

Funktionale nanostrukturierte Grenzflächen und Polymersysteme



Prof. Dr. Brigitte Voit
Tel. 0351 4658-590
voit@ipfdd.de



Prof. Dr. Manfred Stamm
Tel. 0351 4658-225
stamm@ipfdd.de

Der Fokus des ST1 lag 2014 bei funktionalen Polymeren für die organische Elektronik, selbstorganisierenden und responsiven Schichten und Partikeln sowie Nanostrukturen und Hybriden definierter Form und Funktion. 2014 hat sich die Kooperation mit den Partnern des cfaed sowie nationalen und internationalen Kooperationspartnern zu Polymeren für die organische Elektronik vertieft. Deutliche Fortschritte konnten erreicht werden bei der Übertragung der quasi lebenden Negishi-Katalysator-Transfer-Polymerisation auf neue Monomere (Polym. Chem. 2014, 5, 5383) und die Reduzierung des Katalysatoreinsatzes (Angew. Chem. Int. Ed. 2014, 53, 2402). In Zusammenarbeit mit dem Institut für Medien- und Printtechnologie der TU Chemnitz wurden Transistoren auf Polymerfolien durch Drucktechnologien in einem Rolle-zu-Rolle-Prozess hergestellt (J. Mater. Chem. C, 2014, 2, 5149). Auch konjugierte Polymere mit selbstorganisierenden semifluorierten Seitenketten (Handbook Fluoropolymer Sci. Tech., 2014, p.235ff) weisen hier hohes Potential auf.

Im Bereich der funktionalen Hybride wurden Magnetitnanopartikel mittels RAFT effektiv in Polymerpartikel integriert (Macromolecules 47, 2014, 4186), für zerstörungsfreie Prüfmethode in polymeren Hochleistungsverbunden entwickelt (Adv. Eng. Mat. 16, 2014, 1276) und zur Stabilisierung von Nanostrukturen in Blockcopolymeren genutzt (Colloid Polym. Sci. 292, 2014, 2249). Zudem gelang es, eine dichte helikale Packung von Nanopartikeln in Blockcopolymer-Templaten zu erzielen und mittels TEM-Tomographie erstmalig nachzuweisen (Angew. Chem. Int. Ed. 2014, 53, 9090). Es wurden Plättchen mit Janus-Charakter hergestellt, mittels TEM verifiziert und an Grenzflächen verwendet (ACS Appl. Mater. Interf. 6, 2014, 13106). Interessante stäbchenförmige Nanostrukturen entstanden über die Umhüllung von Cellulose-Nanokristallen mittels dendronisierter Glykopolymere (JACS, 136, 2014, 866). Nanostrukturierte Polymere und Nanokomposite waren auch der Fokus der im September 2014 vom IPF in Dresden organisierten 8. Internationalen ECNP Konferenz.

Prof. Dr. Matthias Schubert aus Nebraska-Lincoln wurde Anfang 2014 als erster IPF-

Fellow berufen, was die langjährigen engen Kontakte und die fruchtbare Zusammenarbeit bei funktionellen Polymeroberflächen widerspiegelt. Im Gegenzug wurde Frau Dr. Petra Uhlmann eine Adjunct-Professur an der University Nebraska-Lincoln verliehen. Als Ausweis für die enge und fruchtbare Zusammenarbeit auf dem Gebiet der Glykodendrimere für biomedizinische Anwendungen wurde zudem Frau Prof. Dr. Barbara Klajnert-Maculewicz aus Lodz als IPF-Fellow berufen.

Die vielfältigen Untersuchungen an Polyelektrolytkomplexen wurden in einem Buch mit Beiträgen von namhaften Gruppen, editiert von Dr. Martin Müller, zusammenfasst (Adv. Polym. Sci. 255, 2014). Zudem wurde die Dynamik und Kinetik in funktionalen Polymeren analytisch intensiv untersucht. Hervorzuheben ist hierzu die Entwicklung einer Temperatur-abhängigen SEC zum *in-situ* Studium von reversiblen, dynamischen Bindungen in Polymeren (Adv. Mat., 26 2014, 3561), welche von hoher Bedeutung für das Gebiet der selbstheilenden Polymere ist. Auf der Basis temperaturabhängiger *real-time* FTIR-Daten gelang die Modellierung der Imidisierungskinetik photosensitiver Polyimide und damit eine theoretische Vorhersage und Optimierung der Prozessführung. Diese Materialien spielen als dünne Schichten eine wichtige Rolle in der Mikroelektronik (3D-Integration und Advanced Wafer-Level Packaging). Dünne Polymerschichten und deren Charakterisierung wurden intensiv im Rahmen des 8th Workshop Ellipsometry des Paul-Drude e.V. von 160 Teilnehmern aus 18 Ländern im März 2014 in Dresden diskutiert. Im Rahmen des von der Leibniz-Gemeinschaft geförderten Projektes MikROMIK, das erstmals das Vorkommen und die Verteilung von Mikroplastik (Polymerpartikel < 5mm) in der Ostsee und ihrer Rolle als Träger von mikrobiellen Populationen untersucht, wurden erfolgreich FTIR- und Raman-Imaging-Experimente an im IPF hergestellten Modellproben und realen marinen Proben durchgeführt. Ziel dieser ersten Etappe der Mikroplastidentifizierung ist die Methodenadaption, -optimierung und -validierung.

