

# Funktionale nanostrukturierte Grenzflächen und Polymersysteme



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Auch in 2016 fokussierten die Arbeiten in ST1 auf die gezielte Entwicklung, Charakterisierung und Optimierung von funktionalen Polymeren unter Berücksichtigung von Aspekten der Systemintegration. Durch die Neubesetzung der Leitung IPC mit Herrn Professor Andreas Fery wurden stärker als bisher kolloidale Aspekte in die Materialentwicklungen einbezogen.

Wichtige Fortschritte konnten weiterhin bei Polymeren für optoelektronische Anwendungen erzielt werden. Erstmals wurde thermally activated delayed fluorescence (TADF) in einem Polymeren aus nicht-TAFT Einheiten erzeugt (Adv. Funct. Mater. 2017 online). Durch Design neuartiger Dopanten konnte in Diketopyrrolopyrrol-Halbleiterpolymeren eine rekordverdächtige Erhöhung der Leitfähigkeit um 8 Größenordnungen erreicht werden, und in Naphthalendiimid-Polymere gelang eine feinabgestimmte  $\pi$ -Konjugation (beide Adv. Mater. 2016). Durch Modellierung wurde gezeigt, dass es gelingt, die elektronischen und optischen Eigenschaften durch Ersatz von Heteroatomen in Halbleiterpolymeren nicht zu verändern (Comp. Mater. Sci. 2017). Dotierte Bereiche wurden erfolgreich in vertikalen OFETs mittel Elektronenmikroskopie sichtbar gemacht (Adv. Funct. Mater. 2016).

Interessante Ansätze für Funktionsmaterialien, einmal bezüglich der polymeren Binder für nanostrukturierte Anodenmaterialien in Lithium-Ionen Batterien, aber auch bezüglich der Elektrodenfolien und Polymerelektrolyten für großformatige Bipolar-Batterien, werden in zwei BMBF-Projekten verfolgt. Bioabbaubare Flockungsmittel zur Wasser- aufbereitung werden im Rahmen des BMBF Programms „MachWas“ entwickelt. Mittels in Mikrofluidik-Reaktoren integrierte Hydrogeldots konnten bis zu 3-stufige Enzymkaskaden erfolgreich realisiert werden. Partikuläre Bausteine finden in responsiven Nanoschichten Anwendungen: Beispiel sind temperatur-schaltbare Mikrogele zur Steuerung des Zell-Adhäsionsverhaltens (Biomacromolecules 2016), pH-responsive Blockcopolymer-Mizellen (ACS Nano 2016) oder Janus-Partikel zur Vermeidung von Eis-Bildung (Chem. Mater. 2016). Geeignet gepropfte magnetische Kern-Schale-Partikel konnten erstmals für eine zerstörungsfreie Prüfung mittel ET (Eddy Current Testing) von

Epoxykompositen eingesetzt werden (ACS Appl. Mat. & Interf. 2016).

Im ERC-Projekt METAMECH wird der Ansatz verfolgt, elektronische und optische Funktionsmaterialien über templatgestützte Selbstassemblierung von Hybridpartikeln aus metallischem Kern und polymerer Hülle herzustellen. 2016 gelang es hier erstmals, großflächige magnetische Metamaterialien herzustellen (Faraday Disc. 2016) und plasmonische Cluster konnten als neuer optischer Baustein etabliert werden (ACS Nano 2016). Die Aktivitäten konnten im Excellenzcluster cfaed verankert werden, in das Prof. Fery und Dr. König als Principal Investigators aufgenommen wurden. Einen Schwerpunkt bildet die Untersuchung von Wechselwirkungen und mechanischen Eigenschaften weicher Materie auf der Nano-Skala. Hier gelang es, über die Untersuchung kontrollierter Faltenbildung den E-Modul von 2D Materialien zu charakterisieren (Nature Comm. 2016, Angew. Chem. Int. Ed. 2016). Gleichzeitig wurde AFM-Kraftspektroskopie so weiterentwickelt, dass Mechanik und Wechselwirkung von Nano- und Mikrofasern direkt quantifiziert werden konnten (Polymer 2016, Nanoscale 2016). Zudem gewinnen mechano-responsive Materialien an Bedeutung: So konnten wir im Kontext des Marie-Curie ITN BioSmartTrainee zeigen, dass mechano-responsive Bürstensysteme die Adhäsionsmechanismen biomimetischer Oberflächen aufklären können (ACS Appl. Mat. & Interf. 2016).

Das aktuelle, interdisziplinäre Gebiet der Bio- und Multifunctional Polymer Architectures wurde 2016 in einer Monographie ausführlich dargestellt. Während des 18th International Symposium on Field- and Flow-Based Separations und des 20th European Symposium on Polymer Spectroscopy, welche im Mai bzw. September in Dresden organisiert wurden, konnten die neuesten Entwicklungen in der Charakterisierung und Analyse von Polymeren diskutiert werden.

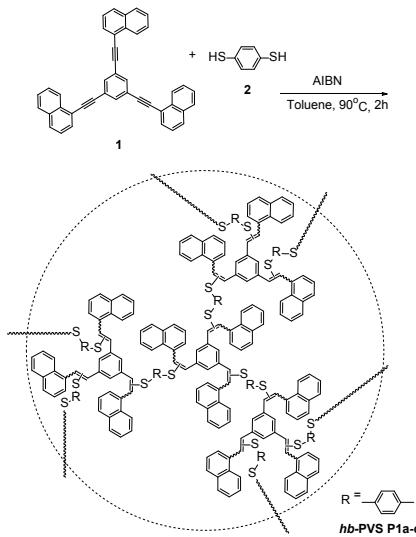
# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

## Hyperbranched polymers with high refractive index for application as light out-coupling layer in organic light-emitting diodes

Qiang Wei, Anton Kiriy, Brigitte Voit

Over the last decades optical and electrical applications have become more and more complex and require the integration of various material classes and concepts. It is nowadays not sufficient to rely only on the performance of the basic constituents of a device but processing, multilayer preparation, materials and interface interactions as well as environmental shielding but also in- and output concepts of the devices need to be addressed. In this regard, high refractive index (HRI) materials, with the capability to increase refraction and decrease reflection, can increase the efficiency of many optic-electronic devices, like organic photovoltaic cells (OPVs), anti-reflective coatings, waveguides, charged coupled devices (CCDs), complementary image sensors (CISs), and organic light-emitting diodes (OLEDs) [1]. Compared with inorganic materials, e.g. rare-earth containing glasses, high refractive index polymers (HRIPs) excel in low cost, light weight, impact resistance, and processability, however, easy to make HRIPs are rarely reported.

In this regard we could show that the facile, metal-free, radically induced "A<sub>2</sub>+B<sub>3</sub>" thiolyne polymerization of 1,3,5-tris(naphthalenyl-ethynyl) benzene and 1,4-dithiolbenzene or other dithiols leads to hyperbranched polyvinylsulfides (PVS) of exceptional high refractive index values [2, 3] (Scheme 1). The concept to further increase the content of high refractive index moieties by focusing on fully aromatic units with high naphthalene content and sulfur linkage allowed to prepare polymeric materials with RI values as high as 1.7839 at the highly interesting D band. Interestingly, the RI values can be further fine-tuned by the monomer ratio which defines the nature of the end groups and the naphthalene unit content, and this goes along with controlling the molecular weights of the polymers from medium/low to very high ( $M_w > 130,000 \text{ g/mol}$ ) (Table 1).



