

Funktionale nanostrukturierte Grenzflächen und Polymersysteme



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Auch 2013 wurden wichtige Beiträge zur Entwicklung von Funktionspolymeren und nanostrukturierten (Hybrid-)Materialien für Zukunftstechnologien geleistet. Sichtbar wurde das insbesondere durch erste Ergebnisse, die in der engen Zusammenarbeit mit dem neuen Exzellenzcluster cfaed der Technischen Universität Dresden erarbeitet wurden. Sie betreffen neuartige, sehr gut verarbeitbare und effektiv vernetzbare organische Dielektrika für OFETs und neue hochverzweigte Polymere mit hohem Brechungsindex für eine effektive Lichtauskopplung bei OLEDs (Macromol. Rapid. Commun. 34, 2013, 1772). Sehr vorteilhaft ist hier, dass die Materialien durch die Kooperation mit Partnern aus der Physik und der Elektrotechnik anwendungsrelevant in Modell-Devices getestet werden konnten. Durch eine exzellente Kombination von experimentellen und theoretischen Arbeiten gelang es zudem, die Abhängigkeit der Lichtabsorption in dünnen Schichten von der Orientierung der Moleküle besser zu beschreiben und zu verstehen (J. Phys. Chem. C 2013, 117, 17285). Zum Thema „Tuning the Properties of NanoCarbon with Fluorination“ startete Ende 2013 ein vom IPF koordiniertes EU-Projekt (NanoCF), das zum Ziel hat, durch Fluorierung graphenartige Schichten mit verbesserten elektronischen Eigenschaften zu entwickeln. Die IPF-Beiträge zur Materialentwicklung im Bereich der Organischen Elektronik konnten ebenfalls sehr erfolgreich bei der Semicon/Plastic Electronics 2013 innerhalb des Organic Electronics Saxony Gemeinschaftsstandes präsentiert werden.

Hohe Aufmerksamkeit erfuhren die Aktivitäten auf dem Gebiet der stark verzweigten Polymere. Dr. Dietmar Appelhans wurde für seine Arbeiten zu „Dendritischen Glycopolymere als vielseitige Materialien für biomedizinische, analytische und materialwissenschaftliche Anwendungen“ mit dem Innovationspreis des IPF und seines Fördervereins ausgezeichnet. In intensiven Kooperationen mit Partnern aus dem Dresdner Raum sowie Gruppen in Polen und Spanien konnte ein deutliches Anwendungspotential dieser Materialien für biomedizinische Fragestellungen herausgearbeitet werden.

Eine fundamentale Fragestellung zum Lösungsverhalten von verzweigten Polymeren wurde in der prominent publizierten Arbeit „Is the universal law valid for hyperbranched polymers?“ (Angew. Chem. Int. Ed. 2013, 52(17), 4659) adressiert. Auch das International Symposium on Separation and Characterization of Natural and Synthetic Macromolecules, das erstmalig in Dresden von Frau PD Dr. Albena Lederer ausgerichtet wurde, legte einen Schwerpunkt auf komplexe, oft auch verzweigte Polymerarchitekturen.

Wie sich die Nanostruktur und deren Funktion mithilfe von Blockcopolymeren steuern lässt, konnte 2013 insbesondere bei der regelmäßigen Anordnung von Nanopartikeln im Film und an Grenzflächen gezeigt werden (Adv. Funct. Mater. 2013, 23, 483, Chem. Mater. 2013, 25, 158). Die Möglichkeiten der Nanostrukturierung von Polymermaterialien konnten sehr gut für die Entwicklung poröser Kathoden für Lithium-Schwefel-Hochleistungsbatterien genutzt werden. Blockcopolymere wurden aber auch zur Herstellung von funktionalisierten Membranen mit vorteilhaften Antifouling-Eigenschaften eingesetzt (J. Mater. Chem. B, 2013, 1, 3397). Die Adsorption von Modellproteinen konnte dabei bei günstigen Trenneigenschaften und Wasser-Durchflussraten deutlich reduziert werden. Die vielfältigen Aktivitäten und die Kompetenz zu Polyelektrolyten wurden in zwei Büchern dokumentiert (Polyelectrolyte Complexes in the Dispersed and Solid State, Part I: Principles and Theory and Part II: Application Aspects, Vol. 255 and 256, M. Müller (Ed.)) und in zwei am IPF veranstalteten Seminaren präsentiert (Biopolymere zur Anwendung in der fest/flüssig-Trennung, November 2013; Biopolymere und Polymere – Charakterisierung und Nutzung zur Stabilisierung und Destabilisierung von Suspensionen und Emulsionen, November 2013). Großes Interesse bei der Industrie fand auch die Simulation des Benetzungs- und Anschmutzverhaltens von Textilien.

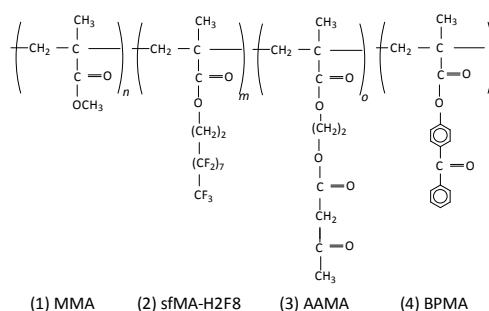
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Tailored methacrylate copolymers for anti-biofouling coatings

Doris Pospiech, Sandra Starke, Tobias Bünker, Anne Wollenberg, Felix Müller, Ulrich Oertel, Ralf Frenzel, Frank Simon, Karina Grundke

Research on anti-biofouling coatings has a long tradition at IPF. In recent years, reports appeared on surfaces with immobilized enzymes for removal of biomolecular films [1], stimuli-responsive surfaces for marine anti-biofouling [2] resulting from the EU project AMBIO [3], as well as numerous reports on superhydrophobic surfaces which were additionally discussed for use in anti-biofouling applications. Based on a former study by Frenzel et al. [4], we developed a family of methacrylate copolymers with different functional comonomers for combined anti-biofouling/fouling-release coatings. Following the concept of fouling-release surfaces with resistance to cell adhesion and the ability to reject dead biologic material as developed by C. K. Ober et al. [see, e.g. [5]]., random copolymers with functional comonomers were created to achieve anti-biofouling activity on transparent glass coatings. Thus, the widespread anti-biofouling problem occurring everywhere that includes diverse biofilm formation [6] was restricted to freshwater biofouling in order to limit the large number of influencing parameters and to elucidate correlations between the chemistry of the coating and the anti-biofouling efficiency. The copolymers included four comonomers: (1) methyl methacrylate (MMA) for mechanical strength, transparency and adhesion to glass substrates; (2) the semifluorinated methacrylate sfMA-H2F8 able to form self-organized films with very low surface free energy [7] for release of foulers (note that this monomer will not be bio-accumulated in contrast to completely perfluorinated compounds due to the possible degradation of CF₂ groups adjacent to CH₂- [8]); (3) 2-acetoacetoxyethyl methacrylate (AAMA) to form complexes with metal ions acting as biocide which was used to reduce the total necessary concentration of metal ion biocides drastically because it is only contained in the outer surface of the coating, and, (4) 4-benzoylphenylmethacrylate (BPMA) as UV-cross-linkable unit to achieve films with long-

term stability in water (chemical structure of the random copolymers given in Figure 1).



