copolymers were prepared with targeted amounts of acrylic acid, aminopyridine, and ureidopyrimidinone comonomers. The polymers behave as rheologically simple melts, however distinct differences are observed between copolymers containing "weak" versus "strong" hydrogen bonding side-groups. H-bond association is also evident in water-swollen hydrogels. Materials containing both permanent (covalent, irreversible) and dynamic (reversible) net points will be discussed as well. Remarkably, H-bonding interactions can effectively stabilize mechanically-strained states leading to a new type of shape memory polymer. Unlike conventional shape-memory polymers, these elastomers containing dynamic bonds lack a well-defined shape-recovery temperature. The transient shape-memory of H-bonding networks can be integrated into micro-features on a surface to influence traction forces. Such adhesion changes can assist in pattern transfer of features, offering a new methodology: shape-memory assisted contact printing.



TITLE Progressive Supramolecular Polymerization of Complementary Subcomponents

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ABSTRACT The development of materials to meet the future demands of society in a sustainable manner depends upon fundamental advancements in chemical sciences and soft-matter technologies. In this regard, supramolecular chemistry provides a unique opportunity to develop distinct (macro)molecular systems covering a wide spectrum of length scales and with emerging properties such as recyclability, facile processability and enhanced resilience. A major limitation in the field, however, has been access to dynamic systems that are capable of operating in aqueous media. A promising approach to address such challenge is the host-guest chemistry of specific macrocyclic molecules including cucurbiturils and cyclodextrins on account of their unique properties. These include the possibility of producing strong and selective heterodimers (also heteroternary adducts) in water in a rapid and facile manner, their responsivity to external stimuli and inertness to biological interfering agents. Such is the focus of this talk, which will show how nanoscale assemblies of different morphologies, including fibers and platelet-like aggregates, can be prepared in a one-pot fashion from complementary components (host and guest molecules) of sub-nanometer dimensions. The binding of selected guest compounds to the host molecule cucurbit[8]uril triggers a step-wise self-assembly process. Initially, a rapid host-guest recognition event yields semiflexible polymer chains. At a later point, aggregation takes place, which results in the formation of low-curvature anisotropic aggregates. Such self-assembly process exhibits unique features on account of tight binding and, most likely, crystallization-assisted self-assembly and will ensure a variety of applications. For example, supramolecular fibers may become ideal materials as drag reducers or viscosity modifiers in applications where small molecule degradable systems are preferred over traditional high molecular weight polymers materials.

INVITED

Supramolecularly-Associated Polymers: From Structure to Dynamics

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Forschungszentrum Jülich GmbH
Jülich Centre for Neutron Science (JCNS-1) and Institute for Complex Systems (ICS-1)

The knowledge of the behavior and the control of reversible supramolecular links are key elements in the design of novel well-processing materials and dual networks making use of covalent and non-covalent crosslinking in adaptive or self-healing materials. For this purpose we study the hydrogen bonding in melts of model polymer systems on both microscopic and macroscopic scale. The systems under investigation consist of low T_g backbones, randomly functionalized either with thymine groups in combination with chains that are telechelically-functionalized with diaminotriazine groups or with urazole groups. The functional groups associate through triple resp. double hydrogen bonding. In the hetero-complementarity case these groups ideally lead to transiently-branched but homogeneous architectures of the comb-type, whereas in the self-complementary case transient networks result. No unspecific aggregation was observed unlike in [1-4]. The interaction of the hydrogen bonding groups and final structures were studied by Small Angle Neutron Scattering (SANS) directly in the polymer melt exploiting hereby the different scattering lengths of hydrogenous and deuterium sections. For the Xray studies (SAXS) the contrast between the polar groups and the polymer chain was sufficient. The formed comb-like block copolymer was described by means of a Random Phase Approximation (RPA) formalism, adapted for the intrinsic dynamic equilibrium between bonded and non-bonded components. The average aggregation number of arms could be measured and the association constant $K_{\text{Thy-DAT}}$ could be evaluated in the bulk as a function of the temperature. The combination of rheology and dielectric spectroscopy confirmed the transiently-branched, hierarchically relaxing comb polymer and could firmly determine the lifetime of the bonds. In the self-complementary case the non-directed urazole linkages allowed to validate quantitatively a recent theoretical model basing on random compact walks of sticker molecules. Both studies gave rise to intrinsically responsive materials and show interesting properties for advanced processing and self-healing applications.

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INVITED

From complexation of oppositely charged polyelectrolytes to supramolecular bottlebrushes and gels

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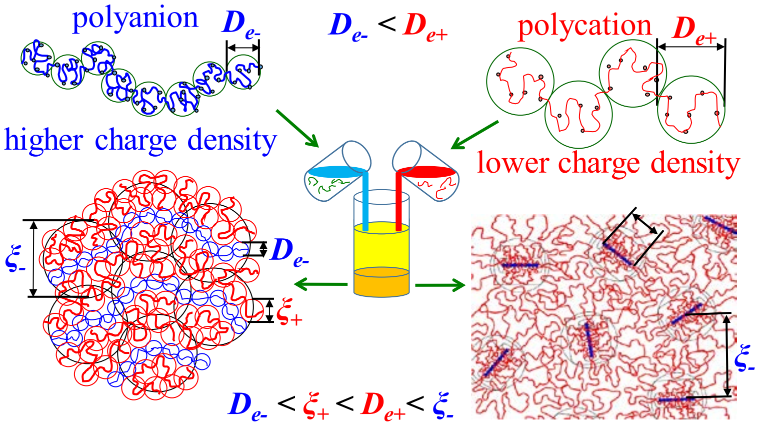
Sergey Panyukov
P. N. Lebedev Physics Institute, Moscow, Russian Federation