**Keywords**  
hyperbranched polymers  
high refractive index  
polymers  
OLED

**Scheme 1:**  
**Polymerizations of B3**  
**(trialkyne 1) and A2 (dithiol**  
**2) to form P1a-c**

item	[C=C]:[SH]	$M_w$ [g mol <sup>-1</sup> <sup>a)</sup> ]	D <sup>b)</sup>	$T_g$ <sup>c)</sup>	Film thickness (nm) <sup>d)</sup>	R <sup>d)</sup>
P1a	3 : 2	7,500	2.9	141	78	1.7839
P1b	3 : 3	134,400	11.3	172	90	1.7778
P1c	3 : 4	32,200	4.9	147	89	1.7683
NPB	-	-	-	-	70	1.7778

Due to the branched structure, even the high molecular weight PVS polymer P1b shows excellent solubility, solution processability and film forming properties as well as high transparency. The rigid, highly aromatic structures further provided excellent thermal properties to the high refractive index polymers (HRIP) like  $T_g$  values up to 172 °C and a 5 % weight loss above 400 °C.

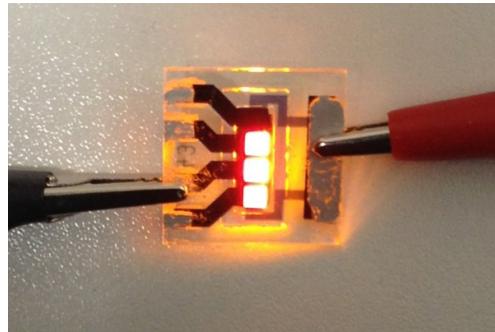
State-of-the art, highly optimized phosphorescent monochrome OLEDs [4] were fabricated on top of HRIP layers to test the compatibility of HRIPs with state-of-the-art OLEDs (Figures 1 and 2). Our results show that the HRIPs, which match fully the refractive index of state-of-the-art low molecular weight organic semiconductor materials like NPB (N,N'-di[naphthalene-1-yl]-N,N'-diphenyl-benzidine), do not deteriorate at all the performance of the OLEDs while maintaining external quantum efficiencies (EQE) of over 20 % for phosphorescent red OLEDs [3]. These results open a pathway towards alternative, low-cost, and scalable out-coupling concepts through refractive index matching of the OLED materials and the HRIPs presented, which are so far not accessible with low molecular weight out-coupling layers. Since our HRIP did

**Table 1:**  
**Characteristic data of hb**  
**PVS P1a-c and NPB**  
**a) Determined by GPC in**  
**chloroform (LS detection);**  
**b) D = Mw/Mn, determined**  
**by GPC in chloroform**  
**c) Tg = glass transition**  
**temperature is recorded**  
**on DSC under nitrogen at a**  
**heating rate of 10 °C min<sup>-1</sup>**  
**d) Refractive index is**  
**represented by Fraunhofer**  
**D (589.3 nm), measured by**  
**ellipsometry**

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not lead to electrical instabilities, they are on the one hand ideally suited for planarizing/smoothening of rough interfaces of light out-coupling structures avoiding electrical losses within the OLED. In addition, they can act as matrix materials for the integration of contrast giving or light scattering structures like (nano) particles which should further increase the light out-coupling efficiency. Further studies showed that such HRIP are also highly suitable for other optical applications like for the preparation of one-dimensional planar all-polymer photonic crystals [5].

**Fig. 1:**  
Picture of the OLED device made with P1b as out-coupling layer  
(prepared by P. Klein,  
IAPP, Dresden)



**Fig. 2:**  
OLED layer architecture;  
NPB = N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine

Ag	80 nm
BPhen:	58 nm
Cs	
BAIQ <sub>2</sub>	10 nm
NPB:	20 nm
Ir(MDQ) <sub>2</sub> (acac)	10 wt%
NPB	10 nm
Spiro-TTB:	44 nm
F6-TCNNQ	2 wt%
Ag	20 nm
Au	2 nm
MoO <sub>3</sub>	1 nm
NPB / P1a / P1b	x nm
glass	1.1mm

Sponsor:  
Supported in part by Center of Excellence  
Centre for Advancing Electronics Dresden  
(cfaed)

## Co-operation:

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# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

## Structural analysis of polyethylene using high temperature size exclusion chromatography with quadruple detection

Laura Plüscke, Robert Mundil, Anatolij Sokolohorskyj, Jan Merna, Jens-Uwe Sommer, Albena Lederer

The pluralism of macromolecules is outstanding and arises from a multitude of parameters and thus potential tools such as kind and chemistry of monomer (natural or synthetic), sequence of repeat units (homo- or copolymer), monomer arrangements (alternating, periodic, statistical etc.) or even polymerization methods to take control of polymer properties. Another significant factor is the control of the macromolecular architecture. Since the beginning of the 20th century polymeric topologies have been discovered ranging from linear to network-like structures and from molecules with moderate occurrence of side chains to very densely branched and dendritic macromolecules which is schematically shown in Fig. 1 [1]. Indeed, branching plays a substantial role in polyethylene (PE), the most important large-scale plastic material in daily use. Here, both bulk and solution properties are affected by the degree and type of branching, which makes the characterization of those parameters highly essential [2, 3].

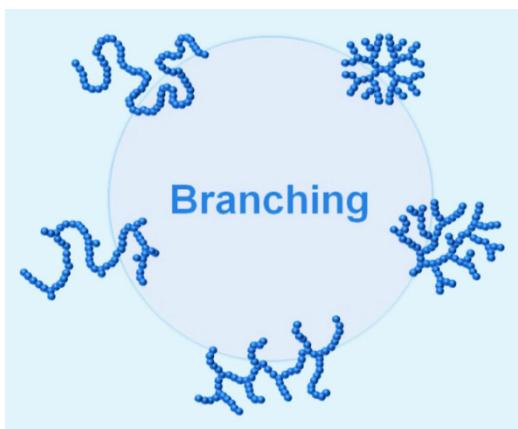
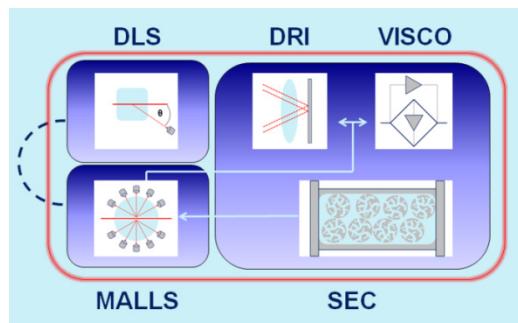