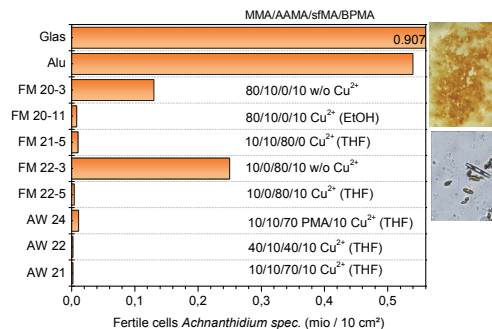
Series of copolymers with different composition were prepared by radical copolymerization and the formation of random copolymers was shown. The molar masses were high enough to ensure preparation of mechanically stable films. These films were spin-coated on glass and aluminum substrates, followed by drying and UV-cross-linking. The occurrence of cross-linking was demonstrated by insolubility of free-standing films [9]. The cross-linked polymer films were treated by solvent annealing with Copper(II)acetate in THF to generate Cu(II) complexes. X-ray photoelectron spectroscopy (XPS) revealed after thorough washing Cu concentrations in the range of 5 wt.-% in the top 10 nm surface. Complexation was indicated by UV-VIS spectroscopy in solutions of AAMA monomer with varying concentration of dissolved copper salts [12]. Cross-linked films with different contents of sfMA as soft, extremely hydrophobic building unit were tested for their anti-biofouling efficiency with typical freshwater foulers, namely *Achnanthydium spec.* (diatom algae) as important example for biofilm-forming freshwater algae, *Desmodesmus subspicatus* (green algae), as well as *Staphylococcus aureus* as typical representative for surface adherent bacteria. AAMA-containing copolymers were examined as Cu(II) complexes and compared to copolymers without Cu(II) treatment. Fig. 2 illustrates the results found for *Achnanthydium spec.* after 7 days of incubation. It can be demonstrated that *Achnanthydium spec.* reacts very sensitive even to very small total amounts of Cu complex in the coatings yielding a significant drop by several orders of magnitude, but also non-treated surfaces showed reduction of diatoms [9].

Keywords
anti-biofouling
freshwater fouling
methacrylate copolymers
staphylococcus aureus
achnanthydium species

Fig. 1:
Chemical structure of the copolymers designed to prevent freshwater biofouling

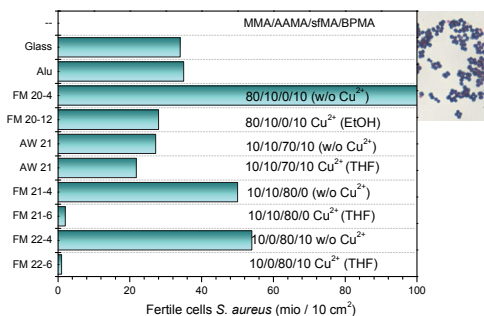
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Fig. 2:
Biofouling results with *Achnanthyidum spec.* on different methacrylate copolymers on glass and aluminum substrates with and w/o Cu^{2+} treatment



Coatings with higher molar contents of the semifluorinated methacrylate gave an additional reduction effect, while substitution of sfMA by the also hydrophobic pentyl-MA was counterproductive. Growth of *Desmodesmus subspicatus* after 7 days incubation could be suppressed to 5-15 %. Figure 3 shows that also the growth of bacteria *S. aureus* (after 24 h incubation time) is moderately inhibited by Cu(II) -containing methacrylate copolymers. The effect is not as pronounced as for *Achnanthyidum spec.* which can be explained by the fact that diatoms are 10-1000 fold more susceptible to Cu as growth inhibitor than bacteria. Moreover, it depends very strongly on the mode of preparation. Incorporation of semifluorinated units also seems to add a positive effect.

Fig. 3:
Results of biofouling experiments on copolymer surfaces with *S. aureus*



In summary, the results obtained so far support the concept of combined biocide/-fouling release. The Cu(II) complexes formed at the outer surface of the polymer coatings did not appear as stable as expected and a certain leaching was observed over time. Thus, it is intended to open the window to new types of monomers adding biocide functions directly to the copolymer. The research will be further pursued in projects with IDUS, BTU and University of Braunschweig with possible applications of other fouling types.

Collaborations:

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Prof. K. Salchert, Brandenburgische Technische Universität Cottbus, Organische Chemie und Naturstoffchemie, Senftenberg, Germany

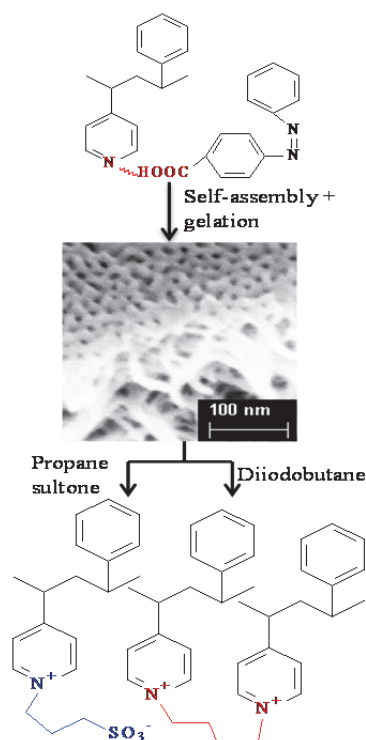
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Antifouling and antibiofouling pH responsive block copolymer based membranes by selective surface modification

Bijay P. Tripathi, Nidhi C. Dubey, Soumyadip Choudhury, Frank Simon, Manfred Stamm

Responsive membranes with nanopores that could be opened and closed by change in environmental condition received much attention in recent past for the applications ranging from water purification to drug delivery. Block copolymers are promising materials for fabricating high throughput and improved amphiphilic responsive filtration membranes. Although nanoporous membranes based on block copolymers offer great chemical tunability, limitations in thermal stability, mechanical performance, and solvent resistance can thwart even broader applications. In order to use these membranes for the filtration of aqueous solutions, additional functional groups inside the pores and on the surface of the membrane may give improved properties with the opportunity for various other applications.



In this work we described a unique and simple approach for the fabrication and selective surface modification of pH responsive PS-P4VP block copolymer based nanoporous membranes with antifouling and antibiofouling property. The isoporous membranes were prepared by combining the supramolecular self-assembly of HABA-PS-P4VP block copolymer complex and nonsolvent phase inversion. Further, the surfaces of prepared membranes were selectively modified by crosslinking quaternization with diiodobutane and zwitterionization with propane sultone under temperature and vacuum condition to achieve highly antifouling and antibiofouling membranes (Fig. 1).

The structure and functionalization of membranes were characterized by different analytical and physico-chemical techniques. Asymmetric structure and ultraporosity of membranes was established by SEM imaging (Fig. 1). The pH responsiveness of the membranes was retained after modification which was proved by water flux measurement under different pH values.

Keywords
pH responsive
membrane
water purification
antifouling
antibiofouling

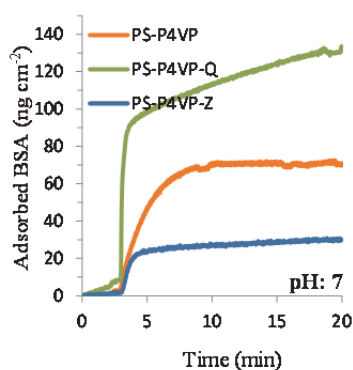


Fig. 1 (left):
Schematic of membrane
preparation and
modification

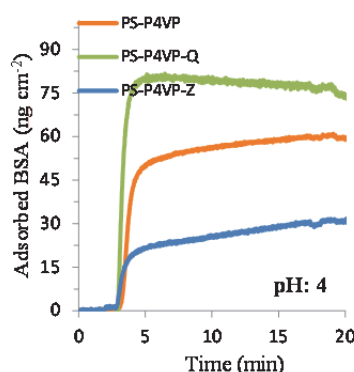


Fig. 2 (right):
Protein adsorption
experiment. by QCM at pH 7
and 4

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Keywords

block copolymers
self-assembly
nanoparticles
periodic arrays
dual nanomaterials
patterning

The performance of these membranes was evaluated with respect to pure water flux, protein fouling by adsorption and filtration, as well as dye rejection properties. The surface modifications of membranes lead to the development of highly antifouling (zwitterionic modification) and antibiofouling (quaternization modification). The protein adsorption data obtained by QCM study is depicted in Fig. 2, clearly indicate that the zwitterionic membrane possess lowest adsorption. The antibacterial property of the membranes was assessed with live/dead staining and fluorescence imaging (Fig. 3). The quaternized membranes showed maximum antibacterial property. > 98% rejection of congo red dye with these membranes reflects its suitability for water purification and separation applications.