We develop a scaling model of coacervates formed by oppositely charged polyelectrolytes. The intramolecular electrostatic interactions in dilute polyanion or polycation solutions are characterized by the so-called electrostatic blobs, D_- or D_+ respectively. Polyelectrolyte sections of electrostatic blob size repel neighboring sections of the same chain with electrostatic energy on the order of thermal energy kT. Conformations of polyanion or polycation chains in their respective dilute solutions with no added salt can be described as stretched arrays of their corresponding electrostatic blobs of size D_- or D_+. The structure of a coacervate formed upon mixing polyanion and polycation solutions depends on the electrostatic attraction between oppositely charged polyelectrolytes balanced by the short-range repulsion. In the symmetric case with $D_- = D_+ = D_e$ the coacervate is a dense packing of these electrostatic blobs with neighboring oppositely charged blobs of size D_e attracting each other with energy on order kT. This attraction is stabilized by short-range non-electrostatic repulsion with energy on the same order kT between all chain sections of size D_e. In the asymmetric case with stronger polyanion intramolecular repulsion $D_- < D_+$ the structure of coacervate is more complex. The highest energy in the coacervate is intramolecular repulsion within polyanions that on scales smaller than inter-polyanion distance $\xi_- \approx D_-^{\nu/2} D_+^{1-\nu/2}$ keeps their conformation of stretched arrays of electrostatic blobs of size D_-. Here ν is the scaling exponent describing interactions of uncharged chain section with solvent (ν=1/2 in theta solvent and ν=3/5 in good solvent). Conformation of polyanions in coacervate is similar to their conformation in semidilute polyanion solutions with the same correlation length ξ_- – stretched array of electrostatic blobs D_- on length scales smaller that correlation length ξ_- and a random walk of chain sections on larger length scales. Weaker charged polycation adsorbs on stronger charged polyanion forming a screening “coat” around it analogous to a semidilute solution of uncharged polymers. The electrostatic attraction of polycations to polyanions is the second largest energy in coacervate and is balances by the short-range repulsion between sections of polycations of size ξ_+ with energy on the order of thermal energy kT. This attraction slowly decreases in strength with increasing distance from polyanion within the polycation “coat” resulting in a slow (logarithmic) decrease of coat concentration. The inter-polyanion correlation length ξ_- is determine by the length scale at which the polycation “coat” compensates the polyanion charge. This compensating polycation coat of coacervates plays the role of counterions of semidilute polyanion solution with the essential difference of negligible translational entropy and important short-range inter-polycation repulsion balancing electrostatic attraction and reducing osmotic pressure of coacervates to zero. The order of interactions from strongest to weakest corresponding from the order of length scales from the smallest to the largest is $D_-<\xi_+<D_+<\xi$_. Opposite charges form bound pairs and larger ionic clusters at higher strength of electrostatic interactions resulting in a formation of first mixed ionic/screening coat coacervate and eventually at the highest electrostatic strength – ionic network of comb/bottlebrush-like polyanion backbones with polycation loops and bridges. We describe how supramolecular assemblies of oppositely charged molecules can form similar bottlebrushes and networks.



Density and Temperature Dependence on Supramolecular Polymer Morphology of Polyethylene and Polybutylene Glycols with Hydrogen Bonding Ends

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19-21 March, 2017

Rheological properties of supramolecular polymers depend on their structure including the size, the number, and the topology of aggregates. A polymer with a hydrogen-bonding motif at both ends is one widely used precursor to build the supramolecular polymers. Due to the complex interplay between chain stiffness, hydrogen bonding interaction, polarity along a chain, 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 with associating ends in wide range of temperature and density using a coarse-grained (CG) model via stochastic approximation Monte Carlo method. Our CG force field is constructed by Boltzmann inversion of the probability distributions of all-atom polymer conformations. This work especially focuses on the transition from ring- to chain-dominated phases since the ring contaminant in a ring-linear blend melt is known to significantly influence its rheology. The phase diagram in a density-temperature space displays two transition lines. One is the first-order transition from ring- to chain-dominated phase and the other is the second-order transition from chain-dominated to free chain phase. For supramolecular polymers at melt-like density it turns out that chain aggregates dominate over rings at room temperature.

Neutron Spin-Echo Spectroscopy for a Molecular View on Supramolecular Chain- and Association- Dynamics

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Using neutron spin echo (NSE) spectroscopy molecular insight in the space and time evolution of the dynamics of supramolecular polymer ensembles are obtained. In particular the influence of chain breaking on the scattering functions is shown and serves as and indicator for the bond breaking rate. The studying was performed on an ensemble of linearly associating telechelic poly-(ethyleneglycol) carrying triple H-bonding end-groups, we show that H-bond breaking significantly impacts the mode spectrum of the associates. The breaking affects the mode contributions and not the relaxation times as was assumed previously. NSE-spectra directly reveal the so far intangible H-bond lifetimes in the supra molecular melt and demonstrate that for both the microscopic and the macroscopic dynamics of the supramolecular ensemble the instantaneous average of the molecular weight distribution governs the systems response at least as long as the Rouse picture applies.