Fig.1:  
Architectures and types of branching in macromolecules



**Keywords**  
GPC/SEC  
light scattering  
viscometry  
polyethylene  
branching

Fig. 2:  
Measuring principle and construction of HT-SEC4

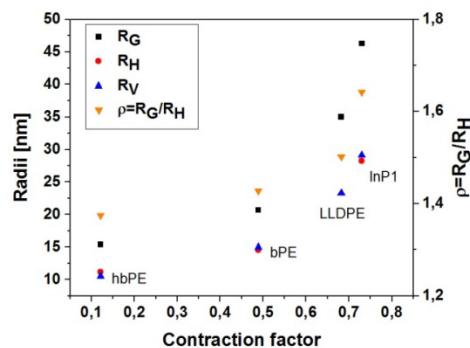
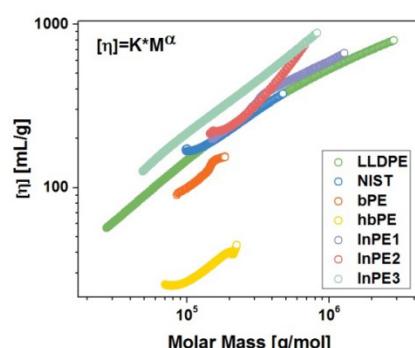
Modern synthesis using Pd(II)- $\alpha$ -diimine catalysts allow the production of well-defined branched PE whose architecture can be easily modified by varying reaction conditions such as pressure or temperature. Moreover, these PEs are very well soluble in solvents like tetrahydrofuran even at room temperature [4]. However, linear PE displays a rather problematic dissolution behavior. In order to compare solution behavior of PE with different topologies elaborate methods like high temperature size exclusion chromatography (HT-SEC) combined with diverse detecting systems are necessary. In our studies we used a novel and unique system based on HT-SEC coupled to four detectors namely multi angle laser light scattering (MALLS), dynamic light scattering (DLS), differential refractive index (DRI) and viscometry (VISCO) which is displayed in Fig. 2. Using HT-SEC4 we were able to receive a broad range of physical parameters and structural factors, which permits the determination of complex structure-property relations of variously branched PE. In our studies we used different types of PE including a linear PE standard (NIST), linear low density PE (LLDPE), PE with linear topology synthesized using a perfluorinated nickel catalyst (inPE1),  $\alpha$ -keto- $\beta$ -diimine nickel catalyst (InPE2) and a nickel chelate catalyst (InPE3). Furthermore, we investigated PE with moderate branching density (bPE) and hyperbranched PE (hbPE) both synthesized using a Nickel- and palladium-chelate catalyst, respectively.

The relation between intrinsic viscosity and molar mass is given by the Kuhn-Mark Houwink power law [ $\eta = K M^\alpha$ ] (see Fig. 3). The exponent  $\alpha$  is a structure-dependent parameter and describes the conformation of the molecule in solution. For our samples the value of  $\alpha$  ranges from 0.55 (hbPE) and 0.65 (bPE) up to 0.90 (InP2). Comparable with

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literature values,  $\alpha$  decreases with increase of the branching density [5, 6]. Moreover, the reduction of viscosity between a linear molecule and a hyperbranched analogue at the same molar mass regime can be clearly seen in Fig. 3. The intrinsic viscosity is decreased fivefold from lnP2 (216mL/g) to hbPE (51 mL/g). The decrease of  $[\eta]$  and  $R_g$  can be seen as a result of branching quantitatively by the introduction of the contraction parameter  $g' = [\eta]HB/[\eta]LN$  respectively. The stronger the branching density of a molecule, the higher the contraction compared to its linear analogue and hence, the smaller the contraction factor. The advantage of our novel quadruple detecting system is the simultaneous measurement of different radii namely the radius of gyration ( $R_g$ ), the hydrodynamic radius ( $R_h$ ) and the viscosity radius ( $R_\eta$ ). Moreover, the ratio between  $R_g$  and  $R_h$  expressed as the  $\rho$ -parameter gives information about the topological properties of our samples. Similar to the Kuhn exponent  $\alpha$ , the  $\rho$ -parameter delivers useful information for the evaluation of the architectural structure of the sample. In Fig. 4 both radii and  $\rho$ -parameter of selected samples are displayed as a function of the contraction factor. First, we notice that  $R_g$  is larger than  $R_h$  and  $R_\eta$  as well as  $R_h$  and  $R_\eta$  are nearly the same size. With increasing  $g'$  the difference between  $R_g$  and  $R_h$ ,  $R_\eta$  becomes larger. This behavior results from the fact that hb polymers have a very dense and compact structure whereas linear macromolecules typically form random coils in dilute solution. The  $\rho$ -parameter increases from 1.38 for hbPE to 1.65 for PE with almost linear topology. On the one hand these results correspond very well to theoretical values ( $\rho=1.25$  for hb polymers with  $AB_2$  monomers and  $\rho=1.7-2.0$  for linear chains), on the other hand the loss of branching density with increasing  $g'$  becomes obvious [7].

**Fig. 3:**  
Kuhn-Mark-Houwink plot  
of PE samples



**Fig. 4:**  
 $R_g$ ,  $R_h$  and  $R_\eta$  against contraction factor  $g'$  of PE samples

Sponsor:  
Deutsche Forschungsgemeinschaft (DFG)

Co-operation:  
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J.-U. Sommer et al., IPF, Institute Theory of Polymers

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# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

## Establishing multienzymatic reactions in microchannels

David Simon, Toni Heroldt, Martin Peiter, Brigitte Voit, Dietmar Appelhans

One of the biggest challenge of today's chemistry is waste treatment or prevention [1]. One solution is the usage of enzymes as catalysts because of the quantitative reaction with low concentrations of side products and the ability to work under adequate conditions (~37 °C, no pressure) in water as solvent [2, 3]. To overcome the drawback of low reusability and stability in harsh conditions, the enzymes have to be immobilized in a three-dimensional environment. In this study we used hydrogels for this purpose. This approach has several advantageous key issues to mimic a natural environment for enzymes and to evoke the substrate-channeling-effect. This effect is characterized by an increased substrate transport between immobilized enzymes in a matrix. This results in an increased enzymatic activity for cascade reactions [4]. Moreover hydrogel-enzymes composites can be easily fixed and patterned on surfaces using photolithography [5, 6].

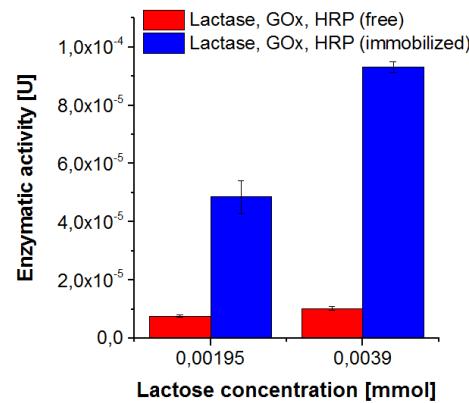
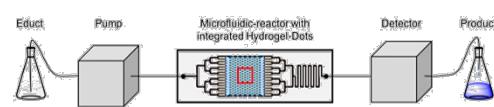
Crooks et al. presented a first minimalist microfluidic reactor at which enzymatic cascade reactions have been immobilized within a PEG-based hydrogels [7]. But there is a lack of long-term stability and reusability of such complex enzyme-loaded hydrogel system. This was the starting point for our study in this research field.

With our co-operation partners at the Technische Universität Dresden we established a microfluidic reaction chamber with enzyme-loaded and hexagonally packed hydrogel dots to minimize mechanical stress and high dwell time of the fluid at the hydrogel-enzyme dots. The established approach is presented in Fig. 1.

We investigated the stabilization and reusability with the immobilization of two enzymatic cascade reactions. Cascade reaction 1, a lactose assay, included lactase (Lac), glucose oxidase (GOx) and horseradish peroxidase (HRP) and cascade reaction 2, a liver assay, included phospholipase D (PLD), choline oxidase (ChOx) and HRP as well. The immobilization of enzymes was simultaneously done during the photo-initiated synthesis of hydrogel dots.