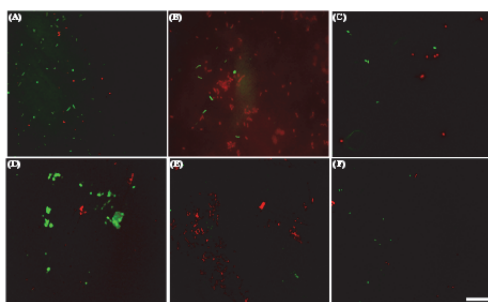


Fig. 3:
LIVE/DEAD fluorescence microscopy images of *E. coli* and *S. epidemidis* on: (A&D) PS-P4VP; (B&E) PS-P4VP-Q; (C&F) PS-P4VP-Z surfaces. The length of the scale bar is 20 μm .

Sponsor:

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A step-wise approach for dual nanoparticle patterning via block copolymer self-assembly

Andriy Horechyy, Petr Formanek, Ulrich Oertel, Manfred Stamm

An application of block copolymers (BCP) for patterning of nanomaterials, such as ordered placement of nanoparticles (NP) of various size, shape and composition into polymer matrix has attracted significant interest of many research groups. Thanks to the variety of morphologies available whose length scale and periodicity can easily be tailored, the BCP have been widely used for the fabrication of hybrid functional nanocomposites containing metal, metal oxide nanoparticles, quantum dots or nanorods, etc. Different experimental approaches have been developed for selective incorporation of NP in one of the BCP micro-domains. Supported by theoretical studies, the binary NP/BCP composites are well established as for today. In contrast, incorporation of two different types of nanoparticles in different domains of the self-assembled BCP matrix is still a challenge.

Here we demonstrate a novel step-wise approach for fabrication of periodic arrays of two different types of nanoparticles (NP1, NP2) selectively localized at different domains of self-assembled block copolymer matrices.[1] Schematically the whole process is shown in Fig. 1. In the first step, polymer-capped NP1 (e.g. AgNP with grafted polystyrene (PS) shell) are mixed with poly(styrene-block-vinylpyridine) (PS-b-PVP) block copolymer in common solvent and cast onto the substrate as thin films. After subsequent solvent annealing, NP1 selectively localize within the PS phase of the self-assembled BCP due to the preferential interaction between the PS shell of the NP1 and PS chains of the BCP. In the second step, water-soluble citrate-stabilized NP2 (i.e. AuNP, PtNP, PdNP) are directly deposited on the PVP domains of NP1/BCP thin films from their aqueous solutions. In such a way, nanostructured thin films with two types of nanoparticles separated by the two distinct block copolymer phases are prepared in a step-wise manner (Fig. 2).

One of the advantages of our approach is that characteristics of either type of nanoparticles can be programmed in advance, which is more

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difficult to achieve for example, when the nanoparticles are prepared in situ. An application of two different methods for nanoparticle incorporation minimizes the nanoparticle clustering and aggregation readily observed for the NP/BCP composites, especially for such with high particle loading [2]. The properties of such ternary NP1/NP2/BCP composites can be easily tuned by changing the nanoparticle loading fraction (NP1) and/or nanoparticle deposition time (NP2) (Fig. 3). The presented method is very simple and well reproducible and can be transferred for various combinations of pre-synthesized nanoparticles and BCP morphologies, leading to development of new functional nanomaterials with mixed functionality originating from either type of nanoparticles.

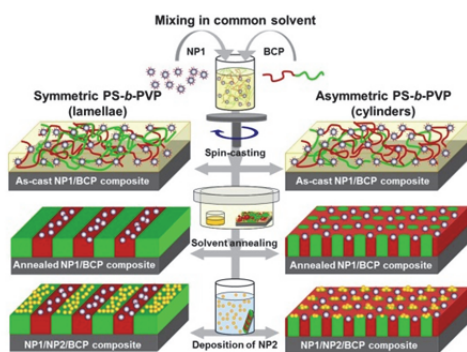


Fig. 1:
Schematics of step-wise approach used for fabrication of ternary NP1/NP2/BCP composites.

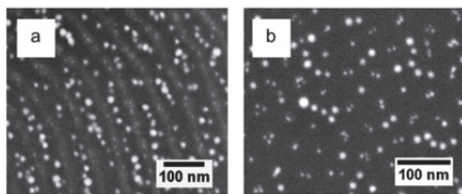


Fig. 2:
SEM images of ternary AgNP/AuNP/PS-b-PVP composites with lamellar (a) and cylinder (b) morphology with different types of nanoparticles localized in different BCP microdomains of self-assembled BCP matrix; due to the difference in size both larger AgNP (d~13 nm) and smaller AuNP (d~3 nm) can be directly visualized distinguished on SEM images.

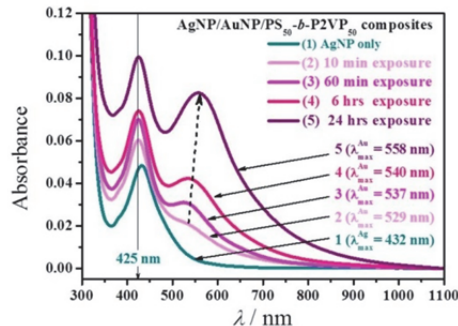


Fig. 3:
UV-Vis spectra of AgNP/AuNP/PS-b-PVP composites loaded with different amount of AuNP (different particle deposition time); the position of plasmon peak originating from gold nanoparticles is red-shifted with an increase of AuNP content.

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Keywords
polyelectrolyte
complexes
CaCO₃, microparticles
poly(2-acrylamido-2-methylpropanesulfonic
acid-co-acrylic acid)
chondroitin 4-sulfate

Nonstoichiometric polyelectrolyte complexes versus polyanions as templates on CaCO₃- based composites synthesis

Simona Schwarz, Frank Simon

Calcium carbonate is an important mineral in nature, having three crystalline polymorphs: calcite, aragonite, and vaterite. Most of the research with respect to CaCO₃ focused in understanding formation of inorganic microparticles in saturated solutions, precipitation kinetics, mechanisms of crystallization and transformations between polymorphs. Organic molecules have the ability to control nucleation of CaCO₃ polymorphs and to organize their growth into desired patterns by controlling hierarchically their structure, shape, size, and orientation [1-3].

Even if there are numerous studies on polyanions control on CaCO₃ growth, the use of nonstoichiometric polyelectrolyte complexes (NPEC) as templates for controlling CaCO₃ crystals growth was not reported before. Polyelectrolyte complexes are obtained by mixing aqueous solutions of oppositely charged polymers; at relatively low concentrations and when one of the components is taken in excess, their formation can lead to colloidal dispersions [4-6]. This study followed the CaCO₃/polymer composite microparticles formation using even some polyanions or NPEC with negative charges in excess (NPEC-n) [7]. We used two polyanions – poly(2-acrylamido-2-methylpropanesulfonic acid-co-acrylic acid) (PSA) and chondroitin-4-sulfate (CSA) – and chitosan as polycation. The influence of polyanion structure, relative inorganic/polymer ratio, tuned by initial solution supersaturation, polymer concentration, and NPEC molar ratio, were investigated. The polymer presence on the composite particle surfaces was evidenced by XPS, and particles charge density and zeta-potential (ZP) [7]. Increasing the inorganic concentration from 0.05 to 0.3 M the particles sizes increased, irrespective of polyanion structure. For the same inorganic concentration, more negatively charged particles were obtained with PSA, probably due to a better polyanion distribution in composite material as a consequence of its flexible chain. Increased amount of PSA increases the polymer content

on the particles surfaces, and therefore a lower content in the inorganic phase (decrease of the relative concentration of calcium expressed as [Ca]:[C]spec). By contrary, the relative calcium concentration increased with CSA concentration increase, the polymer being more uniform embedded into the composite. The chain structures of CSA and PSA were 3D optimized and their interaction with Ca²⁺ ions is represented in Fig. 1.