[1] M. Monkenbusch, M. Krutyeva, W. Pyckhout-Hintzen et. al, PRL **117**, 147802 (2016)

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Using dynamic covalent bonds to fabricate high-performance bio-inspired composites

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Conventional processes commonly used for the fabrication of composites with high volume fraction of reinforcing elements usually require the infiltration of monomers that are subsequently consolidated into a continuous polymer matrix. [1-3] Such infiltration step often leads to long processing times and limits the choices of materials that can be used as soft polymer matrices. In this work, we present a new infiltration-less route in which a co-suspension of organic/inorganic powders is assembled through vacuum-assisted magnetic alignment and the resulting composite consolidated by uniaxial hot pressing at temperatures slightly above the topological transition of the dynamic polymer network. Formation of a strong and stiff continuous phase during hot pressing is enabled by employing polymers that contains dynamic covalent bonds as crosslinking points in their molecular network. We demonstrate that the fabrication process of highly-loaded composites can be significantly simplified using such infiltration-less approach (Figure 1a). As illustrated in Figure 1b, incorporation of 50% in volume of reinforcing platelets within dynamic polymer matrices enhances the flexural modulus and flexural strength by 14-fold and 3-fold as compared to the pure polymer, reaching values as high as 13 GPa and 90 MPa, respectively. These results demonstrate the potential of using infiltration-less routes to enable the fabrication of high-performance platelet-reinforced composites using high volume fraction of reinforcing ceramic particles and polymer matrices that cannot be infiltrated otherwise by other conventional processing methods.

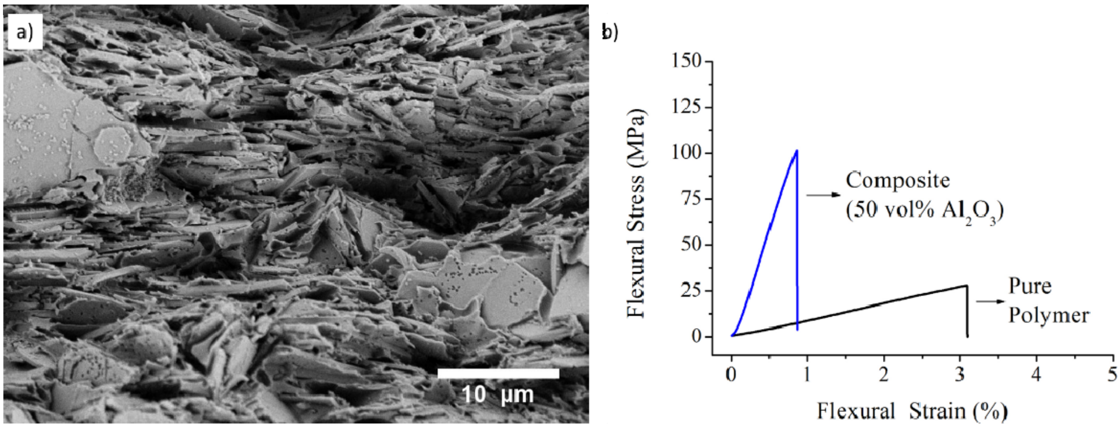

Figure 1. a) Scanning electron microscopy image showing the fractured surface of a composite containing 50 vol% of reinforcing ceramic platelets embedded within a continuous dynamic polymer matrix . b) Representative stress-strain curves comparing the mechanical performance in flexural mode between the pure dynamic polymer matrix and the its composite containing 50 vol% of aligned reinforcing ceramic platelets.

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WEDNESDAY, MARCH 21

INVITED

Strain stiffening in self-assembled biomimetic hydrogels

Rint P. Sijbesma

Soft tissues exploit the interplay between covalent and non-covalent interactions to balance dynamics and mechanical strength. The cellular matrix is well-known to rely on self-assembly to effect motility, but at the same time it can stiffen dramatically in response to strain, thereby protecting from catastrophic deformation.

The design of biomimetic strain-stiffening materials has great potential in tissue engineering due to the wide scope of structural tuning of synthetic molecules as opposed to natural proteins. However, the development of synthetic strain stiffening materials has been limited to covalent polymers and therefore one of the most fundamental aspects of biological hydrogels – their dynamic nature has been overlooked.

Here, we present hydrogels composed of self-assembling amphiphilic molecules that form long, semi-flexible fibers, whose morphology can be covalently fixated. Co-assembly with molecules having reactive groups allows for the controlled introduction of crosslinking points along the fiber contour which can be then cross-linked to obtain strain-stiffening gels mimicking the mechanics of filamentous protein networks.

In the lecture I will explore the effect of covalent fixation on the strain-stiffening properties, and I will show how the fibers can be cross-linked with a thermally responsive PNIPAM polymer to give networks that stiffen under strain as well as by heating.

INVITED

Computer Simulation Studies of Linear and Nonlinear Dynamics and Rheology of Supramolecular Polymer Networks Formed by Associating Telechelic Chains

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We present hybrid molecular dynamics/Monte Carlo simulations of supramolecular polymer networks (SPN) formed by unentangled and weakly entangled telechelic chains with sticky end monomers of finite functionality. The kinetics of sticky monomer association, the topological structure and the resulting dynamic and rheological behavior of the supramolecular systems are studied as a function of the sticker bonding energy and the parent polymer chain length in equilibrium and under shear and planar extensional flows.

In equilibrium percolated transient networks are formed above a threshold bonding energy around $4.3k_BT$. At high bonding energies ($\geq 10k_BT$), the majority of the stickers are fully reacted and the fraction of open stickers is less than 1%. We find the dynamical and rheological behavior of such strongly associated supramolecular networks are dominated by a partner exchange mechanism in which the stickers exchange their associated partners, and so release the imposed topological constraints, through the association and disassociation of sticker clusters. The characteristic time of the partner exchange events grows exponentially with the bonding energy and is up to 2 orders of magnitude longer than the average sticky bond lifetime. As a result, three relaxation regimes, namely the initial Rouse, intermediate rubbery and terminal relaxation regimes, can be clearly distinguished in the stress and chain end-to-end vector relaxation functions. A phantom chain hopping model based on the microscopic understanding is proposed to describe the chain relaxation dynamics in the supramolecular networks.