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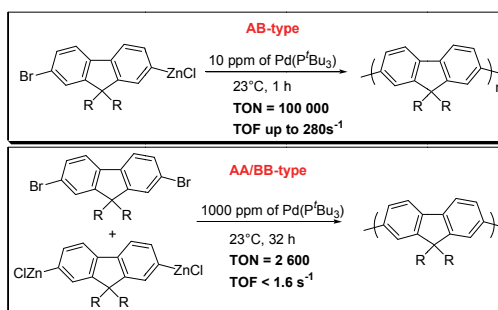
Synthesis of semiconducting, high carrier mobility polymers

Anton Kiriya, Roman Tkachov, Tim Erdmann, Doris Pospiech, Brigitte Voit, Manfred Stamm

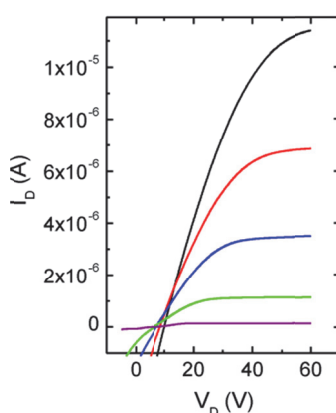
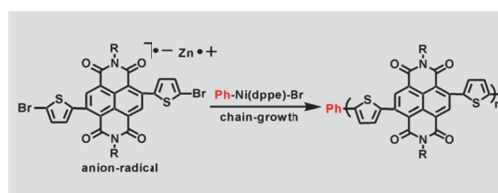
π -conjugated (semiconducting) polymers (CPs) are an important class of materials enabling various optoelectronic applications. For the fabrication of efficient photovoltaic devices, light-emitting diodes and thin-film transistors, high molecular weight polymers are desirable to achieve superior charge transport, morphological, and film-forming properties. For example, a remarkable hole mobility up to $10 \text{ cm}^2/\text{V} \cdot \text{s}^{-1}$ was recently reported for a high molecular weight diketopyrrolopyrrole-based CP whereas the performance of lower molecular weight polymers was reduced. CPs are usually synthesized by step-growth polymerizations, most often by using Pd-catalyzed Stille polycondensations using the so-called AA/BB approach. While achieving low molecular weight polymers is typically simple, the preparation of high molecular weight CPs with these techniques requires judicious balance of A- and B-functional groups, high loading of expensive catalysts, long reaction times and high reaction temperatures. The formation of toxic byproducts is another drawback inherent to Stille polycondensation.

Chain-growth catalyst-transfer polycondensation proved an alternative tool for preparation of CPs and block copolymers [1] with controlled molecular weight, low dispersity and specific end functions. Recently, we have found that Negishi chain-growth polycondensation of a Zn-organic AB-type fluorenic monomer catalyzed by Pd complexes ligated by bulky electron-rich P^tBu_3 occurs rapidly under mild conditions at extremely low catalyst loadings (down to ppm concentrations) and leads to high molecular weight PF2/6 with molecular weights of up to 120 kg/mol (Figure 1) [2]. Such low catalyst loadings are attractive for the preparation of electronic-grade materials free from metal impurities. Unprecedentedly high turnover numbers (TON) (above 70000) and turnover frequencies (TOF) of up to 280 s^{-1} were observed, which are the highest values reported so far in the literature for transition-metal catalyzed cross-coupling

polycondensations. In contrast, the corresponding step-growth polycondensation of functional AA/BB-type monomers provided two orders of magnitude lower TONs and TOFs. Similar trends were observed in AB- as well as AA+BB-Suzuki polycondensations. As it was determined in this work, the much higher polymerization rate and longer catalyst lifetime are due to a faster and safer intramolecular (vs. intermolecular) catalyst-transfer process underlying the chain-growth mechanism. These findings are important for the design of the next generation of polycondensation catalysts.



The $\text{Pd}/\text{P}^t\text{Bu}_3$ catalyst was also applied to polymerize naphthalene diimide-dithiophene based anion-radical monomers (Figure 2).



Keywords
semiconductive polymers
organic electronics
printed devices
high electron mobility
transistors

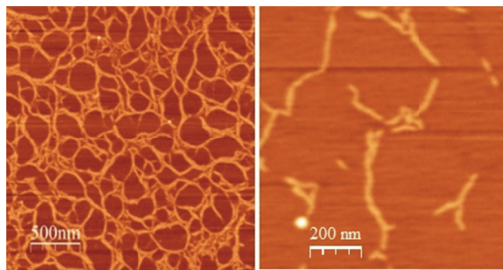
Fig. 1: Chain-growth (top) versus step-growth polycondensations of fluorene-based monomers in the presence of $\text{Pd}/\text{P}^t\text{Bu}_3$ catalyst: much higher efficiency of the former approach is due to the intramolecular catalyst-transfer mechanism inherent to the Chain-growth polycondensation.

Fig. 2: Chain-growth preparation of high molecular weight n-type PNDIT2 (top) which exhibits electron mobilities up to $1 \text{ cm}^2/\text{V} \cdot \text{s}$ (output characteristics of the representative PNDIT2-based OFET fabricated on glass with Au electrodes are shown in the bottom plot).

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Fig. 3:
(a) Representative AFM image of high molecular weight PNDIT2 highlights the ability of PNDIT2 to form large area networks which favor efficient charge transport; (b) PNDIT2 deposited from diluted solution can be resolved as individual chains and few-molecule aggregates due to its extremely high molecular weight (and large contour length).

With this method, the corresponding semiconducting polymer, PNDIT2 with a molecular weight larger than 1000 kg/mol (Figure 3) can be obtained quickly at room temperature and at rather low catalyst concentrations [3].