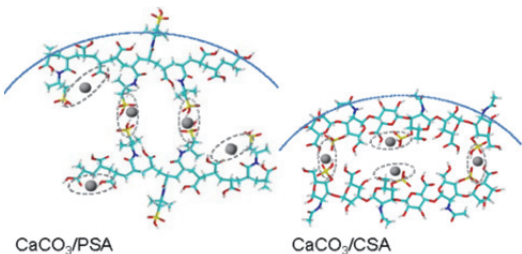


Fig. 1:
3D optimized chain structures of CSA and PSA and their interaction with Ca²⁺ ions

Different ionic crosslinks in CaCO₃/PSA composites can occur: inter-chains, between –SO₃– groups of different PSA molecules, and intra-chain, between –SO₃– and –COO– or two –COO– groups on the same polymeric chain. On CaCO₃/CSA composites, inter-chains crosslinks between –SO₃– groups of CSA and intra-chain between –SO₃– and –COO– groups on the polymer chain are expected. Thus, the composites with PSA may have on the surface some free –SO₃– groups, whereas with CSA the –SO₃– groups are located inside the particles, on the surface being evident amide groups, as shown by XPS [7].

Some characteristics of NPEC-n dispersions and of CaCO₃/NPEC based composites are summarized in Table 1.

polya -nion	n ⁻ /n ⁺	NPEC-n		CaCO ₃ /NPEC	
		ZP ^b , mV	D _n ^c , nm	ZP ^b , mV	D ^d , nm
PSA	0.2	-26.1	172.1	-11.6	10.75
	0.4	-21.5	184.8	-11.4	10.85
CSA	0.2	-30.2	309.9	-12.4	11.40
	0.4	-22.9	323.7	-12.3	11.45

Table 1:
Some characteristics of NPEC-n and of CaCO₃/NPEC based composites

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For the same n/n^* higher values of D_h and ZP were obtained when CSA was used as polyanion. As both polyanions has the same kind of ionic groups in 1:1 ratio, the differences can be ascribed to the polymeric chain structure: PSA is flexible, whereas CSA is semi-rigid. Compared with the starting NPEC-n dispersions, ZP of the particles sharply decreased after composite formation up to close to bare CaCO_3 (~ 10.2 mV). This can be considered as hint of the good NPEC-n embedment into the composites. Higher particles sizes were obtained when NPEC-n were used, compared with the particles prepared with the same polyanions. Complex nanoparticles may restrict the CaCO_3 growth, even if the polyanion in excess can act as ligand for NPEC and CaCO_3 nanocrystals. Fig. 2 shows some SEM images of composite particles with polyanion and NPEC.

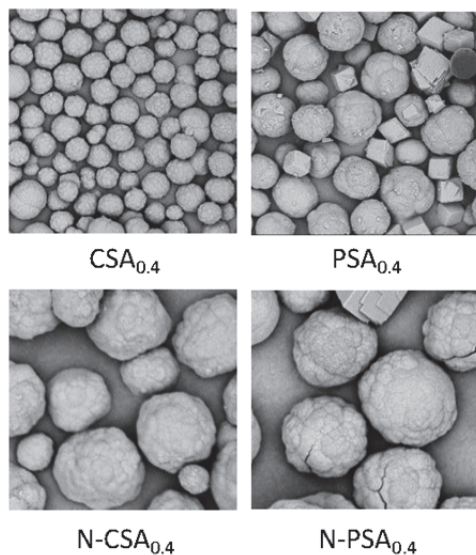


Fig. 2:
SEM images of composite particles prepared with polyanions or NPEC

The particles surface morphologies are very similar for NPEC based composites (Fig. 2), irrespective of polyanion structure, and differs from that of particles prepared with polyanion as template. These findings are in agreement with the values of parameters listed in Table 1, when almost the same values were obtained for the investigated parameters, for all NPEC tested as template in CaCO_3 composite synthesis.

Cooperation:

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Funktionale nanostrukturierte Grenzflächen und Polymersysteme

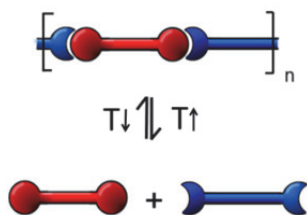
Keywords
self-healing
temperature dependent
SEC
Diels-Alder reaction

In-situ Untersuchungen dynamisch bindender Polymere für selbstheilende Materialien

Josef Brandt, Alben Lederer

Die Anforderungen an moderne Materialien werden immer höher, da sie für stetig komplexer werdende Anwendungen maßgeschneidert sein müssen. Selbstheilende Materialien sind aktuell Gegenstand umfassender Forschungsaktivitäten, da es vielseitige Einsatzgebiete solcher Stoffe gibt und so große Nachfrage vorhanden ist. Konzeptionell beruhen selbstheilende Materialien entweder auf der Einbettung von Heilungsagencien (extrinsisches Heilen) oder dem Einbringen der Fähigkeit zur internen Reorganisation durch reversible und damit dynamische Bindungen, welche kovalent oder auch nicht-kovalent sein können (intrinsisches Heilen). Das Erreichen des intrinsischen Heilungseffektes wird intensiv in vielen Variationen angestrebt, da so, im Gegensatz zu extrinsischem Heilen, homogenere Materialien entstehen und mehrfaches Heilen möglich wird. Abb. 1 zeigt eine thermoreversible Polymerisation, wie sie oft als Ansatz für temperaturinduzierte intrinsische Selbstheilung genutzt wird. Im Falle einer reversiblen Polymerisation über die häufig benutzte Diels-Alder (DA)-Reaktion erfolgt die Polymerisation bei niedrigen und die Depolymerisation bei hohen Temperaturen [1].

Abb. 1:
Schematische Darstellung einer thermoreversiblen Polymerisation



Bei der Entwicklung neuer selbstheilender Polymere ist neben dem synthetischen Aufwand auch die umfassende Analytik der dynamischen Prozesse eine Herausforderung, um Struktur-Eigenschaft-Beziehungen aufzuklären. Diese sind nötig, damit Materialien an Anforderungen spezieller Anwendungen angepasst werden können. Dynamische Bindungsreaktionen von Polymeren können effektiv über die Analyse der Molmassen bzw. der Molmassenverteilungen charakterisiert

werden, welche mithilfe von Größenausschlusschromatographie (SEC) ermittelt werden. Wir arbeiten mit temperaturabhängiger SEC (TD-SEC), um thermoreversible Prozesse in situ verfolgen zu können. Der Aufbau der SEC-Anlage (Abb. 2) ermöglicht es, eine Probe eine beliebige Zeit bei einer gewünschten Temperatur in der Injektionseinheit zu halten und anschließend sofort zu messen, ohne Lösemittel oder Temperatur ändern zu müssen. Dadurch wird der Einfluss störender und ergebnisverfälschender Nebeneffekte minimiert, da Reaktion und Analytik unter identischen Bedingungen erfolgen können.