The nonlinear behavior of strongly associated supramolecular polymer networks under shear and extensional flows are determined by the interplay between the flow-induced chain segment reorientation, nonlinear chain stretching and reduction in the fraction of associated stickers. As a result, there is a clear transient strain hardening or extensional hardening in the startup flows due to the non-Gaussian chain stretching, but a shear and extensional thinning in the steady state due to the decrease in the number of elastically active strands with the increase of flow rate. The transient shear viscosity is found to reach its maximum value at an earlier time than that required to reach the maximum chain stretching, but the transient planar extensional viscosity and the chain stretching reach their plateau or maximum values almost simultaneously. This can be understood from the different dependence of the diagonal and off-diagonal components of the stress tensors on the chain stretching force and orientation vectors.

Structure and association behavior of supramolecular linear polymer melt

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Supramolecular polymerization has emerged as an attractive alternative for the synthesis of functional polymer materials with tailored properties (e.g. self-healing). In particular, supramolecular polymers based on hydrogen bonds are effective, stable and allow the tuning of bonding strength through the choice of specific hydrogen bond matching pairs [1].

In this work we present a combined analysis of small-angle neutron scattering (SANS), linear rheology and pulsed field gradient (PFG) NMR spectroscopy experiments on the supramolecular association and chain structure of well-defined telechelically modified poly(ethylene glycol) (PEG) in the bulk [2]. PEG was functionalized with directed heterocomplementary triple hydrogen-bonding end-groups, thymine (Thy) and diaminotriazine (DAT). The polarity of the backbone polymer is comparable to the end groups and avoids clustering of the groups basing on energetic arguments. Their linear association behavior in the ideal melt state was investigated on the microscopic/molecular level as a function of temperature. By means of a selective labeling scheme, which should ideally lead to the formation of alternating hydrogeneous-deuterated building block sequences if the hydrogen bonding reaction is exclusively heterocomplementary, we showed that the Thy−DAT association is dominant and a Thy−Thy homoassociation is approximately three times less probable. Latter nondirected association gives rise to a considerable amount of random-copolymerization without affecting seriously neither the macroscopic melt viscosity nor the diffusivity of the supramolecular associates. From the q-dependence of a multiblock RPA structure factor, the linear association in the melt is confirmed. Furthermore, this diffusion and viscosity study reveals simple Rouse dynamics of supramolecular polymer chains with molecular weight much larger than the entanglement mass M_e. The Rouse-like dynamics of long supramolecular chains indicates short lifetime hydrogen bonds of the end groups. Our results are in excellent agreement with the related polycondensation theory.

Recent NSE measurements performed on the same system showed the dynamics of the supramolecular chains is Rouse-like at the timescale up to 200 ns controlled by hydrogen bond breaking on the NSE time scale. Moreover, based on the static results [2], the dynamical NSE experiment directly reveal hydrogen bond lifetime, which is one of the key parameters determining macroscopic properties of supramolecular polymer melts [3].

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Single chain model for unentangled associating polymers

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[1] Department of Chemical Engineering, Universidad Politécnica de Madrid, Spain
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Supramolecular networks can be used as sacrificial components in tough physical double networks, as synthetic matrices for tissue engineering, as injectable biomaterials for minimally invasive surgery and in self-healing soft materials. In most of these applications it is very important to understand the mechanical properties of the materials, as well as to predict the diffusion of the network forming constituents. Recent experiments have revealed that a variety of unentangled associative polymers with different architecture (linear and branched) and different nature of the associating interaction (associative protein domains and metal-ligand bonds) exhibit unexplained anomalous diffusion. Recently, we have introduced a new coarse-grained molecular model of star-shaped unentangled associating polymers that explains the observed anomalous behavior and reveals three basic mechanisms of molecular diffusion: caging dynamics, walking diffusion and molecular hopping, all of which depend strongly on polymer concentration, arm length, and the association/dissociation kinetics. The apparent superdiffusive scaling observed in the experiments results primarily from molecular hopping, which prevails over walking when the kinetics of attachment are much slower than the relaxation time of dangling strands. Simple scaling relationships are derived to identify the range of rate constants over which this behavior can be expected. The formation of intramolecular associations or loops in the network promotes this superdiffusive scaling by reducing the total number of arms that must detach in order for a hopping event to occur. In addition, the effect of the number of arms on the diffusivity and relaxation modulus is also studied, the model is extended to different architectures, and the impact of the model predictions on practical aspects like the gel erosion of self-healing time are explored.

Investigation on the local dynamics in supramolecular polymer structures using Magnetic Particle Nanorheology

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Supramolecular polymers consist of macromolecules that exhibit intermolecular non-covalent (dynamic) bonds, typically based on hydrogen bonds, hydrophobic association, π-stacking, complex formation, or ionic interactions. If these interactions interlink different chains, macroscopic transient network structures are obtained. In these systems, the self-assembly and the usually rich reversible dynamics of the supramolecular motifs opens access to new functional materials, potentially exhibiting stimuli-responsiveness and adaptability, thereby making them suitable candidates for self-healing materials.