In general, molecular weights of the resulting polymers can be regulated by reaction conditions (e.g., catalyst concentration and reaction time). This polymerization has several technological advantages as it proceeds fast at mild conditions and does not involve toxic tin-based monomers (usual drawback of widely used Stille polycondensation). Detailed studies revealed that the polymerization involves an unusual combination of chain-growth and step-growth mechanisms. It was found that thus-prepared PNDIT2 exhibits field-effect electron mobilities of up to $\sim 1 \text{ cm}^2/\text{V s}$ as measured in top-gate field-effect transistors (FETs) on glass substrates with Au source/drain electrodes. Preliminary studies demonstrated that the Pd/P^tBu₃ catalyst is remarkably efficient in polymerizing other anion-radical monomers into corresponding homopolymers [4] and block copolymers [5].

Very recently, the groups of Ludwigs, Neher and Brinkmann studied the PNDIT2 samples with narrow dispersity in comparison to broadly distributed commercial N2200 [6]. Preliminary tests demonstrated that the chain-growth-derived CPs allowed better morphology control. An correlation between charge carrier mobility, thin-film morphology and molecular weight distribution was established. Large-scale alignment and improved molecular order was achieved by high temperature rubbing and subsequent post-rubbing annealing. These highly oriented morphologies allowed anisotropic in-plane charge transport probed with top-gate transistors parallel and

perpendicular to the polymer chain direction. Mobility up to $0.1 \text{ cm}^2/\text{V s}$ was observed parallel to the polymer chain, which is up to 10 times higher than that perpendicular to the polymer chain.

Furthermore, a step forward to fully printed polymeric devices was achieved. FETs based on semiconducting polymers are potentially low-cost technology for applications in large-area arrays, for example, backplane/driver circuits for active matrix displays. Advantages of such FETs originate from the potential lower manufacturing costs thanks to device fabrication using common solution-based deposition and patterning techniques such as different (mass) printing technologies like inkjet, gravure, flexo- and offset printing. Furthermore, circuits based on semiconducting polymers are compatible with plastic substrates so that compact, lightweight, structurally robust and flexible electronic devices can be manufactured. In a collaboration with the Institute of Media and Print Technology Chemnitz (TU Chemnitz), transistors with polymeric PEDOT:PSS source/drain electrodes were fabricated on plastic foils by means of mass printing technologies in a roll-to-roll printing press [7]. One of the most innovative achievements of this work is the use of polymeric electrodes instead of traditionally used gold electrodes. Because PEDOT:PSS possesses a too high work function to efficiently inject electrons into n-type PNDIT2 semiconductor used in this work, surface treatment of the printed electrodes with ethoxylated polyethylenimine (PEIE) which reduces the work function of PEDOT:PSS was performed to lower the work function from -5.4 down to -4.5 eV. This provided reduction of threshold voltage and achieved high electron mobility. Thus, fully polymeric PNDIT2 OFETs achieved average linear and saturation FET mobilities of $>0.1 \text{ cm}^2/\text{V s}$. Hence, the performance of n-type, plastic OFET devices prepared under ambient laboratory conditions approaches those achieved by more sophisticated and expensive technologies, utilizing gold electrodes and time/energy consuming thermal annealing and lithographic steps. As such, this is a substantial step toward commercialization of fully plastic transistors.

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Development of new polymers as dielectrics in organic thin-film transistors

Andreas Berndt, Doris Pospiech, Robert Pöttsch, Qiang Wei, Brigitte Voit

Zur Weiterentwicklung und Optimierung von organischen Feldeffekttransistoren (OFETs) - grundlegende Bauelementen für die organische Elektronik - wird am IPF Dresden ein ganzheitlicher polymerchemischer Ansatz verfolgt. Neben halbleitenden (konjugierten) Polymeren tragen vor allem auch die Dielektrika zur Effizienz von Transistoren bei. Im Rahmen des Center for Advancing Electronics Dresden (cfaed) werden hierzu am IPF zwei verschiedene Strategien bearbeitet, zum einen basierend auf Polyphenylenen, zum anderen auf Basis von Methacrylat-Copolymeren.

Hochverzweigte Polyphenylene für den Einsatz als Gate-Dielektrika [1] weisen gute Filmbildungs- sowie dielektrische Eigenschaften auf. Vernetzte Polymerfilme zeigen Durchbruchfeldstärken von bis zu 5.8 MV/cm sowie konstante Kapazitäten über einen breiten Frequenz- und Spannungsbereich. Die Charakteristika von Transistoren, basierend auf vernetzbaren Polyphenylenen als Dielektrikum, Pentacen als Halbleiter und Goldelektroden sind mit Literaturwerten organischer Feldeffekttransistoren vergleichbar. Die Ladungsträgermobilitäten liegen im Bereich von ca. 0.09 bis 0.26 cm²/Vs, Schwellspannungen im Bereich von -12 bis -14 V und I_{on}/I_{off} -Verhältnisse im Bereich von 230 bis 420. Aktuell werden diese sowie strukturell vergleichbare hochverzweigte Polymere (Abb. 1, links) für optoelektronische Anwendungen entwickelt [2,3]. Dabei liegt der Fokus auf Transparenz und einem hohen Brechungsindex. Erste Erfolge zeigen thermisch stabile Polymere, welche sich zu homogenen transparenten dünnen Filmen verarbeiten lassen und Brechungsindizes von bis zu 1,7839 aufweisen.

