

CPP 1: Nanoparticles and Composite Materials I

Time: Monday 9:30–13:30

Location: H34

Invited Talk

CPP 1.1 Mon 9:30 H34

Rich variety of polymer dynamics in nanocomposites — ●GERALD JOHANNES SCHNEIDER — Jülich Centre for Neutron Science, Forschungszentrum Jülich, Outstation at FRM2, Lichtenbergstraße 1, 85747 Garching

Nanocomposites show prominent features in comparison with their respective ingredients. These manifest themselves in a broad range of applications ranging from reinforced rubber to energy related devices. Despite their importance, the respective molecular mechanisms are very complex and remain poorly understood. Particularly this is the case, when attractive interactions of the chains with the surfaces are involved, and e.g. immobilization of chains within an adsorbed layer in the close vicinity of the particles is expected.

In a step toward a better understanding of nanocomposites, the talk illuminates the microscopic polymer dynamics exploiting the high spatial and time resolution of neutron scattering experiments. Using neutron spin echo and time-of-flight spectroscopy, a broad dynamic range – from the segmental relaxation up to the center of mass diffusion of the polymer chains – is explored. This allows for an accurate and detailed picture of the influence of the interaction strength on the chain dynamics and in particular on the molecular motion within the interphase, i.e. in the small layer of adsorbed chains.

CPP 1.2 Mon 10:00 H34

Investigation of particle-induced confinement effects on free volume in PEP-Silica Nanocomposites — ●CHRISTIAN OHRT¹, TÖNJES KOSCHINE¹, STEPHAN HARMS¹, KLAUS RÄTZKE¹, FRANZ FAUPEL¹, LUTZ WILLNER², and GERALD SCHNEIDER³ — ¹Materialwissenschaft-Materialverbunde, Universität Kiel, 24143 Kiel — ²Jülich Centre for Neutron Science 1 and Institut for Complex Systems Forschungszentrum Jülich, D-52425 Jülich — ³Forschungs-Neutronenquelle Heinz Maier-Leibnitz 85747 Garching Germany

PPolymer nanocomposites are widely used due to improved properties compared to pure polymers. Some of the improved properties can be a result of a so called interphase, a part with a modified free volume, resulting from the interaction between nanoparticles and polymer or they can be a consequence of the restricted mobility of polymer chains due to the nanoparticles, usually termed confinement. Positron annihilation lifetime spectroscopy (PALS) can be used to investigate the influence of nanoparticles in a polymer matrix on the free volume. We analysed the change in free volume due to confinement in a weakly repulsive system consisting of poly(ethylene-alt-propylene) (PEP) with different molecular weights and silica nanoparticle concentrations by PALS and thermal properties by DSC. DSC showed no change in glass transition temperature, whereas PALS showed an increase in o-Ps lifetimes for low temperatures and a decrease for high temperatures with increasing filler concentration, which can be explained by a mixing rule of o-Ps lifetimes of the pure constituents. Thus no interphase is formed and the dynamics of the polymer are not affected by confinement.

CPP 1.3 Mon 10:15 H34

An unusual viscosity behaviour of the nanocomposites — ●MARTA LUNGOVA, WIM PYCKHOUT-HINTZEN, and DIETER RICHTER — Forschungszentrum Jülich, Germany

Many polymers have been modified by adding the suitable nanoparticles resulting in a higher modulus and viscosity. However, some systems showed the opposite effect [1]. The reduced viscosity was also observed on the system of linear PEO with PEO-grafted silica nanoparticles where in a similar way, the size of the nanoparticles is in the range of the tube diameter of the bulk polymer. The viscosity reduction becomes more evident with increasing Mw but crosses-over to the opposite, reinforcement effect, for high Mw of the matrix. This is apparently a function of the ratio between the radius of the nanoparticle and the Rg of the bulk polymer.

The SANS experiment (ILL, France and FRM II, Germany) showed that the polymer shell of the nanoparticle tends to be more swollen in the matrix of low Mw whereas with increasing Mw of the bulk the shell collapses and particles separate from the matrix resembling rigid particles with the typical reinforcement effect. The dynamics of the bulk polymer measured by NSE (ORNL, USA) were slowed down in a system with higher viscosity.

This work is a part of the European project DYNACOP supported

by Marie Curie Action.

[1] Mackay M. et al, Nat.Mater., 2003, 762-6.