Enzymatic activity was detected by conversion of UV/Vis dye ABTS ( $\lambda = 405$  nm) with  $H_2O_2$  catalyzed by HRP. Cascade reaction 1 showed an increased activity, while the enzymes are immobilized by hydrogel dots (Fig. 2). Thus the expected substrate-channeling-effect was directly proven. Furthermore, the long-term stability of this trienzymatic cascade reaction is still given after a storage time of 21 days (40 % of relative activity compared to the starting 100 % relative activity). Finally, the cascade reaction 1 was successfully integrated in the microfluidic channel and the reusability was proven for 4 measurement cycles, while the activity remains at 40 % of starting activity. For cascade reaction 2 the substrate-channeling-effect does take place as well. The immobilized enzymes showed a 1.5 times increased activity compared to the free enzymes. Even the long-term activity compared to the free enzymatic cascade reaction is dramatically increased by the immobilization in hydrogel dots. Activity of immobilized enzymes could be still measured after 30 days compared to the complete activity loss of the free enzymes after 6 days. In summary, we demonstrated the successful immobilization of two trienzymatic cascade reactions with the desired long-term stability and reusability. Cascade reaction 1 was already successfully integrated in a microfluidic reactor and used for several cycles.

**Keywords**  
enzymatic reaction  
immobilization  
hydrogel  
microfluidic reactor



**Fig. 1:**  
Schematic buildup of the microfluidic reaction system. The microchannels were made of PDMS and the detection was done by UV-Vis spectroscopy. The hydrogels (red square) were synthesized in a hexagonally ordered pattern on the glass surface.

**Fig. 2:**  
Comparison of enzymatic activity of the immobilized enzymatic cascade reaction compared to the free cascade reaction. The activity was measured by conversion of ABTS and measured with UV-Vis spectrometry.

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Sponsor:

Deutsche Forschungsgemeinschaft (DFG),  
Graduiertenkolleg 1865 "Hydrogel-based  
Microsystems"

Co-operation:

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## Magnetite core-shell nanoparticles in non-destructive flaw detection of polymeric materials

Mimi Hetti, Doris Pospiech, Matthias Bartusch, Brigitte Voit

Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles (NP) are well-known for their superparamagnetic behavior making them ideal for numerous applications in biomedicine, biosensing, bioseparation, engineering, for magnetic shape-memory materials, in magnetic resonance imaging, magnetic data storage and many more [1]. Special surface modifications allow to tune the behavior in various media and to adjust the properties for the special application [2]. The project summarized here aimed at the development of magnetite nanoparticles with polymeric shell for use in structural health monitoring of fiber-reinforced composites. Non-destructive monitoring of microscale damages before failure is an important task and requires introduction of special properties like electric conductivity, magnetic response or thermal conductivity which can be employed for sensing. Here, magnetization was used to yield material response. The project was realized stepwise as illustrated in Fig. 1 including 1<sup>st</sup>) development of suitable polymer-modified magnetite NPs and their characterization; 2<sup>nd</sup>) their utilization in epoxy resin matrices to explore the possibility of magnetic monitoring; 3<sup>rd</sup>) their application on reinforcing ultrahigh molecular weight polyethylene (UHMWPE) fibers, and, finally, preparation of high performance composites with the modified UHMWPE wovens. The experimental work was supported by simulations of model organic molecules with a magnetic metal atom followed by scanning tunneling microscopy [3]. Additional Monte Carlo simulations revealed the influence of copolymers on the surface tension of interfaces and the compatibilization between nanoparticles and polymers [3]. The magnetite NPs were prepared by coprecipitation of  $\text{FeCl}_2/\text{FeCl}_3$  with ammonium hydroxide according to [2]. Poly(glycidyl methacrylate) (PGMA) was chosen as polymer modification due to the high amount of reactive epoxy groups. PGMA was synthesized by atom transfer polymerization, and attached to 3-mercaptopropyltriethoxysilane-modified magnetite NPs by grafting-to reaction [4, 5], or alternatively, by grafting-from [5]. Properties

of selected magnetite NPs with different modification are summarized in Table 1. The cluster size could be tuned by the reaction conditions and was examined by dynamic light scattering and transmission electron microscopy [5]. PGMA modification reduced the NP agglomeration. The saturation magnetization determined by vibrating sample magnetometry (VSM) of PGMA-modified  $\text{Fe}_3\text{O}_4$  NPs was higher than reported in literature [6], and correlated well to the magnetite content. Negligible hysteresis in the magnetization vs. magnetic field curves indicated superparamagnetic behavior, as expected.

NP type	Cluster particle size $Z_{av}$ (DLS) [nm]	Saturation magnetization $M_s$ [emu/g]	Magnetite content [wt%]
$\text{Fe}_3\text{O}_4$	135	77	97
$\text{Fe}_3\text{O}_4$ -oleic acid stabilized	56	67	87
$\text{Fe}_3\text{O}_4$ -PGMA1	304	69	87
$\text{Fe}_3\text{O}_4$ -PGMA2	173	63	79
$\text{Fe}_3\text{O}_4$ -PGMA2		47	56
$\text{Fe}_3\text{O}_4$ -treated UHMWPE woven	-	0.6	not det.
Epoxy-2.5 wt% $\text{Fe}_3\text{O}_4$ -PGMA1	-	42979	
Epoxy-2.5 wt% $\text{Fe}_3\text{O}_4$ -PGMA1	-	0.7	

**Keywords**  
**magnetite nanoparticles**  
**core-shell nanoparticles**  
**non-destructive sensing**  
**high-performance**  
**composites**

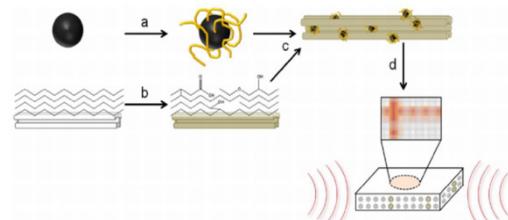
**Table 1:**  
**Properties of selected magnetite NPs with different modification**

Mixing PGMA-modified magnetite NPs into a standard epoxy matrix gave after curing saturation magnetizations between 1.9 and 0.7 emu/g which correlated to the magnetite content [4]. Moreover, it could be shown that the co-reaction of the PGMA glycidyl groups in curing yielded composites with sufficient dispersion and adhesion of the NPs and therefore unchanged ultimate tensile strength after incorporation of the NPs, indicating that the introduction of magnetic response at high property level of composites can be realized. Application onto atmospheric plasma-treated UHMWPE woven also resulted in measurable magnetization and thus, magnetizable textile structures [3]. Both results gave a solid base for the following sensing experiments. Epoxy resins with PGMA-modified magnetite NPs were examined by eddy current testing (ET) in collaboration with BAM Berlin. This technique induces a magnetic reluctance defined as ET signal which was not observed in the control sample without NPs. Different kinds of artificial defects were introduced in the samples and the method was able to detect surficial and sub-surficial flaws at the low NP concentrations ( $\leq 1$  wt%) used by scanning over the rectangular surface, as illustrated by the resultant C-scan in Fig. 2. In fiber/woven-reinforced composites where the final magnetite concentration is significantly lower, the

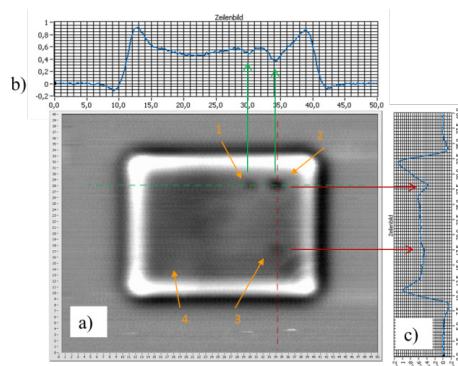
# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

method still has to be adjusted to detect small defects, however, the fibers were well visualized. The results obtained in this study for the first time open a new and very promising pathway for non-destructive flaw detection in polymeric composites.