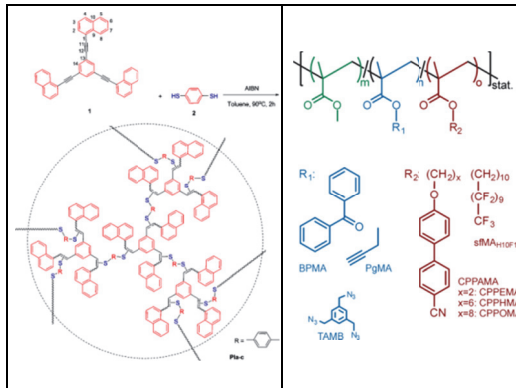
Für dielektrische Anwendungszwecke werden derzeit Methacrylat-Copolymere mit maßgeschneiderten Eigenschaften synthetisiert und charakterisiert (Abb. 1, rechts) [4].

Keywords

dielectrics
polyphenylene
methacrylate copolymers
liquid crystalline side chains
breakdown field strength
relative permittivity
refractive index

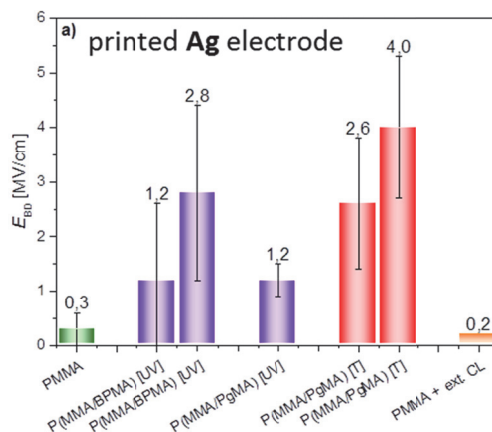
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Abb. 1:
Chemische Struktur hochverzweigter Polymere für OLED-Anwendungen (links) sowie chemische Struktur der als Dielektrika entwickelten Methacrylat-Copolymere mit verschiedenen Vernetzungsstrategien (blau) und flüssigkristallinen Comonomeren (rotbraun) (rechts).



Da zur Herstellung der Devices insbesondere Lösungsverfahren wie Spincoating und Inkjet Printing zum Einsatz kommen, sind effiziente Vernetzungsmethoden erforderlich, um eine hohe Durchbruchfeldstärke zu gewährleisten. Auch mit diesem Polymersystem konnten bereits sehr gute Werte von bis zu 4.0 MV/cm realisiert werden, im Vergleich zu unvernetztem PMMA mit 0.3 MV/cm, wobei sowohl das Dielektrikum als auch die verwendeten Elektroden aus Lösung abgeschieden wurden (Abb. 2).

Abb. 2:
Durchbruchfeldstärke (unter Verwendung gedruckter Silberelektroden): PMMA (grün), UV-vernetztes PMMA (blau), thermisch vernetztes PMMA (rot), PMMA mit 1,6-Bis(trichlorsilyl)hexan als externer Vernetzer (orange).



Eine weitere Anforderung an die neu entwickelten polymeren Dielektrika sind hohe relative Permittivitäten (high- k). Hierzu sollen unter anderem high- k BaTiO₃-Nanopartikel zum Einsatz kommen. Diese wurden synthetisiert und oberflächenmodifiziert. Bei der Herstellung dünner Polymer-Nanocomposit-Filme ist auf eine homogene Verteilung der Partikel mit möglichst geringer Agglomeration zu achten, um glatte Filme zu erhalten, da dies einen entscheidenden Einfluss auf die Grenzfläche zwischen Halbleiter und Dielektrikum

hat. Des Weiteren werden flüssigkristalline Comonomere in die Polymerstruktur integriert, um diese Grenzfläche weiter zu optimieren. Durch Ausbildung geordneter Strukturen in der dielektrischen Schicht sollen Struktur, Morphologie und folglich die Eigenschaften des Halbleiters verbessert und somit die Effizienz der OFETs gesteigert werden. Zukünftig sollen so OFETs mit maßgeschneiderten Komponenten wie Halbleiter und Dielektrikum entwickelt werden, die aufeinander abgestimmt sind. In Zusammenarbeit mit der Arbeitsgruppe von Dr. Kiriy, die sich mit der Entwicklung und Optimierung neuer Halbleiterpolymere beschäftigt, soll dieses Ziel realisiert werden.

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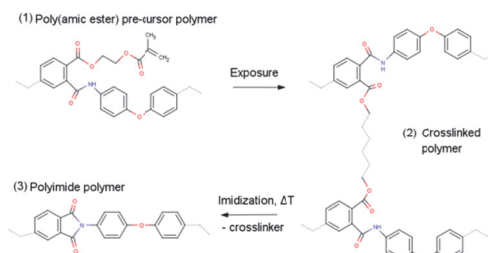
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Modelling imidization kinetics of photosensitive polyimides in solid state for microelectronic applications

Frank Windrich, Mikhail Malanin, Klaus-Jochen Eichhorn, Brigitte Voit

Nowadays manufacturer of microelectronic products, especially in the field of 3D-Integration and Advanced Wafer-Level Packaging have to deal with a complex combination of materials and substrates. Downstream processing in this technology field is often limited to a specific temperature range. Therefore it is desirable to reduce process temperatures of polymer passivation processes to a minimum. Polyimides (PI) are one of the most important classes of high performance polymers in this area of packaging technology, but require curing temperatures of 300°C and higher, which is above acceptable temperature ranges for temperature sensitive applications. Recently, low-temperature cure polyimide formulations are available, which combine a low-temperature process with the excellent properties of polyimides. Using imidization catalysts the cure temperature for these materials can be reduced to less than 250°C. For optimization purposes it is desirable to have a model of the imidization reaction, which allows describing the process in solid state quantitatively. The objective in this work was to determine the imidization kinetics in-situ and describe the reaction quantitatively. The impact of photo-crosslinking on the kinetics was evaluated. As a result a cure model has been developed to describe the imidization process regarding temperature and time, which allows achieving information about the final degree of imidization for a specific cure process in advance. A commercially available photosensitive low-temperature curable ester-type polyimide precursor was studied in this work. A typical polyimide process used for microelectronic packaging consists of 3 steps. First, the polyimide pre-cursor material is spin coated from solution (1). Second, the layer is structured by photolithography (2) and finally the polymer film is converted to a polyimide by a thermal process (3). In Fig. 1 the chemical changes during the process steps (1) – (3) are shown.