CPP 1.4 Mon 10:30 H34

Structural investigation of polymer-metal nanocomposite films using time-of-flight grazing incidence small angle neutron scattering — ●YUAN YAO¹, EZZELDIN METWALLI¹, JEAN-FRANCOIS MOULIN², MARTIN HAESE-SELLER², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany — ²HZ Geesthacht at FRM II, Lichtenbergstr.1, 85748 Garching, Germany

Soft polymer films with embedded magnetic nanoparticles have attracted immense interest for wide potential applications in functional nano-devices. Well-aligned highly-oriented hybrid films of polystyrene(deuterated)-block-polybutyl methacrylate symmetric block copolymer are used to guide polystyrene grafted maghemite nanoparticles within the polymer matrix. Parallel and perpendicular lamella structured films, embedded with different nanoparticles concentrations (from 0 up to 15 wt%), are prepared by spin coating process. Both surface and buried structural information of the metal-polymer hybrid film are gained using TOF-GISANS. The nanoparticles are positioned in one polymer domain and a distortion of the lamella structure evolves with increasing nanoparticle concentration. The nanoparticles arrangement and possible particle assemblies within the polymer matrix is influenced by the lamella orientation.

CPP 1.5 Mon 10:45 H34

Structure and morphology of hybrid thin films for non-volatile memories — ●JIRÍ NOVÁK¹, GIULIA CASULA², RUPAK BANERJEE¹, CHRISTIAN FRANK¹, ALEXANDER GERLACH¹, KATHARINA BROCH¹, PIERO COSSEDDU², ANNALISA BONFIGLIO², and FRANK SCHREIBER¹ — ¹Universität Tübingen, Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen — ²University of Cagliari, DIEE, Piazza d'Armi, 09123 Cagliari, Italy

Recently, hybrid thin films comprising metal nanoparticles (NPs) embedded in an organic semiconductor (OSM) matrix became attractive as constituents of non-volatile resistive memories [1,2]. The control of the structure of hybrid films via growth parameters is of crucial interest to tailor the electric properties of the memory elements.

We present a structural study on the formation of Al NPs atop thin organic films (small molecule OSM N1400 by Polyera). The films were prepared via thermal evaporation on Si substrates for various organic film thicknesses and at various Al growth rates. The combined GISAXS, X-ray reflectivity, and AFM study shows that the Al cluster distance and size depend mainly on the organic layer morphology controlled by its thickness. On the other hand, the Al NPs layer structure is weakly sensitive to the Al deposition rate. This is in a strong contrast to, e.g., growth of Au on top of DIP layers, where rather Au growth rate and substrate temperature play a crucial role [3].

[1] L.D. Bozano *et al.*, *Adv. Funct. Mater.*, **15**, 1993 (2005); [2] Liping Ma *et al.*, *Appl. Phys. Lett.*, **82**, 1419 (2003); [3] F. Schreiber, *Phys. Stat. Sol.*, **201**, 1307 (2004);

CPP 1.6 Mon 11:00 H34

In situ SAXS measurements on the imbibition of polymer melts into aligned CNT arrays — ●MARINA KHANEFT¹, LUCAS BECKER¹, THORSTEN HEINLEIN², HERMANN TEMPEL², JÖRG J. SCHNEIDER², and BERND STÜHN¹ — ¹Experimentelle Physik kondensierter Materie, Technische Universität Darmstadt — ²Eduard Zintl-Institute für Anorganische und Physikalische Chemie Technische Universität Darmstadt

We present results on the imbibition of the polymer into aligned carbon nanotube (CNT) arrays and describe the filling kinetics of the polymer. The aligned CNT structures were prepared by CVD method. We considered two types of CNT arrays: well ordered CNTs prepared within porous alumina template (PAOX). CNTs have a diameter around 40 nm and are arranged on a hexagonal lattice as were the pores of PAOX template. A second kind of CNT array consists of randomly arranged tubes with small diameter (<10 nm) grown on a quartz surface by catalytic CVD approach. The imbibitions process of polystyrene (PS) into the CNT array is followed with time-resolved small angle X-ray scattering (SAXS). We observed polymer infiltration into tube inte-

rior and interstices between CNTs. For CNT array grown in PAOX template, filling kinetics inside and outside tubes can be analysed separately. Infiltration only in inner part of CNTs can be achieved by polymer filling of CNTs situated in PAOX. Interstices between tubes can be filled after removing the template. We found the filling kinetics demonstrates two well separated processes: the formation of a precursor film and completion of the imbibition process.