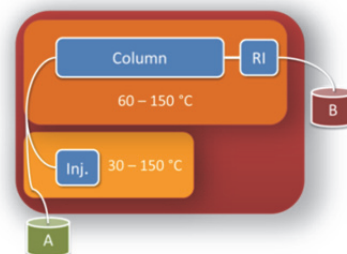


Abb. 2:
Aufbau der GPC im temperaturabhängigen Modus
(A: Eluent, Inj.: Injektionseinheit, RI: Brechungsindexdetektor, B: Abfall)

Auf diese Art kann der Verlauf der Reaktionen kinetisch verfolgt und deren Vollständigkeit durch quantitative Auswertung der Chromatogramme ermittelt werden. Die Methode ist bei der Art der Analyten sehr tolerant und kann somit prinzipiell für viele verschiedene Problemstellungen benutzt werden [2]. In aktuellen Forschungen wurde sie bereits erfolgreich für die Aufklärung von Effekten zur Kontrolle der thermoreversiblen DA-Reaktion genutzt [3].

Abb. 3 zeigt die ermittelte Vollständigkeit der retro-DA-Reaktion („Bonding Decrease“) in Abhängigkeit von Temperatur und Größe der Strukturblöcke zwischen den Diels-Alder-Funktionalitäten. Zusätzlich konnte die Reversibilität von DA-Reaktionen mittels DLS nachgewiesen werden, da der hydrodynamische Radius ein guter qualitativer Indikator für die Bindungsreaktionen ist (Abb. 4) [4].

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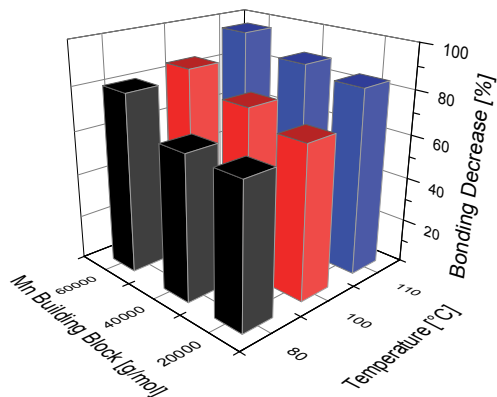


Abb. 3:
Einfluss von Molmasse der Strukturblöcke und Temperatur auf die Vollständigkeit der retro-DA Reaktion

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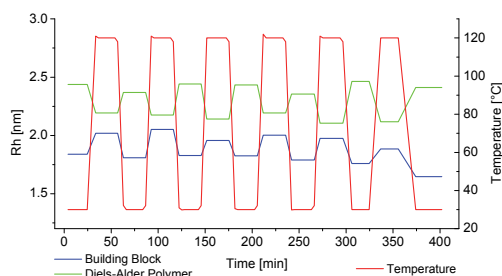


Abb. 4:
Hydrodynamischer Radius des DA-Polymers und Building-blocks in Abhängigkeit der Temperatur bestimmt mittels dynamischer Lichtstreuung (DLS) (Polymerisation jeweils bei 30 °C, Depolymerisation bei 120 °C)

Die gewonnenen Erkenntnisse sind für die Entwicklung speziell angepasster dynamisch bindender Polymersysteme von großer Bedeutung.

Kooperationen:
Prof. Dr. C. Barner-Kowollik, Karlsruhe Institute of Technology (KIT)
Dr. F.-G. Schmidt, Evonik Industries AG

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Keywords

graphite fluoride
room-temperature
fluorinated graphite
fluorine pattern
solid-state NMR
DFT calculations

Fluorine patterning in room-temperature fluorinated graphite determined by solid-state NMR and DFT calculations

Anastasia Vyalikh, Ulrich Scheler

2D crystals have recently drawn considerable attention for both the investigation of fundamental physical properties and for the implementation in the next generation of electronic devices. Of particular interest is graphene, a single-layer carbon compound, characterized by numerous spectacular properties. However, despite the advantages determined by its unique electronic properties, the absence of a band gap has limited its applicability in electronics. Fluorination of the surface of graphene allows to open and to control the band gap, thus the fluorinated graphene becomes a more interesting electroactive wide band gap material than the pristine graphene. It has been shown that electronic, optical, and magnetic properties of fluorinated graphite and fluorinated graphene can be tuned by the fluorine content and the fluorination pattern.

To get insight into a mechanism of pattern formation upon room-temperature fluorination we studied acetonitrile-intercalated graphite fluorides C_2F_x (Fig. 1) using a combination of high-resolution solid-state nuclear magnetic resonance (NMR) and density functional theory (DFT) calculations. The ^{13}C MAS NMR data confirmed that the room-temperature fluorination has not changed the planar configuration of the graphite sheets and that all carbon sheets were subjected to fluorination. However, in the material with the lowest fluorination degree, graphite-like domains have been found. We modelled different fluorination patterns on a graphene plane, whose geometries have been allowed to optimize, and their ^{19}F NMR parameters have been calculated by DFT. Comparing the theoretical parameters with the experimental data allowed to assign the ^{19}F NMR spectra (Fig. 2) and to quantify the structural motives obtained upon fluorination. It has been found that all possible fluorination motives (including CF chains of both zigzag and armchair configurations, fluorinated cyclohexane rings, and isolated CF pairs) may exist in the

materials studied in the present work. Thus, our data exclude the presence of uniform structural motives, such as chains, in room-temperature fluorinated graphite. The ^{19}F NMR shielding parameters calculated in the present work can be used as classification criteria for assignment of ^{19}F NMR chemical shifts in fluorinated carbon materials. The results obtained in the present work provide a basis for predicting the electronic properties, dynamics, and energetics of fluorinated graphene and graphite materials.

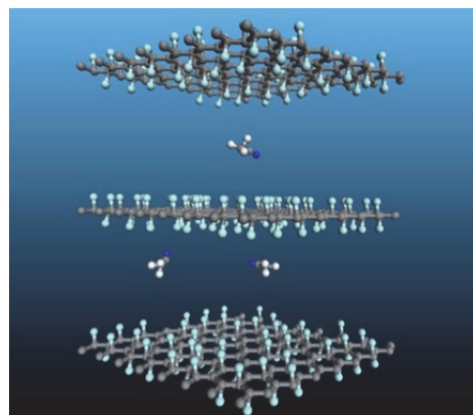


Fig. 1:
Structure of acetonitrile-intercalated graphite fluoride (Materials Studio, Accelrys®)

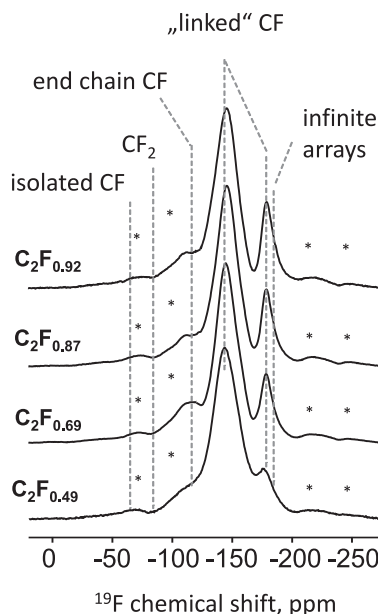


Fig. 2:
Experimental ^{19}F MAS NMR spectra (30 kHz) of acetonitrile-intercalated graphite fluorides

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Sponsor:

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Electroconductive carbon nanotube-cellulose composites for sensing application

Haisong Qi, Jianwen Liu, Shanglin Gao, Edith Mäder, Christina Scheffler

Science and technology have moved toward renewable raw materials and more environmentally friendly and sustainable resources and processes. As the most abundant natural polymer in nature, cellulose is widely used in textiles, papers, and fields of energy. Recent advances in nanomaterials and technologies are rapidly delivering new functional cellulose based materials containing nanoparticles over a broad range of applications. Carbon nanotubes (CNTs) have unique electrical, mechanical and thermal properties, and are widely used as reinforcing agents in polymers to fabricate electronic devices, sensors and so on.

In order to combine the excellent properties of both CNTs and cellulose, CNT-cellulose composites are fabricated by dissolving cellulose and dispersing CNTs homogeneously in aqueous alkaline-urea solution [1]. It is a simple, efficient and environment friendly process. The CNT-cellulose composite films prepared from this process are as flexible as normal papers (Fig. 1).