Keywords
imidization
polyimide
kinetics

Fig. 1:
Photosensitive ester-type polyimide chemistry

The imidization process was monitored in the temperature range of 160-250°C by in-situ transmission FT-IR spectroscopy using spin coated films on silicon substrates. The experimental data was fitted by time, temperature and conversion dependent first-order kinetic/diffusion model, which is described in more detail in [1-3]. The model takes into account the change of the reaction rate with temperature and degree of imidization using an apparent rate constant. Fig. 2 shows the regression results for an exposed PI precursor film (exposure dose 200mJ/cm², isotherm conditions).

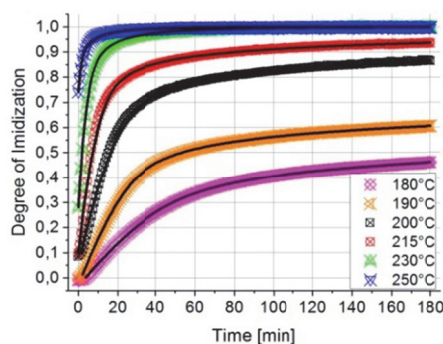


Fig. 2:
Regression results for exposed PI precursor layer (exposure dose 200mJ/cm²)

The imidization reaction shows a chemically-controlled and a diffusion controlled region with significant different reaction rates. Due to vitrification the PI film becomes glassy when the T_g reaches the process temperature, which truncates the molecular mobility of the reacting groups. The reaction therefore becomes diffusion controlled and slows down rapidly. The model equation was applicable to photo-crosslinked polyimide films and to non-exposed films. Higher exposure doses lead to a more crosslinked polymer network, which is necessary for the photolithographic stability of the material during processing. The dose parameter is crucial for the application of these films. Due to network formation during

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Keywords
microswimmer
hydrogel
actuator

photo-crosslinking the molecular mobility of the reacting poly(amic ester) groups within the PI pre-cursor is further reduced and limits the imidization rate in the chemically-controlled region (k_{chem}) compared to non-exposed films. This is caused by an entropic effect and was quantified using Eyring's equation. The activated complex loses degrees of freedom, which can be detected in a reduced activation entropy and finally in a lower imidization rate in the chemically-controlled region (see Fig. 3)

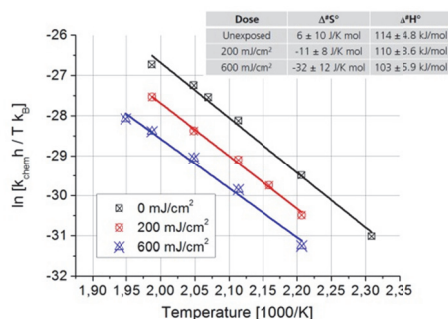


Fig. 3:
Eyring plot of k_{chem} in dependence on exposure energy

The main outcome of the cure model is that for high imide contents at low process times a minimum remaining proportion of chemically-controlled reaction rate is necessary, which requires a certain temperature. The FT-IR results show that >99% degree of imidization can be achieved with a curing process for 3h at 230°C for unexposed films. If the crosslinking degree, caused by high exposure doses, is too high a further increase in cure temperature is necessary to ensure enough energy to yield >99% polyimide. At lower exposure doses the overall decrease of reaction rate may be compensated by an increase in reaction time.

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Stimuli-responsive microjets with reconfigurable shape

Georgi Stoychev, Leonid Ionov

Biological micro-swimmers such as bacteria or sperm cells are generally composed of flexible or moving parts, which thrust the propulsion of the micro-organism. The movement of biological swimmers is often provided by oscillation of a flexible tail powered by energy rich chemical reactions and some of them contain small nozzles where jet forces are generated. In addition, they are able to respond to gradients of temperature, chemical, pH, light and others. Artificial self-propelled micro-nanomotors are engineered by multiple methods leading to a rich variety of architectures such as, nanowires, microtubes, spherical particles, helical structures, and more. Those autonomous micromotors offer great possibilities for research from fundamental mechanisms of motion at the micro- and nanoscale to potential bio-medical and environmental applications. In contrast to biological swimmers, artificial micromotors are commonly formed by rigid structures based on inorganic materials. Here, we present the fabrication of flexible thermo-responsive polymer microjets. Our micro-swimmers are formed by self-folding films consisting of thermoresponsive poly(N-isopropylacrylamide) (PNIPAM), which swells below 32°C and shrinks above this temperature, hydrophobic polycaprolactone (PCL) and thin layer of Pt, which catalyzes decomposition of hydrogen peroxide. These self-propelled microjets can reversibly fold and unfold in an accurate manner by applying changes in temperature of the solution where they are immersed. This effect allows them to start and stop multiple times by controlling the radius of curvature of the microtube. This property, added to its semi-transparency, makes this type of microjet especially attractive for studying fundamental questions such as the effect of curvature on the bubble nucleation and its correlation with the speed of microjets.