To get an enlightening insight into the structure and dynamics of supramolecular polymer networks, approaches via nanorheology are promising. Here, tracer particles with size of a few nanometers are used to extract local dynamic rheological information on the matrix by analyzing their translational or rotational motion. In our previous works, it was shown that active *Magnetic Particle Nanorheology* (MPN) is successful to extract local dynamic properties of complex matrixes such as the frequency-dependent loss and storage moduli, the viscosity, or characteristic relaxation times.[1,2] In short, by this method, magnetically blocked nanoparticles are excited by an AC magnetic field, and the complex magnetic susceptibility data is evaluated to result in the desired dynamic information of the investigated matrix.

In this contribution, we report on an application of this method to transient networks of star-shaped polymers with metal coordinating arm-end groups, with a view to investigate the binding strength and network topology systematically as a function of variable transition metal ions. For this purpose, star-shaped PEG precursors are end-group functionalized with terpyridine moieties that are then complexed to different metal ions such as Mn^{2+}, Zn^{2+} and Co^{2+}.[3] The strength and connectivity of the polymer networks are characterized by evaluation of bond lifetimes, complex formation constants, mesh sizes, as well as viscoelastic properties.

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Chemistry Department

Institute of Physical Chemistry

Influence of Polymer Polarity and Association Strength on the dynamics of supramolecular model Polymers

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In the recent decade, materials capable of responding to internal or external stimuli including the ability to autonomously self-heal became an important field of applied material science. One of the most prominent examples are supramolecular polymers [1], which combine the overall good chemical–mechanical properties of polymers with the inherent dynamic reversible supramolecular interactions. Amongst others, hydrogen bonding (H-bonding) represents such a reversible mechanism [1].

The presented work focused on the self-assembly via H-bonding of polymer model systems in the bulk. Investigations were done on polymers with a polypropylene oxide (PPO) and polyethylene oxide (PEO) backbone, respectively. Diaminotriazine (Dat) and Thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy) as functional end groups. Different experimental techniques such as SAXS and rheology were combined to study in particular the correlation between the backbone polarity and the different end-groups association strength, as Upy is highly self-associative in comparison to the heterocomplementary pair Thy/Dat.

Results on the structure show that PEO and PPO functionalized with the pair Thy/Dat self-assemble as linear chains [2], while both polymers functionalized with Upy show a sphere particle morphology corresponding to a Upy rich-phase, indicating phase separation. The corresponding Upy cluster radius is larger on PPO than on PEO due to the lower chain hydrophobicity. This means that the bonding energy was affected by the different polarities. Moroever, an analysis on the dynamical behavior indicates not only the formation of a supramolecular structure, but also a dramatic change from predominantly viscous as observed for Thy/Dat groups [2,3].

A.B. acknowledges DFG for a research grant (BR5303)

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Overcharging and reentrant condensation of thermoresponsive ionic microgels

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The complete understanding of the mechanism driving colloid-polyelectrolyte complexation still represents a fundamental problem of great interest in soft matter. Polyelectrolyte adsorption onto oppositely charged surfaces represents the core of this problem and a number of theoretical studies, using different approaches, have been published on this subject[1-3].

During the past few decades, colloid-multivalent ion complexation has been investigated by using either model systems, such as solid hard colloids[4], soft colloids of biological interests[5], or hydrophilic globular proteins[6]. In all cases two distinct but intimately related phenomena accompany and drive the self-assembly, i.e. charge-inversion and reentrant condensation.

Although these phenomena have been observed in a variety of polyelectrolyte-colloid mixtures in different conditions, in all previously reported works the charge density on the colloid surface was fixed, or, at least, it could not be changed without changing the ionic strength or the pH of the suspending medium. Thermoresponsive microgels, whose synthesis is initiated by charged groups and is equivalent to an end-group functionalization, are characterized by a thermodynamic volume phase transition (VPT) that gives the opportunity to tune finely the adsorption of polyelectrolytes simply by changing temperature. Indeed, by controlling the particle volume, the VPT affects dramatically the microgel charge density and hence the polyelectrolyte adsorption.

We investigated the complexation of thermoresponsive anionic poly(Nisopropylacrylamide) (PNiPAM) microgels and cationic ε-polylysine (ε-PLL) chains. By combining electrophoresis, light scattering, transmission electron microscopy (TEM) and dielectric spectroscopy (DS) we studied the adsorption of ε-PLL onto the microgel networks and its effect on the stability of the suspensions. We show that the *volume phase transition (VPT) of the microgels triggers a large polyion adsorption*. Two interesting phenomena with unique features occur: a temperature-dependent microgel overcharging and a complex reentrant condensation. The latter may occur at fixed polyion concentration, when temperature is raised above the VPT of microgels, or by increasing the number density of polycations at fixed temperature. TEM and DS measurements unambiguously show that short PLL chains adsorb onto microgels and act as electrostatic glue above the VPT. By performing thermal cycles, we further show that polyion-induced clustering is a quasi-reversible process: within the time of our experiments large clusters form above the VPT and partially re-dissolve as the mixtures are cooled down.

Finally we give a proof that the observed phenomenology is purely electrostatic in nature: an increase of the ionic strength gives rise to the polyion desorption from the microgel outer shell.

By showing that the VPT of thermoresponsive ionic microgels can be employed to trigger polyion adsorption and tune reentrant microgel condensation, our work lays the foundation for a groundbreaking strategy to tune electroadsorption ruled by temperature and that can be employed in a variety of fields spanning wastewater and soil remediation, nanoencapsulation of small charged nanoparticles, and selective drug delivery.