**Fig. 1:**  
Concept and working steps: a) preparation of magnetite NPs and their chemical modification; b) plasma treatment of UHMW PE fibers and yarns; c) impregnation of plasma-treated UHMW PE fibers/yarns with modified magnetite NPs; d) embedding of magnetite-covered UHMW PE fibers/yarns into epoxy, curing and magnetic measurements



**Fig. 2:**  
Examination of an epoxy resin sample with 1 wt% PGMA-modified magnetite NPs with eddy current technique:  
a) C-scan image of the ET measurements with four artificial defects;  
b) ET signal profile along the dotted green line;  
c) ET signal profile along the dotted red line (printed with permission of the American Chemical Society)



**Sponsor:**  
European Center for Emerging Materials and Processes Dresden (ECEMP), Sächsische Aufbaubank, Project A2 Innovatives molekulares Design für eine volumenorientierte Bauteildiagnostik (MolDiagnostik), funded by European Union and the Free State of Saxony by the grant number SAB/EFRE 100116427.

**Co-operation:**  
Dr. M. Bartusch, Prof. C. Cherif,  
Dr. R.-D. Hund, Technische Universität Dresden, Institute of Textile Machinery and High Performance Material Technology  
R. Pohl, R. Casperson, Bundesanstalt für Materialforschung und -prüfung, Berlin  
Dr. V. Neu, Leibniz-Institut für Festkörper- und Werkstoffforschung, Institut für Metallische Werkstoffe, Dresden  
Prof. G. Cuniberti, Dr. F. Moresco, Technische Universität Dresden, Professur für Materialwissenschaft und Nanotechnik  
Prof. J.-U Sommer, IPF

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# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

## Optische Metamaterialien auf großen Flächen: Templat-gestützte Selbst-assemblierung von Metamaterialien durch die Nutzung mechanischer Instabilitäten

Yannic Brasse, Bernhard A. Glatz, Fabian Goßler, Roland Höller, Tobias A. F. König, Christian Kuttner, Martin Mayer, Patrick T. Probst, Max Schnepf, Anja Maria Steiner, Andreas Fery

Ziel des European Research Council Projekts Metamech ist es, Schichten mit optischen Metamaterialeigenschaften großflächig zu erzeugen. Optische Metamaterialien zeichnen sich dadurch aus, dass ihr effektiver Brechungsindex durch das Design der Materialien auf der Nanoskala eingestellt werden kann. Dadurch können auch negative Brechungsindizes, die in homogenen Materialien nicht vorkommen, oder sehr effizient polarisationsdrehende Schichten realisiert werden. Während bisher die Herstellung solcher Materialien nur mit sehr aufwendigen Lithographieverfahren möglich war, die nicht auf große Flächen anwendbar sind, verfolgt Metamech einen völlig anderen Ansatz. Dazu werden metallische Nanopartikel mit Polymerhüllen überzogen und anschließend in großflächig hergestellte Polymer-Faltenstrukturen eingebracht. Die Falten führen zu einer templatgestützten Selbst-assemblierung der Partikel, wodurch sich ähnliche Strukturen wie durch die bisher verwendeten Lithographieverfahren herstellen lassen [1-5]. Uns ist es so vor kurzem gelungen mit diesen Methoden erstmals Metaoberflächen herzustellen, die großflächig magnetische Resonanzen bei optischen Frequenzen aufweisen, ein wichtiger Schritt hin zu negativen Brechungsindex-Oberflächen (Abb. 1) [3].

Während aktuell vor allem Grundlagen erforscht werden, könnte die großflächige Herstellung von optischen Meta-Oberflächen spannende Perspektiven für die Kontrolle von Licht auf Oberflächen mit Anwendungen für Sensorik, Kommunikationstechnik oder Energiegewinnung bieten.

Förderer:  
ERC Starting Grant, PI Andreas Fery

Kooperation:  
Prof. S. Förster, Physikalische Chemie, Universität Bayreuth  
Prof. M. Karg, Kolloide und Nanooptik, Universität Düsseldorf

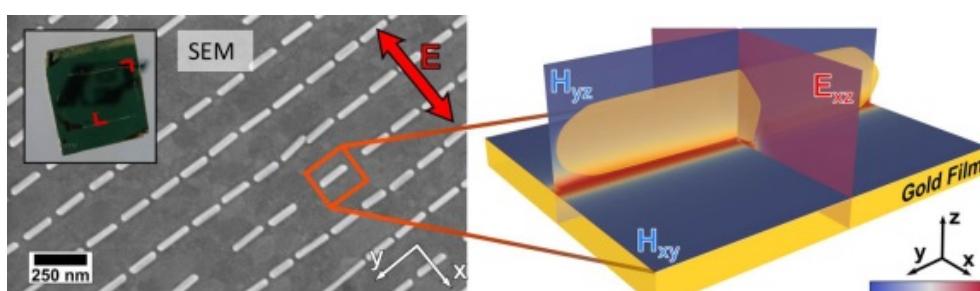
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**Keywords**  
**physical chemistry**  
**optics**  
**metallic nanoparticles**  
**self-assembly**  
**macroscopic**

**Abb. 1:**  
**Template gestützte Partikelselforganisation von goldenen Nanostäbchen auf einem goldenen Metallfilm als makroskopische magnetische Metaoberfläche.**

**Links:** Fotografische Aufnahme mit IPF-Logo und elektronenmikroskopische Aufnahme (SEM) der magnetischen Metaoberfläche (durchsichtig für das menschliche Auge).

**Rechts:** Schematische Zeichnung und Finite-Elemente Simulation der elektrischen und magnetischen Felder. Die magnetische Eigenschaft des Systems wird erst durch eine elektromagnetische Kopplung des Nanostabes mit dem Metallfilm erhalten.



# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

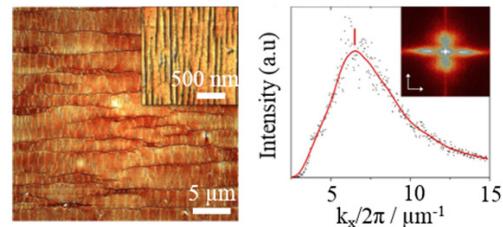
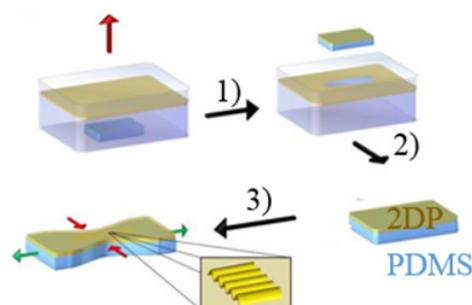
**Keywords**  
2D-materials  
mechanical  
characterization  
wrinkling

## Präzise Messung mechanischer Eigenschaften von 2D-Polymerfilmen

Bernhard Alexander Glatz, Christian Kuttner, Andreas Fery

Die Entdeckung von Graphen zeigte das enorme Potential von 2D-Materialien für Optik, Elektronik und Mechanik. Ziel chemischer Synthese ist in diesem Gebiet, die Prinzipien und Vorteile von 2D-Materialien auf andere Stoffklassen auszuweiten und so das Eigenschaftsspektrum zu erweitern und für verschiedene Anwendungen maßzuschneidern. Besonders die mechanische Charakterisierung solcher molekular dünner Schichten ist jedoch mit extremen Herausforderungen verbunden. So wurden bisher Verfahren benutzt, für die Kräfte für die Deformation freitragender Schichten mittels rasterkraftmikroskopischer Methoden detektiert wurden. In dem kürzlich erschienenen Artikel in *Nature Communications* geht die Gruppe Fery einen anderen Weg [1]: Da die in der Gruppe Feng hergestellten 2D-Materialien großflächig vorliegen, können ihre mechanischen Eigenschaften mittels Faltenbildung bestimmt werden: Dazu werden wie in Abb. 1 gezeigt die Filme zuerst auf Elastomere transferiert und anschließend wird das Elastomer samt Film deformiert, was zur Bildung von Falten mit einer charakteristischen Wellenlänge führt. Diese hängt von der Dicke der 2D-Schicht, sowie von den mechanischen Eigenschaften von Elastomer und Film ab. Alle Parameter bis auf die mechanischen Eigenschaften sind bekannt oder unabhängig bestimmbar, sodass der Young-Modul des 2D Materials abgeleitet werden kann. Die Methode ist auch für andere ultradünnen Systeme wie Schichtsilikat-Taktoide geeignet [2] und könnte sich zu einem neuen Standard für die mechanische Charakterisierung von 2D-Materialien entwickeln.

**Abb. 1:**  
**Probentransfer und SIEBIMM-Verfahren:** Der 2D-Film wird mittels eines PDMS-Elastomerblocks aus dem Wasserbad herausgehoben und getrocknet. Im anschließenden Schritt erfolgt die uni-axiale Dehnung der Probe, was Falten des Films in der Nano-Ebene erzeugt.



**Abb. 2:**  
**Ergebnisse der mechanischen Messung.** Links: Topographisches Höhenbild der Falten (mit eingebetteter Vergrößerung). Rechts: Fourier-transformiertes Spektrum der Wellen-Periodizität des linken Bildes.

Förderer:  
European Research Council (ERC), Projekt-Nr: METAMECH-306686

Kooperation:  
Prof. X. Feng, Technische Universität Dresden  
Dr. Z. Zheng, Technische Universität Dresden

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## Electron microscopy for organic electronics

Petr Formanek, Michael Göbel,  
Manfred Stamm, Andreas Fery

Organic electronics is a rapidly developing field with a huge potential for future applications in everyday life like entertainment, biosensors, internet-of-things and green energy (organic photovoltaics). The activities of IPF in this field focus on organic solar cells (OSC) and organic field effect transistors (OFET).

The performance of OSCs and OFETs strongly depends on geometry, morphology and structure of materials and layers used. Since the typical feature sizes of OSCs and OFETs are in the range of micrometers to nanometers, electron microscopes are necessary to visualize them. Because the different organic materials frequently have very similar interaction with electron beam, their images in electron microscope have poor contrast so that advanced analytical methods are the only chance to visualize the material morphology. Ref. [1], [2] demonstrate how scanning electron microscope (SEM), energy-dispersive x-ray spectroscopy (EDX), transmission electron microscope (TEM), energy-filtering in TEM (EFTEM) and focused ion beam (FIB) substantially contributed to clarification of material science problems and to explanation of device performance.

One of the novel device architectures is vertical organic field effect transistor (VOFET). While the advantage of VOFETs is better performance than that of traditional OFETs, their geometry and understanding of operation are more complicated. Fabrication of VOFETs requires lithography which may lead to issues with mask alignment (Fig. 1) FIB and EDX provide invaluable insight into these effects.

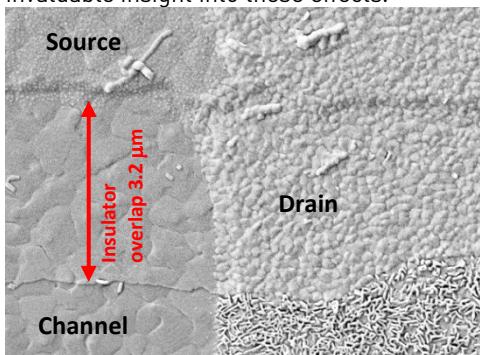
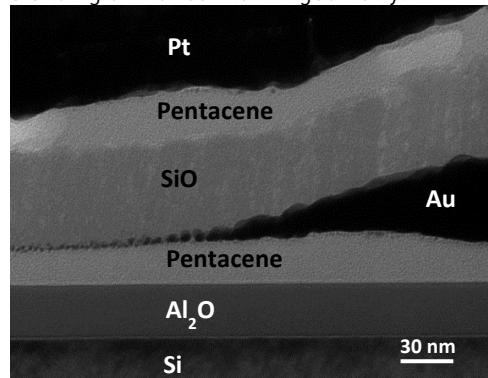


Fig. 1:  
Top-view SEM image of vertical OFET revealing an insulator overlap of approx. 3.2  $\mu\text{m}$

In the studies of contact doping in VOFETs [1], SEM (Fig. 1) was used to measure the overlap of the insulator which served as a fixed parameter in device modelling. EDX confirmed the location of doping layer underneath the source electrode (suppl. info of [1]). The thickness of the different layers of the VOFET was measured in TEM images (Fig. 2) of cross-sections prepared by the FIB lift-out. These characterizations lead to much more complete understanding of the real VOFET geometry.



In case of OSC, blends of fullerene:dicyano-vinylquinquethiophen ( $\text{C}_60:\text{DCV5T}$ ) were inspected with energy filtered TEM as preliminary studies to [2].

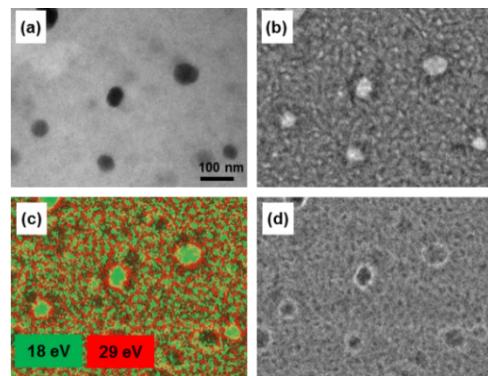


Fig. 3a shows conventional image of  $\text{C}_60:\text{DCV5T}$  blend deposited at 72 °C. Except for spherical crystals of  $\text{C}_60$  no further morphology is visible. Only energy-filtered images at plasmon losses of 18 eV and 29 eV (Fig. 3b, c) reveal smaller domains. FIB lift-out was used to prepare a cross section of  $\text{C}_60:\text{DCV5T}$  blend layer deposited at 132 °C. Elemental mapping using EFTEM served to clarify the vertical distribution of elements (Fig. 4). Notable is a thin DCV5T layer underneath DCV5T crystals which are surrounded by  $\text{C}_60$ . Morphological characterization combined with microscopic and mesoscopic simulations revealed that