15 min. break

Invited Talk CPP 1.7 Mon 11:30 H34
Photonic structures based on responsive nanoparticle/microgel hybrids — ●THOMAS HELLWEG — Universität Bielefeld, Physikalische und Biophysikalische Chemie (PC III), Universitätsstr. 25, 33615 Bielefeld, Germany

Microgels based on responsive polymers can be combined with metal nanoparticles leading to materials with responsive optical properties (1). Ordering of nanoparticles into assemblies which are well-defined on the nanoscale and at the same time of macroscopic dimensions is one of the most pressing challenges in materials science. If particles are aggregating in a random fashion, often uncontrolled electronic coupling effects occur, which result in less defined electronic, optical or magnetic properties or in a complete loss of the specific nanoparticle effects and a re-entrance of bulk material properties. Creating ordered nanoparticle structures is one means of avoiding such uncontrolled coupling. In this context hybrids of microgels and nanoparticles are offering interesting pathways for 2 and 3 D assembly (2,3). The present contribution will describe the properties of these hybrids and discuss strategies of their assembly.

- (1) Karg, M. und T. Hellweg, *Current Opinion in Coll. Interf. Sci.*; 14, 438–450, 2009
- (2) Müller, M., M. Karg, A. Fortini, T. Hellweg und A. Fery, *Nanoscale*, 4:2491–2499, 2012
- (3) Karg, M., T. Hellweg und P. Mulvaney, *Adv. Func. Mater.*; 21:4668–4676, 2011

CPP 1.8 Mon 12:00 H34
Photoinduced phase transitions in gold-microgel hybrids — ●SARAH T. TURNER, STEFAN WELLERT, and REGINE VON KLITZING — Stranski Laboratory, Dept. of Chemistry, TU Berlin, Germany

The ability to reversibly switch between a collapsed and expanded state in response to an external stimulus makes hybrid microgels attractive for applications such as sensoric and drug delivery systems. We studied the photoinduced light-to-heat conversion and consequent volume phase transition of hybrid gold-microgels. In order to use such hybrid systems as a potential barrier in polyelectrolyte multilayers, details about the degree of shrinking related to the gold loading and laser intensity are required. An optimal gold nanoparticle concentration per microgel was found to exist, as too low a concentration does not allow enough heat formation to induce a volume phase transition and too high a concentration hinders the full swelling of the microgel below the lower critical solution temperature. The distribution and loading of the gold nanoparticles is investigated via transmission electron microscopy and the change in the plasmon resonance of the gold nanoparticles upon microgel shrinking is investigated by temperature-controlled UV-Vis absorption spectroscopy. The plasmon resonance frequency of the gold nanoparticles was excited by one laser (532 nm) while a second was used to simultaneously measure dynamic light scattering (633 nm) by blocking the scattering signal from the first laser with an optical filter.

CPP 1.9 Mon 12:15 H34
Wrinkle-Assisted Self-Assembly of PNIPAM Coated Nanostars as SERS Platforms for Sensing of PAHs in Gas Phase — MAREEN MUELLER, ●MORITZ TEBBE, NICOLAS PAZOS-PEREZ, and ANDREAS FERY — Department of Physical Chemistry II, University of Bayreuth, 95440, Bayreuth, Germany

Plasmonic nanoparticles are excellent candidates for their potential use in microelectronic, optical and biomedical applications. Their electromagnetic behaviour is highly dependent on their specific particle size, shape, and surrounding environment. Various different synthetic methods allow us to fine tune the particle shape and size thus, the materials properties. However, the lack of capability to form reproducible organized structures is still a challenge to solve in order to use them in new technologies. Template-assisted self-assembly is a versatile platform to generate particle assemblies in high quality and with high reproducibil-

ity. Compared to lithographically prepared templates, controlled surface wrinkling on elastomers is an alternative approach to produce structured surfaces with periodicities in the range of nanometres. The use of wrinkled surfaces as templates for nanoparticle alignment via printing, results in highly ordered nanoparticle arrays. In this work a new surface enhanced Raman spectroscopy (SERS) platform based on the extended organization of poly-N-isopropylacrylamide (pNIPAM)-coated gold nanostars over large areas into parallel lines is presented.[1] This system yields high and homogeneous SERS intensities, and simultaneously traps PAH traces, e.g. pyrene, as pollutants from the gas phase. 1. Mueller, M., et al., *Langmuir*, 2012. 28(24): p. 9168-9173.