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Nanostructured, thermoresponsive and biocompatible hydrogels based on Poly(2-oxazoline)s for 3D bioprinting and biofabrication

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In recent years, many attempts have been made to develop improved biocompatible gels for many different applications such as 3D bioprinting, in-gel printing or injectable drug depots. The placement of different cells within biomaterials into spatially defined structures, better known as 3D bioprinting, finds increasing interest among engineers, scientist and clinicians.[1] However, the understanding of the nanostructured arrangement is necessary to use the full potential of such materials and to be able to tailor their properties. Recently, we reported on a shear thinning, biocompatible and thermoresponsive bioink candidate.[2] Small angle neutron scattering (SANS) experiments herein suggest a bi-continuous sponge like structure of the polymer supramolecular network at elevated temperatures with characteristic domain sizes and correlation lengths between 50 and 350 Å differing from other thermoresponsive polymer-based hydrogels.[3] Therefore, these gels can be seen as potential one component nanocomposites for biomedical applications.

Our aim is to develop and establish a highly adaptable and biocompatible hydrogel platform based on amphiphilic Poly(2-oxazoline)s (POx), a prominent member of pseudo-polypeptides. In the last decades, they have been intensely investigated especially for biomedical applications.[4] These materials have to fulfill various requirements like consistent quality, sufficient quantity and customizable biological and physical properties.[5]

Here we report on our approach to investigate the influence of the polymer composition on the hydrogel nano- and microstructure by SANS. Furthermore, we want to correlate the findings with the macroscopic behavior of the gel and hereby create a better understanding of our hydrogel system.

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ABSTRACTS

Poster contributions

P1

Ambient temperature non-covalent curing of waterborne polymer dispersions: Polyelectrolyte interpolymer complexation

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Sustainable development is one of the great challenges of the 21st Century. Without any doubt, this complex issue must be addressed at many different levels, including prolonging the lifetime of equipments, vehicles and infrastructures. Corrosion is major factor reducing these lifetimes. Use of protective coatings is one of the ways to prolong them and contribute to the sustainability. The protective coatings are usually produced by solution polymerization using high amounts of solvents that increases substantially the released amount of volatile organic compound (VOC) in the atmosphere. On the one hand, the sustainable development requires eliminating or at least severely reducing, the use of solvents in coatings. On the other hand, this confronts the new legislative in EU about reducing of the emissions of solvents. As an answer to this, waterborne polymer coatings have been developed. However, their performance still is not on the level of solventborne ones, mainly due to the particulate nature of polymer aqueous dispersions that influence negatively formation of continuous protective films.

In this project the interest is focused on the improvement of the quality of the protective films by investigation of the interparticle complexation induced by strong and irreversible ionic interactions between the individual latex particles during film formation process, in order to develop an ambient temperature non-covalent curing method of waterborne coatings. The interactions is planned to be induced between differently charged polymer particles and triggered by variation of pH of the polymer dispersions prior to final film preparation.

The challenge of this work relies in the fact of combining particles of same composition and opposite charges. An ionic complexation was formed combining negatively charged latex, synthesized using small amount of sodium styrene sulfonate functional monomer, and positively charged latex, synthesized using 2-(dimethylamino)ethyl methacrylate functional monomer. To control the complexation process, the charge density on the polymer particles, the extent of the electric double layer and the size of the particles were studied and their effect on the mechanical strength, chemical and thermal resistance and barrier properties of the ionically complexed protective coatings were determined.

P2

Unfolding luminescent polymers in flow

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Many fascinating examples of mechanosensitive materials can be found in nature. For example, the von Willebrand factor (VWF) protein unfolds in response to increased extensional flow rates in the bloodstream near sites of injury in the blood vessel wall, allowing the protein to bind to platelets and thereby form a clot to prevent further blood loss. In the past fifteen years, chemists in the burgeoning field of mechanochemistry have sought to create polymeric materials with similarly specific and productive responses to mechanical force, such as stress-sensing and damage repair. Whilst great progress has been made in this area, many of these mechanoresponses have high threshold forces for activation (~nanonewtons), and the use of ultrasound sonication to study their activation under force has limited the development of a more quantitative, mechanistic understanding of these phenomena.

We present our preliminary results on the unfolding of luminescent, self-associating polymers at relatively low forces (~piconewtons) in a flow-focusing cross-slots microfluidic device, which permits precise control over the applied extensional strain rates. The polymers are functionalised with terpyridines (Tpy) as pendant side-chains. In the presence of Eu^{3+} ions, pendant terpyridines bind to the metal ion, forming luminescent, force-sensitive complexes and simultaneously inducing the folding of the polymer chain. Under extensional flow we expect the polymers to stretch and unfold, as terpyridine ligands dissociate from the metal ion. The resulting decrease in luminescence intensity across the flow-focusing junction can be monitored in situ with a camera, providing a map of the polymer's mechanochemical response to different forces in a single image. Furthermore, we envisage that force-induced unbinding of supramolecular groups would be useful for triggering further mechanoresponsive behaviour.

P3

INCORPORATION OF HYDROGEN BONDING FOR HIGH PERFORMANCE WATERBORNE COATINGS

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Over the past few decades, with the growing awareness of the need to limit the negative environmental consequences of the chemical industry, there has been a drive towards increasing the sustainability of many industrial processes. In polymer science, for example, the traditional solventborne processes are gradually being phased out and replaced by polymerizations in dispersed media, where the use of solvents is avoided by using water as dispersant. Although the market for waterborne coatings is increasing, there are certain commercial applications, such as automotive coatings, which still remain mainly in the realm of solventborne polymers due to their superior mechanical properties. Thus, in order for the complete replacement of solvent based polymers in coatings products, the development of high performance waterborne coatings is needed.