Keywords

cellulose
carbon nanotube
electroconductive
functional composites
biomaterials
sensors

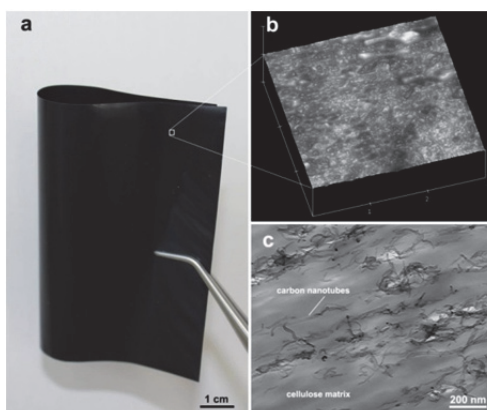


Fig. 1:
Morphology and
microstructure of the CNT-
cellulose film regenerated
from NaOH-urea aqueous
solution: a, photograph; b,
AFM image [X×Y×Z: 3 × 3 ×
0.8 μm³]; and c, TEM
image

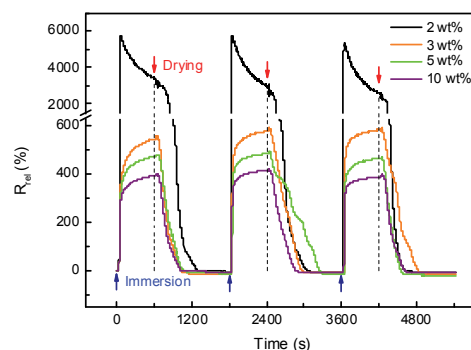
Uniform dispersion of CNTs, in combination with favourable CNT-cellulose matrix interaction, causes the better ductility and higher toughness of the materials, as well as the enhanced thermal stability. The network formation of CNTs in cellulose matrix not only introduced good conductivity to the materials,

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but also led to the impressive multifunctional sensing abilities to tensile strain, temperature and environmental humidity. Especially, the sensitivity of the films exhibits highly linear and repeatable correlation to tensile strain. The useful linear strain range for these films is 7 - 13 % strain with the value of gauge factor in the range of 0.6 - 1.2. This unique characteristic indicates their excellent sensing ability as strain gages.

Interestingly, these CNT-cellulose films have been shown to serve as highly sensitive, well reversible and reproducible sensors for water [2]. They exhibit rapid response and high sensitivity, with a sensitivity of 5500 ~ 500 % for films with CNT loading from 2 ~ 10 wt% (Fig. 2).

Fig. 2:
Relative resistance change (R_{rel}) of CNT-cellulose films with different CNT content during immersion/drying cycles in water/air (20 °C)



The sensibility of CNT-cellulose films is mainly caused by the hygroscopic swelling of the cellulose matrix. This unique performance is well reproducible and durable. Thus, these CNT-cellulose films offer a solution to sense liquid water in a reliable and efficient way, which can be widely used in many fields such as detection of water leakages and water content determination. Based on their unique characteristics and excellent sensing abilities, other forms (such as fibre, textiles, etc.) of CNT-integrated cellulose composites could also serve as water sensors, which provide the promise to design various smart materials.

By using the homogeneous dispersion of CNTs and cellulose in alkaline-urea aqueous solution, CNT-cellulose composite aerogels are fabricated by flash freezing-lyophilization process [3]. All the composite aerogels show both a nanostructured solid network (specific surface areas between 140 and 160 m²/g) and a broad pore size distribution (including macro-pore, mesopore and micropore) (Fig. 3).

They have good thermal stability and mechanical properties. The Young's modulus of them can be tuned to reach about 90 MPa. The CNT-cellulose aerogels with 3 - 10 wt% CNTs have an electrical conductivity of $2.3 \times 10^{-4} \sim 2.2 \times 10^{-2} \text{ Scm}^{-1}$. The conductivity threshold at CNT volume fractions of the CNT-cellulose aerogels is as low as 3×10^{-3} . Furthermore, these aerogels show good sensitivity to ambient pressure, which provides the potential for detection of gases or volatile organic compounds.

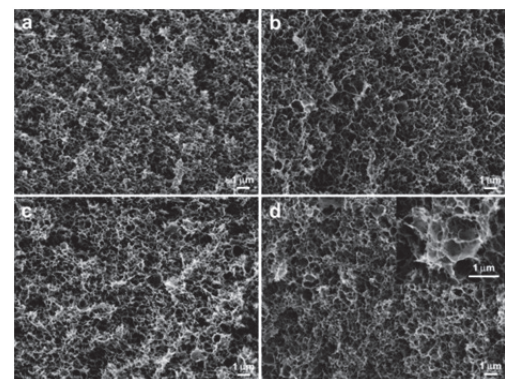


Fig. 3:
SEM images of the CNT-cellulose aerogels with different CNT contents: (a) 0; (b) 3 wt%; (c) 5 wt%; and (d) 10 wt%

Sponsor:
Deutsche Forschungsgemeinschaft,
"Multifunctional cellulose based fibres,
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Simulation of textile wetting using fluid implicit-particles (FLIP)

Alfredo Calvimontes

Spreading, wetting, penetration and capillary are topics of great interest to understand washing. Current models allow to understand wetting on relatively simple surfaces. However, it is necessary to study these phenomena using models that represent more realistically the morphology of the materials being studied. All mathematical methods and programs that simulate currents are based on equations describing fluid mechanics. Fluid simulations usually attempt to reproduce the effects of Navier-Stokes equations that describe fluid flow [Eq. 1]. A typical representation of the incompressible form of these equations, after some simplification, is:

$$\frac{\partial u}{\partial t} = f - (u \cdot \nabla)u - \frac{1}{\rho} \nabla p + \nu \nabla^2 u \quad (\text{Eq. 1})$$

$$\nabla \cdot u = 0 \quad (\text{Eq. 2})$$

where u is the velocity field, p the pressure term, f represents the external forces, ρ the density and ν the kinematic viscosity. The first term of the right side of Eq. 1 accounts for convection of the fluid, and the last term accounts for velocity diffusion due to the fluid's viscosity. The second equation ensures that the fluid is divergence free and thus incompressible.

Because of its complexity, computer fluid dynamics can only be solved using an iterative, numerical approximation, which requires a powerful computer. Calculation time varies, depending on the problem at hand, between fractions of seconds and months.

Fluid simulations are based on three fundamental concepts of fluid dynamics: the continuity, momentum and energy, i.e. mass conservation, Newton's second law, and conservation of energy. The forms of the equations could vary according to the following viewpoints of fluids: Lagrangian [2-4], Eulerian [3-4] and Lattice-Boltzmann. However, they are equivalent through some simple mathematical manipulations.

The FLIP (Fluid-Implicit Particle) algorithm uses Lagrangian particles to represent the

fluid and a Lagrangian grid of quadrilateral zones to calculate the intersections among the particles [5-7]. It is a mixture of a particle representation of the fluid and a grid for the solution of implicit moment equations. FLIP is formulated to give consistency between the solution of the Lagrangian equations of motion on the grid, and the equations of motion of the particles.

Using FLIP it is possible to simulate the interaction of liquid flows and solids. Topographical data obtained by any measurement method can be used during the simulation as solid substrate. Other solids can be also included in the simulation. The physical properties of the solids (density, center of mass, friction coefficient, etc.) and the liquid forces, as well as the gravity can be controlled during the simulation.

This method can be also used to simulate the interaction between liquids on a solid substrate. The physical properties of the FLIP-liquids (particle size, grid size, density, viscosity, internal pressure, friction coefficient, etc.) and the liquid forces, as well as the gravity can be controlled during the simulation. To simulate fabric wetting it is necessary to have a digitalized fabric structure. Depending on the purpose of the investigation, it is possible to use topographic maps obtained by means of optical methods, i.e. chromatic sensor, confocal microscopy, stereophotogrammetry, etc.