Funktionale nanostrukturierte Grenzflächen und Polymersysteme

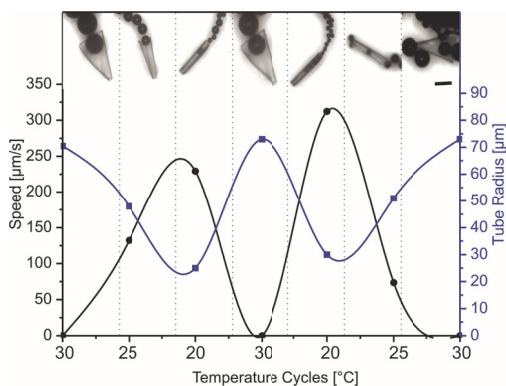
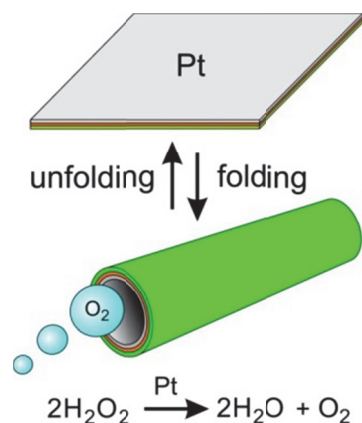


Fig. 1.
Scheme of stimuli-responsive microjets with reconfigurable shape (left) and dependence of their speed of movement on temperature (right).

Co-operation:
Prof. O. Schmidt, Dr. S. Sanchez, V. Magdanz,
IFW Dresden

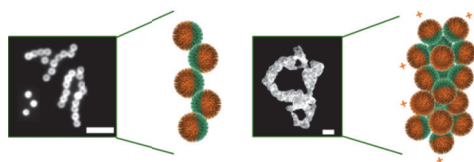
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Hairy Janus particles: Marriage of opposites and assembly

Alla Synytska, Alina Kirillova, Georgi Stoychev

Self-assembly of colloidal particles is a particularly fascinating topic because they are located at the border between nano- and macro-worlds. With the help of colloidal particles one can transfer rules of self-assembly on the nanoscale level for the design of macroscopic structures. A variety of new building blocks of different shapes, compositions, patterns and functionalities is now available for the creation of new superstructures.

Very interesting from experimental and theoretical points of view is the self-assembly of asymmetric colloidal particles such as Janus particles. Janus particles (named after the two-faced Roman god) have attracted significant attention due to their multifunctionality and resemblance to the molecular amphiphiles such as surfactants, phospholipids, and block copolymers. Due to their unique anisotropy, Janus particles have found their applications in different fields, including stabilization of emulsions, chemical catalysis, drug delivery, display technology. Their controlled synthesis with even switchable properties and control over assembly towards new materials is a particular challenging task. Therefore in this work we synthesized different kinds of amphiphilic hairy Janus particles (Fig. 1, two polymers are grafted onto the opposite sides of the core) and have studied their self-assembly mechanisms (Fig. 2).



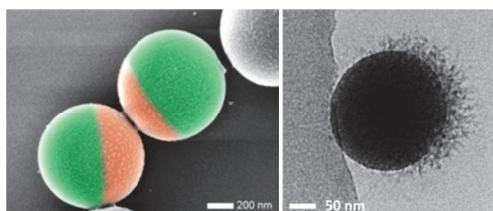
Keywords
Janus particles
self-assembly
stimuli-responsive
multifunctional

Fig. 1.:
Representative SEM (left, PDMAEMA side – green, PLMA side – orange) and cryo-TEM (right, PDMAEMA is hairy side) images of PDMAEMA/PLMA Janus particles

We found that amphiphilic PEG/PLMA-JP (Fig. 2 left) and PDMAEMA/PLMA-JP (Fig. 2 right) form chain-like aggregates in water dispersions, which is because of the Janus character of the particles.

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Fig. 2.:
Proposed structure of the chain-like structures formed by PEG/PLMA-JP (left) and PDMAEMA/PLMA-JP (right) Janus particles in DI water: Fluorescence microscopy images and representative cartoons. Scale bars: 5 μm



In fact, PEG/PLMA-JP and PDMAEMA/PLMA-JP Janus particle have one hydrophilic side, which is swollen in water, and one hydrophobic side. As result these particles tend to stick to each other by their hydrophobic sides in water in order to minimize unfavorable contacts between PLMA and water. This leads to formation of linear chain-like structures. The character of these agglomerates depends, however, on the kind of Janus particles. PEG/PLMA-JP form thin one-particle chains (Fig. 2 left).

PDMAEMA/PLMA-JP form linear 3D helical structures (Fig. 2 right). We believe that PEG is highly swollen and doesn't allow the particles to come too close to each other with their PLMA sides. As result the area of possible contact between hydrophobic sides is reduced that leads to formation of linear chains (Fig. 2 left). In the case of PDMAEMA/PLMA-JP a more complex aggregation behavior is observed due to the fact that PDMAEMA is swollen in water and is positively charged. The particles tend to touch by their hydrophobic sides; however, there are possibilities for them to have more neighboring particles due to the large size of the polymer patches. In the case of 'stickier' PLMA larger structures are formed (Fig. 2 right). When the electrostatic repulsion of the PDMAEMA sides is hindered by increasing the ionic strength, even larger linear structures are formed. A similar mechanism was observed in the work of Granick et al., where they used the same effects to construct linear 3D helical structures from amphiphilic particles, however, without hairy morphologies. These studies are expected to broaden the general knowledge about the design principles of building blocks for the fabrication of functional materials as well as the principles by which they interact with each other. The obtained knowledge will open new horizons in

design of advanced reconfigurable materials with an essential feature: freedom and flexibility to reshape.