To give a solution to this problem and improve the mechanical properties of the film, a chemical-covalent crosslinking reaction is often carried out after the film formation process. The problem is that most of the crosslinking reactants are toxic [1]. In this work we explore the possibibility of crosslinking the system with physical interactions based on interpolymer complexation. Such interactions are widely used to provide structural integrity to natural polymers. One of the most powerful and interesting interactions is hydrogen bonding where a electron-donor group like oxygen interacts with an electron acceptor group[2-5].

Here, emulsion polymerization of MMA-BA has been performed utilizing polyvinyl alcohol has as a steric emulsifier. This leads to formation of particles with substantial number of hydroxyl groups grafted to the surface. Upon film formation, hydrogen bonding between the PVA units leads to films of increased mechanical strength. In order to maximize the hydrogen bond interactions additional hydrogen bonding acceptors such as poly (vinyl pyrrolidone) are added and the effect on mechanical properties is explored.

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P4

Studying the role of bridging ligands in organometallic nanoparticles

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Polymers are one of the most important classes of materials in the modern life. The demand for specific and controlled properties of polymers has encouraged the development of various techniques for their controlled polymerization and cross-linking. In recent years the field of single chain organic nanoparticles has attracted the interest of the scientific community due to their promising applications and ease of synthesis.[1] By coordinating metals to a binding polymer matrix under dilute conditions, intramolecular cross-linking could be achieved, leading to single chain collapse and the formation of organometallic nanoparticles (ONPs).[2]

Polycyclooctadiene (PCOD) and polybutadiene (PBD) can coordinate rhodium chloride dimer complexes, leading to a change in the polymer's properties; *e.g.* its conductivity.[2] Our current study focuses on the effect of the anion bridging ligands in the electronic properties of the ONPs. This work may enable a deeper understanding of the conductivity mechanism and furnish a series of new ONPs with potentially novel applications.

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P5

Effect of the nanofiller topology on the dynamics of all-polymer nanocomposites.

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Nanoparticles are added to polymeric matrices to form nanocomposites with enhanced mechanical, optical or electrical properties. The performance and macroscopic properties of polymer nanocomposites depend on the dynamics of the polymer matrix affected by the filler topology and concentration. However, despite the efforts, the confinement effects of nanoparticles on polymer motions are still not fully understood, especially in the case of soft nanoparticles.

Recently, a notable dilation of the entanglement tube diameter in polyethyleneoxide (PEO) linear chains when mixed with poly(methylmethacrylate) (PMMA) single-chain nano-particles (SCNPs) was observed[1]. In that case, however, the two components have a large dynamic asymmetry, being the PMMA SCNPs frozen compared to PEO.

To isolate the topology effect we studied systems where the polymer matrix and the filler have the same chemistry (polyisoprene) and thus are dynamically symmetric. We have done a systematic variation of the filler topology and concentration and probed the polymer matrix chain dynamics using a combination of PFG-NMR and dielectric spectroscopy. We used two star polymers with 8 and 18-arms and compared them to the linear case of the same size, i.e. 2 arms. Our results show an acceleration of the linear matrix chain mobility with the additive concentration, but less so with the additive topology.

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P6

Laterally-resolved properties of all-polymer composites thin films by high-resolution atomic force microscopy.

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The synthesis and physical characterization of soft polymeric nano-objects, in particular, single-chain nanoparticles (SCNPs) has been an intensively discussed area in recent years.[1] These new materials have shown interesting and challenging physical properties as well as potential future applications, not only as stand-alone objects but also as components of multiple advanced systems. For example, combining SCNPs with conventional polymers gives rise to all-polymer nanocomposites, *i.e.* systems where both the matrix and the load have a polymer nature.[2] These systems would benefit from advantages as ambient temperature and solution processing, which ultimately could lead to an enhanced dispersion of the load while retaining the usual interesting properties of polymers (*e.g.* flexibility, resistance to corrosion and low cost). Moreover, considering that SCNPs are soft nano-objects, it becomes interesting to evaluate from a basic point of view how different could be all-polymer nanocomposites from conventional polymer/inorganic nano-filler composites and from traditional polymer blends. In this work, we present the preparation and in-depth characterization of all-polymer nanocomposites thin films by high-resolution Atomic Force Microscopy (AFM). Our nanocomposites thin films were prepared by spin coating onto silicon wafers a polymer solution containing poly(vinyl methyl ether) (PVME), acting as the matrix, and SCNPs of poly(methyl methacrylate-*co*-2-(acetoacetoxy)ethyl methacrylate) P(MMA-*co*-AEMA) at different weight ratios. Using AFM measurements with ultra-sharp probes, we were able to study the lateral dimension of individual SCNPs in the nanocomposite, when the content of SCNPs was less than 5 wt%. As the content of SCNPs was increased, we observed how aggregation developed (Figure 1). The dimensions of the nano-objects were determined from the AFM images using a custom built code that allowed automatization and fast processing. Finally, besides the interesting topological information obtained by standard AFM measurements, we also explored the mechanical and electrical contrast in these nanocomposites by using PeakForce Tapping (PF-QNM) and nanoDielectric Spectroscopy (nDS), respectively.