Textile surfaces can be also generated using mathematical methods or using Computer-Aided Design (CAD) software. Structure generators are more sophisticated programs to construct can do woven models with high synergy effects regarding discretization, visualization and property computation.

The combined simulation of various fluids (water, liquid soils), rigid dynamic solids (soil particles) and static solid substrates (textiles) may allow the study of washing phenomena and detergency by controlling physical variables, such as density, velocity, viscosity, pressure, temperature, roughness, porosity, adhesion/repulsion forces, etc. However, for now the most important limitations to the application of this method are the high hardware specifications and the extremely long computational time.

Keywords

textiles
wetting
fluids simulation
dissipative particle
dynamics

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Fig. 1:

A FLIP spot grows on a woven plain fabric surface by spreading and planar capillary. The simulation can be compared with the real fabric after soiling with a water soluble ink. As well as in the experiment, the FLIPs spread on the fabric filling firstly the void spaces above the wefts (horizontal yarns).

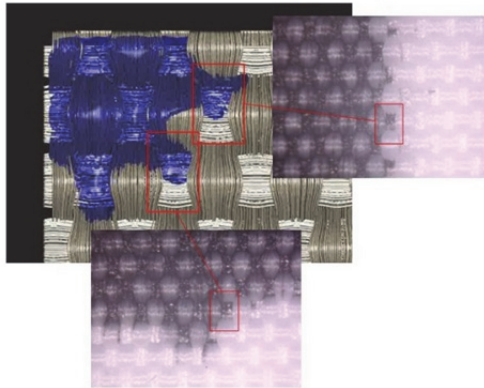
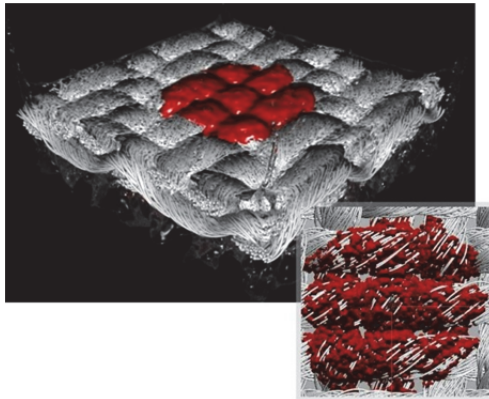


Fig. 2:

FLIP method can be used to simulate the effect of water flow through soiled fabrics by controlling the water velocity and pressure as well as the soil viscosity, soil-fabric adhesion and water-soil interaction forces. The simulation resulted in 10% of soil removal (frame).



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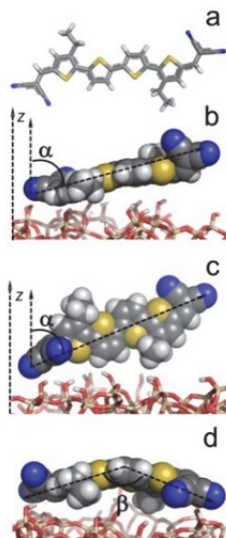
Adsorption layers of conjugated oligomers: The importance of oriented molecules for light absorption in organic thin films

Olga Guskova, Klaus-Jochen Eichhorn,
Jens-Uwe Sommer

The development of organic photovoltaics involves the design and application of new materials. Promising low band gap donor materials in small molecule solar cells, containing low-weight oligothiophenes have demonstrated rather high power conversion efficiencies [1]. In particular, functionalized quarter/sexithiophenes with electron-withdrawing dicyanovinyl end groups [DCV4/6T] exhibit enhanced electron affinity, which results in more efficient exciton dissociation in heterojunctions [2,3]. Along with subatomic design, the orientation of the molecules is a crucial parameter that affects the transformation of light into electricity.

In the present work different experimental and theoretical techniques are applied to study (i) how the chemical structure influences the molecular orientation in thin films of DCV4T-Et2 with two ethyl side chains at thiophenes one and four (the chemical structure of the material is presented in Fig. 1a) and DCV4T-Et2:fullerene blends on silica surface, (ii) how a nearly flat-lying orientation of DCV4T-Et2 in pristine and blended films can be reached, and (iii) what mechanism is responsible for the desired flat-lying molecular orientation, which is important to further improve the light absorption [4].

The morphology of the pristine DCV4T-Et2 and the mixed DCV4T-Et2:fullerene films is investigated by grazing incidence X-ray diffraction (GIXRD), variable angle spectroscopic ellipsometry (VASE) and atomic force microscopy (AFM). In Fig. 2a, the GIXRD pattern from the crystalline regions of the pristine DCV4T-Et2 films shows an intense Bragg reflection at $2\theta = 10.8^\circ$ and several very small reflections at larger 2θ angles. Accordingly, DCV4T-Et2 grows highly crystalline in a nearly flat-lying (DCV4T-Et2 molecule is 2.4 nm long, the Bragg reflection at $2\theta = 10.8^\circ$ can be originated by molecules which are 70° tilted with respect to the substrate normal) orientation in pristine thin films leading to strong thin film absorption.



In contrast to GIXRD, VASE can probe the mean orientation of all molecules in amorphous films. In Fig. 2b, the spectra of n (index of refraction) and k (extinction coefficient) of the pristine film are shown. Based on these data the mean tilt angle of the molecular transition dipole moment μ can be estimated. From the quantum chemical calculations [4] follows that the transition dipole moment of DCV4T-Et2 is aligned parallel to the molecular long axis. Hence, the mean tilt angle of μ is equal to the mean molecular tilt angle α . In pristine DCV4T-Et2 films the molecular tilt angle α is in the range of 70° (with respect to the substrate normal, Fig. 2b, c). This nearly flat-lying orientation is appropriate to induce high light absorption since μ is only tilted by 20° (in mean) to the electric field vector of the photon in the case of perpendicular illumination.

Complementary to the experimental findings, the molecular dynamics (MD) simulation results reveal two different orientations of the DCV4T-Et2 molecules: the first one is tilted configuration (Fig. 1 b, c); the last one includes almost flat-lying molecules (Fig. 1 d). In the latter case the molecule/substrate interactions slightly changes the rotational angle of the terminal functional groups and can lead to the small bending of the conjugated backbone. In both cases the longest molecular axis is oriented along the substrate. The molecular tilt angles are in a good agreement with the experimental results (Fig. 1 b, c).

Keywords
plastic electronics
multiscale simulation
thin films
morphology
oligothiophenes

Fig. 1:
(a) Optimized geometry of the DCV4T-Et2 molecule (quantum-chemical calculations, B3LYP/6-31G(d,p)-basis set) and (c-d) three typical orientations of a single DCV4T-Et2 with respect to the silica surface (MD snapshots, all-atomistic molecular dynamics simulation, PCFF-force field). Here z is surface normal, α - tilt angle between thiophene backbone and the z -normal. Panels (b, c) show the tilted molecules with $\alpha = 65.8 \pm 2.5^\circ$ and $53.4 \pm 1.9^\circ$, respectively. The bending angle $\beta = 157.2 \pm 1.1^\circ$, panel (d). Carbon is shown in grey, nitrogen in blue, sulphur in yellow, hydrogen in white, oxygen in red and silicon in beige. For more details see reference [4].