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Co-operation:
Prof. L. Isa, ETH Zürich

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Helical packing of nanoparticles confined in cylindrical domains of a self-assembled block copolymer structure

Andriy Horechyy, Petr Formanek, Manfred Stamm

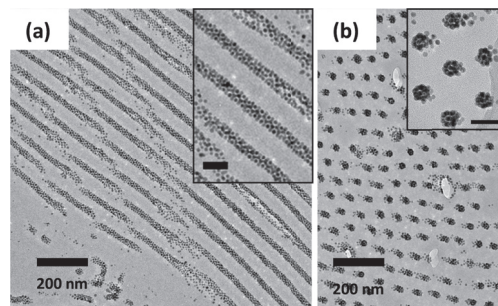
Theoretical models predict that a variety of self-assembled superstructures of spherical particles may result when particles are confined in a 1D space [1]. Such superstructures may include simple chain-like or zigzag particle arrangements, as well as a wide spectrum of more complex chiral and achiral particle assemblies. Formation of such superstructures has been experimentally observed for hard spherical particles confined in hollow cylindrical channels or in grooves on patterned substrates. These superstructures are of particular interest when formed by the nanoparticles (NP), like plasmonics or QDs, whose unique, often size-dependent properties are superimposed with those originating from their packing geometry.

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. Thus, a large number of diverse methods to generate NP/BCP nanostructures and control over the nanoparticle location within the BCP matrix are well established and widely described. However, most of the literature reports do not designate the structures formed by the nanoparticles themselves, revealing in most cases random particle arrangements within host domain of self-assembled BCP matrix.

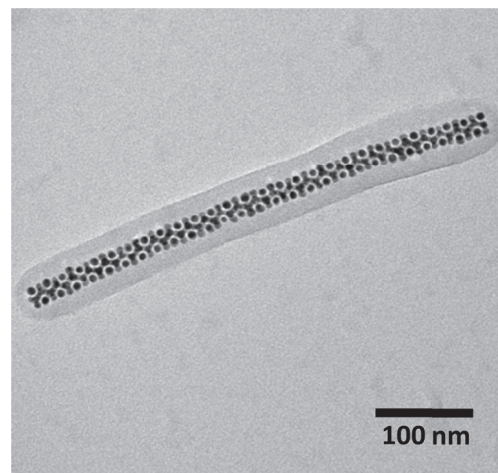
Theoretical modeling and simulations of NP/BCP systems predict that uniform spherical nanoparticles with preferential attraction to the one of the blocks can also self-assemble within the host domain and generate a variety of ordered structures and morphologies. However, these nanoparticles assemblies were predicted as metastable or unstable and occur in very narrow parameter range, thus never observed before [2].

In the present work we demonstrate for the first time that the polymer-coated silver nanoparticles (AgNP) confined in the self-assembled cylindrical domains of a block

copolymer self-assemble into a superstructure with densely nanoparticle packing as shown in Fig. 1 [3].



Moreover, these nanoparticles assemblies can be isolated in form of individual polymeric nanofibers (NF) [4] with NP close packing being preserved inside the nanofiber (Fig. 2).



The exact nature of the ordered three-dimensional nanoparticle structure was resolved using TEM imaging combined with an electron tomography technique on an isolated NF loaded with AgNP. The 3D reconstruction of AgNP packing inside the nanofiber reveals a central chain of AgNPs along the long axis of the NF surrounded by a stack of rings of five nanoparticles, whereby adjacent rings are twisted 36° with respect to each other (Fig. 3). This twist of adjacent particle layers gives rise to a spiral or helical arrangement of the nanoparticles, where the central nanoparticle chain is surrounded by five helical chains (one such chain is highlighted in red in Fig. 3).

Keywords
block copolymers;
helical packing;
nanoobjects;
nanoparticles;
self-assembly

Fig. 1:
TEM images of self-assembled morphologies formed in an AgNP/PS-b-P4VP sample loaded with 10 wt.% AgNPs: (a) view along the plane of the PS cylinder axis, (b) view normal to the plane of the PS cylinder axis. Scale bars of the inset images correspond to 50 nm.

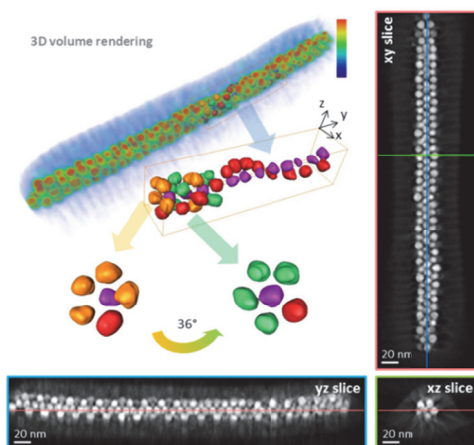
Fig. 2:
TEM image of a single NF isolated from the AgNP/PS-b-P4VP composite with closely packed ordered structure formed by AgNP.

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Keywords
 fullerenes
 dyad
 computer simulation
 self-assembly
 hydrophobic interaction
 electrostatic interaction

Obtained results provide unique possibilities for further fundamental research in this direction and open up the new ways for discovery of novel hierarchical superstructures in NP/BCP systems. Moreover, such complex nanoparticle arrangements are very interesting in terms of their structure-related properties, like optical behavior or energy transfer, and provide new opportunities for the application-oriented research of such materials.