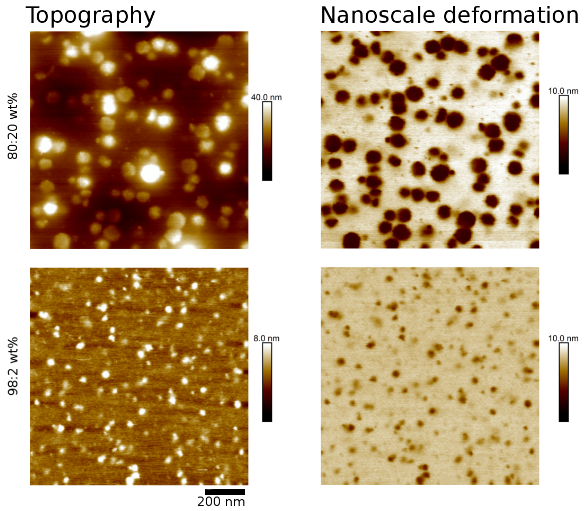

Figure 1. Topography (left column) and nanoscale deformation (right column) of two all polymer nanocomposites thin films. PVME:P(MMA-*co*-AEMA) SCNP weight ratios are indicated for each case. The 200 nm dimension bar applies for all images.

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P7

Quantification of different contributions to dissipation in various rubber nanoparticle composites

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A detailed understanding of the molecular origin of dissipation in rubber nanoparticle composites is important for an effective optimization of such materials for tire tread applications. An approach to resolve and quantify different contributions to dissipation based on strain sweeps measured at different temperatures is presented. Recently, a modified Kraus equation has been successfully used to approximate loss modulus (G'') data depending on strain amplitude (γ).[1] This approach allows an interpretation of the molecular origin of different contributions to dissipation. Results for different filler rubber combinations are presented. The used model quantifies strain-dependent dissipation $G''(\gamma)$ curves generally well. Interestingly, the results support the finding that the filler network in highly filled rubber nanoparticle composites shows visco-elastic properties as concluded earlier from reinforcement data $G'(\gamma)$.[2,3] There are obviously three main origins of dissipation in rubber nanoparticle composites related to different contributions in $G''(\gamma)$ data:(i) deformation of intact glassy bridges in filler network dominating at small strain amplitudes, (ii) breaking of glassy rubber bridges dominating at intermediate strain amplitudes, and (iii) contributions to dissipation which are filler network independent remaining at very large strain amplitudes1. The dependences of these three dissipation contributions on filler content and temperature confirm nicely the existence of glassy rubber bridges in the filler network. The consistency of this physical picture with experimental findings for dissipation and reinforcement in many rubber nanoparticle composites seems to be a strong evidence for the validity of the underlying assumptions.

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P8

The new high-resolution neutron spin-echo spectrometer (J-NSE) at MLZ

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Neutron spin echo (NSE) spectrometers provide the ultimate energy resolution in quasi-elastic thermal and cold neutron scattering spectroscopy. High-resolution means the extension of the Fourier-time (τ) up to the regime of μs. The extension of the resolution towards larger Fourier-times critically depends on the reduction of the field-integral inhomogeneity down to the some ppm over the neutron paths within the used beam and detection cross sections and solid angles. The combined effect of the main precession devices (solenoids) and present correction coils is the limiting factor. We could bias this hardship by optimizing the shape of the precession magnetic field - and thus reducing the intrinsic inhomogeneity introduced by the cylindrical main solenoids - guided by the original idea of Zeyen [1] and by new semi-analytical approach [2] combined with numerical optimization. Following this strategy a set of new magnetic coils has been designed for the neutron spin-echo spectrometer (J-NSE) at MLZ. The new coils are fringe field compensated with zero net dipole moment, superconducting solenoids. We present here the first results on the performance of the new J-NSE: Due to the lower intrinsic field inhomogeneity in the beam area the amount of required correction is reduced by over a factor 2, as expected from numerical calculations. At the end of the installation phase in autumn 2017 the new performance of the J-NSE already allowed to use a magnetic field integral of 1.0 Tm corresponding to a Fourier-time of 100 ns at λ 8 Å. Together with an increased wavelength-band from 10% to 20% we will strive for 500 ns at 15 Å in the first neutron cycles of 2018. The improved resolution may be used to reach larger Fourier-times and/or to benefit from significant intensity gains by the use of shorter neutron wavelength from a given τ. Thus the new J-NSE will meet the needs to look into the microscopic dynamics of functional polymers, and more, with a much enhanced new quality.

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Magnetodielectric effect in compliant magnetorheological elastomers

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Magnetorheological elastomers comprise micrometer-sized iron particles dispersed in compliant elastomer matrices. The ferromagnetic filler particles can rearrange in external DC magnetic fields. This leads to significant modulation of their physical properties. Magnetorheological properties are the well-known example. We have experimentally studied magnetodielectric properties of magnetorheological elastomers in stepwise time-varying dc magnetic fields at room temperature. It is found that imposition of magnetic field significantly increases both the effective lossless permittivity of these composite materials as well as their effective conductivity. These magnetodielectric effects are more pronounced for larger concentrations of soft-magnetic filler particles and softer elastomer matrices. The largest observed relative change of the effective dielectric constant in the maximum magnetic field of about 0.6 T is of the order of 1000%. In particular, we measured the largest, to the best of our knowledge, magnetodielectric effect in polymer based composite materials at room temperature. The largest observed absolute change of the loss tangent is approximately 0.8. The transient response of the magnetodielectric effect to step magnetic-field excitations is studied in dependence on the step amplitude. A significant hysteresis of the magnetodielectric effect on the externally applied magnetic field is observed. The findings are attributed to the rearrangement of ferromagnetic filler particles in external magnetic fields.