**Keywords**  
organic electronics  
organic solar cell  
organic field effect  
transistors  
transmission electron  
microscope  
scanning electron  
microscope  
energy-dispersive x-ray  
spectroscopy  
energy-filtering in TEM  
focused ion beam

Fig. 2:  
Cross-section TEM image of vertical OFET at the edge of the source electrode

Fig. 3:  
Top-view TEM image of  $\text{C}_60:\text{DCV5T}$  blend deposited at 72 °C. (a) Conventional image, (b, c) energy-filtered images at 18 eV, 29 eV loss respectively, (d) false-color overlay of the EFTEM images. The phase separation on nanoscale is visible only in the EFTEM images

# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

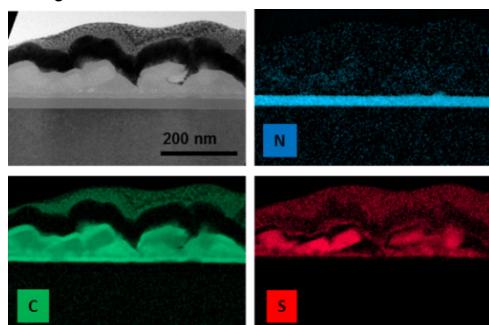
## Keywords

composite material  
interphase  
aminolyses  
IR spectroscopy imaging

**Fig. 4:**  
Cross-section TEM image of C60:DCV5T blend deposited at 132 °C. Conventional image (top left) and corresponding elemental maps revealing spatial distribution of C60 and DCV5T.

decisive quantity controlling the internal quantum efficiency is the energetic disorder caused by material mixing [2].

In summary, the few presented examples demonstrated how valuable electron microscopy is for the material science and device design.



## Sponsors:

Federal Ministry of Education and Research (BMBF),  
Heliatek

## Co-operation:

Dr. T. Mönch, Dr. A. A. Günther (now Hauke),  
Dr. M. Sawatzki, Prof. K. Leo, Technische Universität Dresden, Institut für angewandte Photophysik  
Dr. K. Walzer, Heliatek GmbH, Dresden

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## Molekulare Strukturaufklärung von reaktiven polymeren Grenzschichten

Cordelia Zimmerer, Gert Heinrich

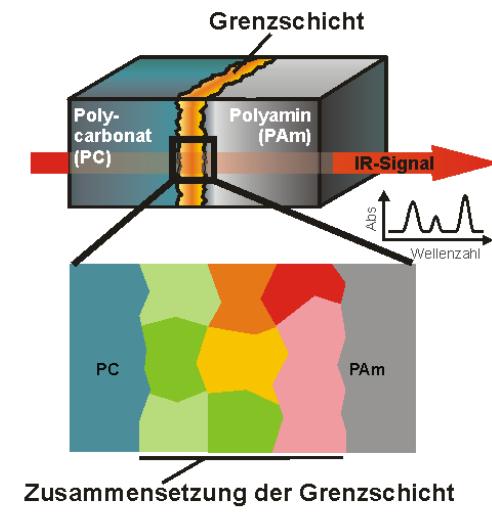
Durch die Kombination verschiedener Materialien können neue Gebrauchsgüter und Bauteile geschaffen werden, die sich vielseitiger, zuverlässiger und zugleich auch ressourcenschonender einsetzen lassen. Um diese Merkmale zu erreichen, ist eine starke und dauerhafte Verbindung der Materialien auf molekularer Ebene, d.h. durch Ausbildung kovalenter Bindungen, erforderlich. Um verschiedene Polymermaterialien auf diese Weise zu verbinden, muss neben dem Vorhandensein von reaktiven Gruppen in den Ausgangsmaterialien stets eine energetische Barriere überwunden werden. Sind diese Bedingungen erfüllt, können die Materialien miteinander reagieren und Block-copolymere als Interphase ausbilden. Prozessintegriert werden diese Reaktionen häufig in Schmelze bzw. als Festphasenreaktionen durchgeführt. Festphasenreaktionen laufen so lange ab, bis ein Reaktionspartner aufgebraucht ist oder kein Energieeintrag mehr stattfindet. Aus der Kenntnis der abgelaufenen bzw. ablaufenden chemischen Reaktionen, deren Zwischen- und Reaktionsprodukte, der Phasenzusammensetzung von Produktgemischen und deren Morphologie kann auf wichtige Eigenschaften des Verbundes geschlossen werden. Die Charakterisierung der Grenzschicht, insbesondere hinsichtlich der gewünschten Ausbildung chemischer Bindungen ist somit zwingend erforderlich, um die Eigenschaften der Verbunde sicherzustellen. Die große Herausforderung besteht dabei in der Gewinnung molekularer Strukturinformationen aus der oftmals nur wenige Nanometer dicken Grenzschicht.

Die Infrarot (IR)-Spektroskopie ist eine der wenigen anwendbaren Methoden, mit der zerstörungsfrei inter- und intramolekulare Wechselwirkungen in der extrem dünnen Grenzschicht erfasst werden können. Das IR-Spektrum zeichnet sich durch einen sehr hohen Informationsgehalt zur molekularen Struktur aus und muss daher mit komplexen und iterativen Methoden schrittweise analysiert werden.

In Abb. 1 ist das Schema zur IR-spektroskopischen Messung des Verbundes zwischen dem hydrophoben Polycarbonat (PC) und

# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

einem primären Polyamin (PAm) als Polyelektrolyten und deren Reaktionsprodukten in der Grenzschicht dargestellt.



**Abb. 1:**  
Strukturaufklärung der Grenzschicht mittels IR-Spektroskopie

Die Grenzschicht wird lateral aufgelöst mittels IR-Imaging untersucht. Bei der Interpretation der Spektren kann nur teilweise auf vorhandene Referenzdaten, z. B. in entsprechenden Tabellenwerken [1], zurückgegriffen werden. Um die möglichen Verbindungen und Strukturgruppen sicher zu identifizieren, wurden schrittweise adäquate Modellsubstanzen synthetisiert und analysiert. Diese Herangehensweise hat sich bereits bei der Analyse der komplexen IR-Spektren von ähnlichen Systemen bewährt [2].

Die chemische Reaktion von PC mit Polyvinylamin (PVAm) führt zur Kettensspaltung des PCs an einer Carbonat-Gruppe und der Bildung eines Block-copolymers. In dieser Grenzschicht können verschiedene Kopplungsgruppen auftreten. Vorrangig wird die Urethangruppe gebildet, welche eine kovalente Verknüpfung zwischen beiden Materialien darstellt (Abb. 2). Allerdings entstehen auch beim Abbau der PC-Ketten verschiedene Nebenprodukte, deren Struktur aufgeklärt werden soll. So werden für die Bildung eines Allophanates zwei Carbonat-Gruppen umgesetzt. Bei der Biuret- oder Harnstoffbildung wird die PC-Kette ebenfalls mehrmals pro Carbonat-Einheit gespalten. Es bildet sich kein Block-copolymer und damit keine kovalente Bindung zwischen den Materialien, PC wird

dann vorrangig an der Grenzschicht erodiert. Dieses Beispiel zeigt, dass zur Bewertung des Verbundes die Kenntnis der molekularen Struktur und der Konzentrationsprofile in der Multiphasengrenzschicht zwingend erforderlich sind. Kinetische Studien und Grenzschichtmodelle an Mischphasen wurden zur Aufklärung der Vorgänge mit thermischen und chromatographischen Referenzmethoden kombiniert. Es konnte gezeigt werden, dass

- eine komplexe Interphasenzusammensetzung für PC mit verschiedenen Polyaminsystemen vorliegt,
- starke intermolekulare Wechselwirkungen zwischen Reaktionsprodukten und Edukten existieren
- verschiedene Mischbarkeiten und Gefügeausbildung (Kristallinitäten) der Produktphasen auftreten und
- eine zeitliche Abhängigkeit der Bildung der Produktphasen nachweisbar ist.