CPP 1.10 Mon 12:30 H34
effective interactions in polymer-nanoparticle composites and their resulted phase structures — ●XUEZHENG CAO¹, HOLGER MERLITZ^{1,2}, and JENS UWE SOMMER^{1,3} — ¹Leibniz Institute für Polymerforschung Dresden, D-01069 Dresden, Germany — ²Department of Physics and ITPA, Xiamen University, Xiamen361005, P.R.China — ³Technische Universität Dresden, Institute of Theoretical Physics, D-01069 Dresden

We have studied polymer induced effective interactions between nanoparticle-nanoparticle and nanoparticle-substrate using molecular dynamics simulations. To analyze the entropic depletion potential, the polymer matrix above overlap concentration is regarded as a melt of concentration blobs. Convincing numerical evidence for the universal validity of scaling theory to describe the depletion potentials over a broad concentration range was found, and the directly measured depletion forces were well described with a scaling model in which the attraction between particles is caused by the depletion of concentration blobs. Adding enthalpic attraction between polymer-nanoparticle or polymer-nanoparticle can prevent the depletion effect. A thermodynamically stable dispersion of nanoparticles within polymer solution is verified to be possible by tuning the attraction strength between polymer and nanoparticle. We show that nanoparticles have a higher degree of order close to the substrate by increasing system temperature. This can be understood by scaling arguments showing the interplay between correlation blob and adsorption blob of polymers.

CPP 1.11 Mon 12:45 H34
Conformational Transitions in Polymer Brushes — ●DIRK ROMEIS^{1,2} and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden, Germany — ²Technische Universität Dresden, Germany

Due the large density gradients in polymer brushes strong interaction forces are present leading to stretched chain conformations with the end-to-end distance scaling linearly with the degree of polymerization. In such an environment slight modifications of individual brush chains have great effects on their conformations [1,2]. We developed a quasi off-lattice SCF Model, that accounts for finite extensible polymer chains composed of differently sized and interacting spherical monomers. It allows for a realistic description of polymer brushes up to high grafting densities and the results are in excellent agreement to corresponding MD simulation [3], including packing, fluctuation and depletion effects. Using this approach we analyzed the behavior of individually modified guest chains in polymer brushes and encountered conformational transitions revealing a scaling behavior that can be rationalized using an analytical model. [1] Merlitz H. et. al. [*Macromolecules* **41** 5070, 2008] [2] Merlitz H. et. al. [*PRL* **102** 115702, 2009] [3] Romeis D. et. al. [*JCP* **136** 044903, 2012]

CPP 1.12 Mon 13:00 H34
Thermally stable composites of block-copolymer/metal nanoparticles. — ●IRYNA PEREPICHKA, DMITRII PEREPICHKA, and BRUCE LENNOX — Department of Chemistry, McGill University, Montreal (QC) Canada

Metal nanoparticles are widely studied for their applications in medicine, cosmetics, sensing, data storage, etc. Use of nanoparticles as catalysts in organic synthesis is another promising direction. However, many reactions require high temperatures, at which most nanoparticles solutions are unstable. Thus, producing metal nanoparticles that would not agglomerate during organic reaction is challenging.

We have synthesized gold and copper nanoparticles that are stable at above 150 C in various organic solvents. Role of ligands in nanoparticles stabilization has been studied. We have shown that combination of metal nanoparticles and diblock copolymers results in stable nanoformulations. Use of thus prepared Cu and Au NP as catalysts for aromatic C-C coupling reactions will be discussed.

CPP 1.13 Mon 13:15 H34

Charge transfer and recombination in hybrid solar cells with CuInS₂ nanocrystals studied by light-induced electron spin resonance — •CHRISTOPHER KRAUSE, RANY MIRANTI, DOROTHEA SCHEUNEMANN, FLORIAN WITT, JOANNA KOLNY-OLESIAK, HOLGER BORCHERT, and JÜRGEN PARISI — University of Oldenburg, Department of Physics, Energy and Semiconductor Research Laboratory, 26129 Oldenburg

Organic-inorganic hybrid solar cells made of semiconductor nanocrystals embedded into an organic material have made considerable progress in recent years. The highest efficiencies of such kind of solar cell are currently reached with cadmium based semiconductor nanoparticles, which have the drawback of a high toxicity. Therefore

we investigate the application of CuInS₂ nanoparticles as a promising new candidate for organic-inorganic hybrid solar cells. By ligand exchange procedures we are able to modify the surface of the nanoparticles in order to enable an efficient charge transfer and control the number of trap states arising from dangling bonds. In this contribution, light-induced electron spin resonance (LESR) measurements on composites of CuInS₂ nanoparticles with P3HT and PCBM will be presented. LESR is used to study the charge transfer at the hybrid donor/acceptor interface and its dependence on the ligand shell. Besides proving a successful photo-induced charge transfer we can use this method to investigate the density of trap states by analyzing the recombination kinetics of photo-generated long-lived charge carriers at different temperatures.