Funktionale nanostrukturierte Grenzflächen und Polymersysteme

Fig. 2:

(a) GIXRD patterns of 100 nm thin pristine DCV4T-Et2 film and (b) anisotropic optical constants modeled from VASE data. For more details see reference [4]

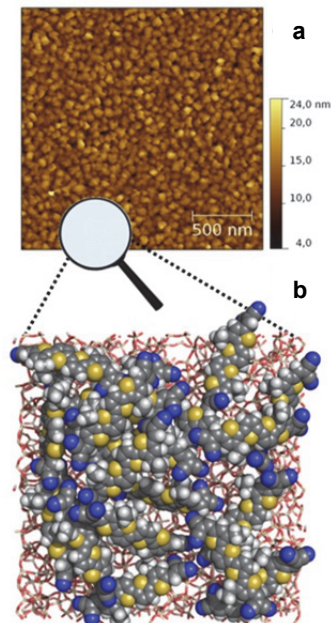
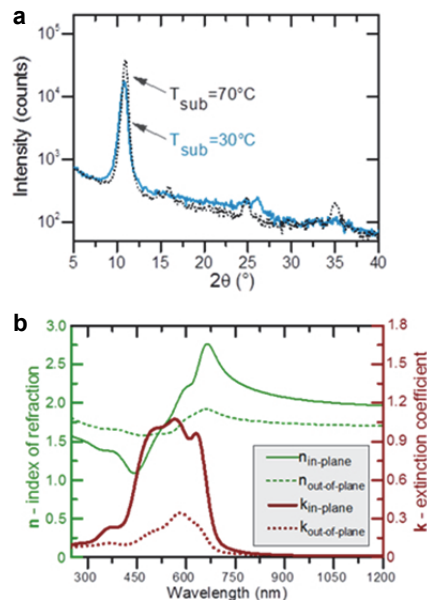


Fig. 3:

Thin film morphology: (a) - $2\ \mu\text{m} \times 2\ \mu\text{m}$ sized AFM image of the 100 nm thick pristine DCV4T-Et2 film deposited at $T_{\text{sub}} = 30^\circ\text{C}$ on SiO_2 -Si-wafer and (b) - $6\ \text{nm} \times 6\ \text{nm}$ sized MD snapshot of the DCV4T-Et2 monolayer on SiO_2 -surface (all-atomistic molecular dynamics simulation, PCFF-force field). For more details see reference [4].

Due to the crystalline-like growth of the pristine DCV4T-Et2 films the surface of the film exhibits a grainy structure as probed by AFM (Fig. 3 a). Unlike the nearly perfect crystals of inorganic semiconductors, such mosaic picture of organic electronic materials can be explained by weak intermolecular and molecule/substrate interaction. The simulation results show that the driving force of orientation of the DCV4T-Et2 oligomers on silica is controlled by the hydrogen bonding between substrate silanol groups and the cyano-groups on the conjugated molecule (Fig. 3 b, MD 'magnification' approximately 100 000 times). The tendency to form the sub-clusters with aligned (primary quasi-2D geometry) tilted molecules is clearly demonstrated. Although the formation of well-ordered truly crystalline films (or layers) of DCV4T-Et2 on silica in the simulations is not detected due to the low number of molecules contained in the system, such sub-clusters possibly are prototypes of ordered stacks perpendicular to the surface, which are obtained in our experiments.

Cooperations:

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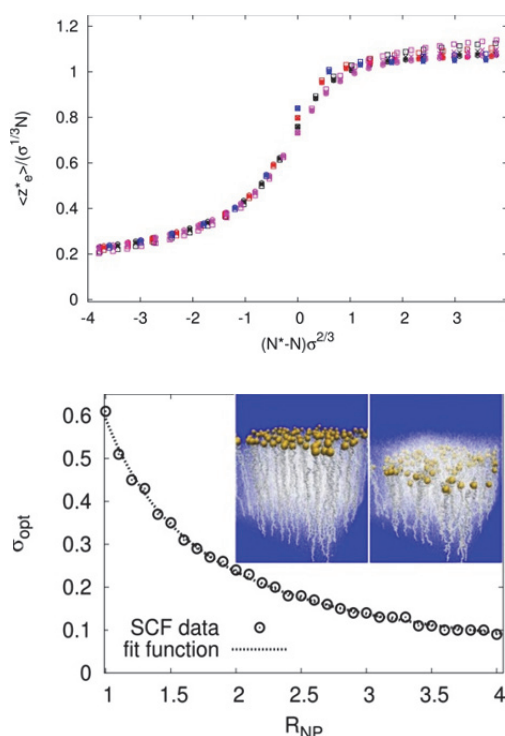
Funktionale nanostrukturierte Grenzflächen und Polymersysteme

Entwicklung einer neuen selbst-konsistenten Feldmethode zur Beschreibung von Schaltungen der Kettenkonformationen in dicht gepfropften Polymerbürsten

Dirk Romeis, Jens-Uwe Sommer

Durch dichtes Aufpfropfen langkettiger Polymermoleküle an einer Oberfläche entstehen Polymerbürsten. Aufgrund der Bedingungen in einer solchen Bürste werden die Einzelketten stark gestreckt und die Verteilung der freien Enden innerhalb des Bürstenprofils ist sehr sensitiv gegenüber Veränderungen der Umgebung (Lösungsmittelqualität, Temperatur) als auch bezüglich Modifizierungen der Einzelketten selbst (Kettenlänge, chemische Zusammensetzung) [1]. In diesem Zusammenhang ist es von besonderem Interesse, das Verhalten dieser Ketten zu verstehen und so ihre Konformationen zu kontrollieren um Oberflächen zu erzeugen, welche eine gewünschte Reaktion auf äußere Anregungen zeigen. Um dieses Verhalten detailliert untersuchen zu können, haben wir eine numerische Methode entwickelt [2, 3], welche sowohl die Konformationsfluktuationen als auch die endliche Streckbarkeit und mögliche Modifizierungen der Ketten berücksichtigt. Diese Methode ist gleichzeitig sehr effizient bezüglich des Rechenaufwands und erlaubt es somit, einen sehr großen Bereich des Parameterraumes systematisch zu studieren. In diesem Zusammenhang wurde das Verhalten von Kettenkonformationen unter Änderung des Polymerisationsgrades, unterschiedlicher Lösungsmittelselektivität und einer veränderten Größe des freien Endmonomers untersucht, siehe Abb. 1 und 2. Als besonders interessant erweist sich die Veränderung des freien Endmonomers. Wie bereits in Molekulardynamik-Simulationen gezeigt werden konnte [4], kann ein vergrößertes Endmonomer (z.B. in Form eines Nanoteilchens), welches gleichzeitig eine unterschiedliche Wechselwirkung mit der Umgebung zeigt, zu einem empfindlichen Schaltverhalten zwischen dem 'versteckten' und dem 'exponiertem' Zustand des Endmonomers führen. Mit Hilfe der neu entwickelten numerischen Methode konnte dieses Schaltverhalten in einem großen Parameter-

bereich untersucht werden. Insbesondere konnte damit eine optimale Pfropfdichte in Abhängigkeit der relativen Größe des Endmonomers gefunden werden, bei welcher die Empfindlichkeit des Schaltvorgangs maximal wird (Abb. 2). In Ergänzung der numerischen Arbeiten wurde auch ein analytisches Modell entwickelt, welches die Ergebnisse qualitativ beschreiben kann.



Keywords
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Abb. 1:
Mittlere Höhe des freien Endmonomers einer Kette mit dem Polymerisationsgrad N^* in einer Bürste mit einem Polymerisationsgrad von N in skaliert Darstellung. Die Pfropfdichte ist mit σ bezeichnet. Verschiedene Symbole / Farben entsprechen Bürsten mit verschiedenen Polymerisationsgraden N / Pfropfdichten σ . Es ist zu erkennen, dass es zu einem Kollaps der modifizierten Kette für $N^* < N$ kommt.

Abb. 2:
Für Ketten, deren Endmonomer durch ein Nanopartikel unterschiedlicher Größe R_{NP} (Radius des Nanopartikels im Verhältnis zu dem eines Monomers) ersetzt wurde, gibt es eine optimale Pfropfdichte σ , bei welcher die Schaltung zwischen 'verstecktem' (kollabiert) und 'exponiertem' (gestreckt) Zustand besonders sensitiv ist. Aus [3] und [4].

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