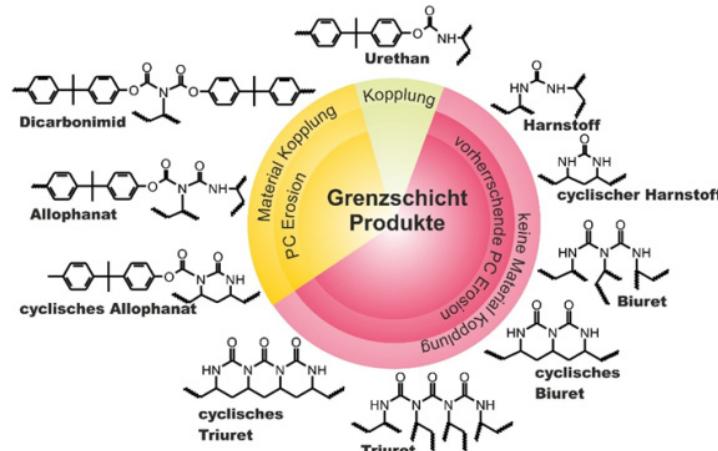
Nachfolgende Arbeiten konzentrieren sich auf die Übertragung der Kenntnisse auf den reaktiven Verarbeitungsprozess und damit die Herstellung von Verbunden mit gezielt einstellbaren Adhäsionseigenschaften.

Kooperation:

Prof. G. Steiner, Klinisches Sensoring und Monitoring, Technische Universität Dresden,  
Prof. V. Sablinskas, Universität Vilnius, Litauen

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**Abb. 2:**  
Aminolyseprodukte PC mit PVAm und deren Einfluss auf die Verbindung der Materialien



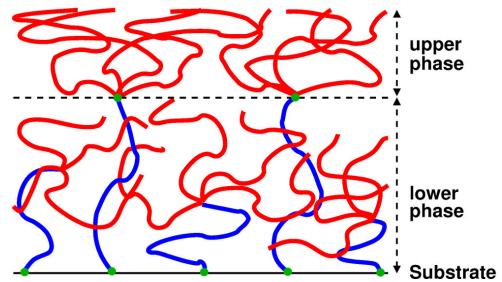
# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

**Keywords**  
polymer brushes  
dendrimers  
MD simulations

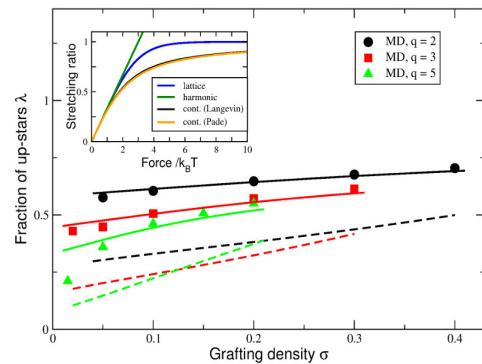
## Brushes made of dendritic polymers: Theoretical models and computer simulations

Holger Merlitz, Jens-Uwe Sommer

The theory of polymer brushes, composed of linear polymers, which are densely grafted onto a substrate, has been thoroughly investigated during the past decades. More recently, brushes made of polymers of rather complex architectures have moved into the focus of research. In fact, numerous biological systems are featuring brush-like interfaces with branched structures, and advances in the synthesis of dendrimers with well defined properties are opening new opportunities for the design of functionalized surface layers. Among the most striking differences between brushes made of linear chains and those made of dendritic polymers is the increased complexity of the latter: To balance the vertical density profile, a certain fraction of dendrimers has to retract into the lower parts of the brush, while others are stretching up to the surface. Such a vertical partitioning of the molecular conformations – the result of a spontaneous symmetry breaking – has been observed in recent numerical lattice-based self-consistent field (SCF) computations [1, 2] and in molecular dynamics (MD) simulations of our group [3]. Unfortunately, simple theoretical models so far resisted both a qualitative and a quantitative description of these structural features. With the development of our dual-phase mean-field model in continuum space [4], that gap had been closed, and as a consequence, similar dual-phase models, based on lattice space descriptions of the dendrimers, have been presented [5, 6]. It turned out that these new theoretical tools were consistently predicting some of the basic brush properties such as layer thickness or density, while they differed rather significantly in their partitioning fractions of extended and retracted molecules, i.e. in the internal structure of the brushes. Moreover, even rather sophisticated simulation studies using numerical lattice-SCF and MD simulations yielded inconsistent results for these population fractions [7, 6].



**Fig. 1:**  
**Dual phase MF model for a brush made of starlike polymers:** The upper phase consists of arms of the extended star population, while the lower phase accommodates the retracted stars [8]



**Fig. 2:**  
**Fraction of extended starlike polymers as a function of grafting density for different functionalities q.** MD-simulations (data points) and continuum space MF-theory (solid curves) agree, but a lattice-based MF model (dashed curve) differs considerably [8]

In a recent review article, we have summarized the state of the art of the theory of dendrimer brushes with a comparison of currently available models and their predictions [8]. In this work, convincing evidence is given that the differences in elasticity of the polymers, which arise from the respective model assumptions (lattice space vs. continuum space), are among the main reasons for the observed inconsistencies. In fact, lattice polymers, despite of their finite extensibility, are, over a wide range of stretching ratios, softer than polymers in continuum space [9], which leads to differences in the total free energy of the brushes at a given partition of their molecules. The lattice-chain (blue) is softer than the continuum space chain (yellow).

# Funktionale nanostrukturierte Grenzflächen und Polymersysteme

In another recent study, in which a comparison of the corresponding predictions for brushes near the  $\Theta$ -point is carried out, we have interchanged lattice- and continuum space contributions to the free energy models and obtained considerable deviations in the resulting population fractions [10]. Yet, these variations were still insufficient to account for the full quantity of differences which are observable in corresponding numerical simulations. This implies that additional effects of the volumetric interactions between the monomers are contributing to the structural features of branched polymer brushes. In summary, we are now in the possession of an entire toolbox of theoretical models to describe brushes made of branched polymers. In certain parameters - prominently the partition fractions of molecules that are either in extended or retracted states - i.e., the vertical stratification of these brushes, the models yield different predictions. A reliable model of the internal structure of these brushes is necessary in order to arrive at accurate predictions of their potential as environment-responsive surface layers, and their characteristic features of switching properties under well defined conditions. Experimental data, which would allow quantitative comparisons with theoretical predictions, are currently unavailable, but systematic studies of the characteristic differences between theoretical approaches are continuing.

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## Sponsor:

Deutsche Forschungsgemeinschaft (DFG),  
SPP 1369, NSF China, Grant No. 11274258, 111-  
Project (B16029)

## Co-operation:

Prof. C.-X. Wu, Department of Physics, Xiamen  
University, China