Fig. 3.
 3D reconstruction obtained by the tomography of AgNP packing inside the NF formed by the PS-*b*-P4VP block copolymer. The 3D volume rendering shows the entire structure, in which the reconstructed density is color coded according to the colorbar, where the AgNPs appear red (high density) and the BCP appears blue (low density). From the tomogram some of the AgNPs are segmented to visualize their spiral arrangement. The slices show sections through the center of the 3D volume in the three directions in space.



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Co-operation:
 Prof. B. Nandan, IIT Delhi, India
 Dr. D. Wolf, Triebenberg Laboratory, TU Dresden, Germany

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C₆₀-dyad aggregates: Self-organized structures in aqueous solutions

Olga Guskova, Srinivasa Rao Varanasi, Jens-Uwe Sommer

The study of aggregate properties of pristine fullerenes (Fig.1 a) in a liquid environment is a problem deserving increasing theoretical interest.

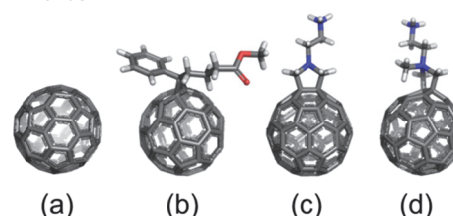


Fig. 1:
 The objects of the study: a bare C₆₀ fullerene (a), phenyl-C₆₁-butyric acid methyl ester (PCBM) with polar -C(O)-O- group (b), charged fulleropyrrolidine derivatives (c, d); for fulleropyrrolidines the "attached" organic moieties are 2-pyrrolidin-1-ylethylammonium, monocation (b), 2-(1-methyl-pyrrolidin-1-yl)-ethylammonium, dication (d). The chloride, iodide or perchlorate anions are counterions (are not shown). Grey, red, white, blue cylinders represent carbon, oxygen, hydrogen and nitrogen atoms/bonds, respectively.

The C₆₀-solvent interactions and fullerene solubility is a primary factor contributing to the rapid advancement of fullerene chemistry for material science applications, where fullerenes are considered as extremely promising components for bottom-up fabrication of photonic materials and as colloidal suspensions for various medical fields.

But the key to nanotechnology is not only making miniature structures out of individual components. It may be forcing those structures to build themselves. For example, in polar solvents, including water, the fullerenes are virtually insoluble. When such different in chemical sense substances come into contact with each other, buckyballs demonstrate their phobia of water forming colloidal nm-sized clusters ("nano-C₆₀" [1]) with omnifarious shapes and geometries – spheres, vesicles, needles, rods, tubules, disks, stars, fibers. The hydrophilic decoration of a water-fearing carbon cage via attaching a wide range

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of well-hydrated groups is becoming a popular route to promote and modulate the aggregative behaviour [2, 3]. As a consequence, synthesized dyad possesses at least two levers, which supply the molecule its unusual physico-chemical properties of being simultaneously hydrophobic and hydrophilic (Fig.1 b-d) and open scientists a new avenue into molecular manipulation of fullerenes. Since the question about predominant intermolecular interaction in the fullerene agglomeration is still puzzling, it is important to consider the interaction types responsible for the dyad self-assembly with a “magnifying glass” of the modern science – a molecular dynamic simulation with atomistic resolution. In our case simulated many-molecule systems contain 32 fullerene dyads solvated with several thousand water molecules (Fig.2).

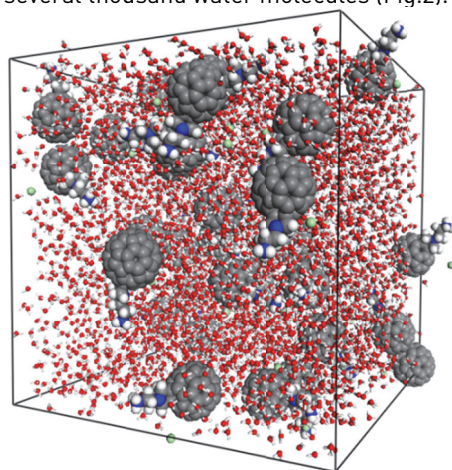


Fig. 2:
An initial point for molecular dynamics – 32 fulleropyrrolidine cations, 32 chloride anions and 5000 water molecules randomly distributed in a cubic simulation box. Grey, red, white, blue, green spheres represent carbon, oxygen, hydrogen, nitrogen and chlorine atoms/ions, respectively. The details of the model can be found in Ref. [4].

In focus are the phenomena that determine the shape of the final ensemble in water [4]. A gentle interplay of acting forces (surface tension/electrostatics) guides molecules of fullerene dyads to organize themselves into micelles in aqueous solutions (Fig.3).

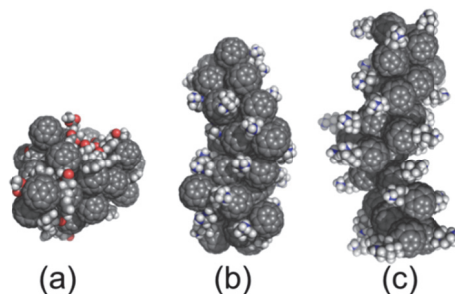


Fig. 3:
Snapshots of simulated aggregates of (a) PCBM, (b) fulleropyrrolidine monocation, (c) fulleropyrrolidine dication forming in aqueous solution; water molecules (a-c) and chloride ions (b, c) are omitted for clarity.

A different type of clustering phenomenon is seen for neutral and charged C_{60} -derivatives. Fullerene with hydrophilic but neutral short ester-side group preferentially forms spherical aggregates in water similarly to pristine C_{60} particles (Fig.3a). Fulleropyrrolidines self-assemble in turn into elongated structures because of the presence of charged groups and counterions that help molecules to template themselves into non-spherical structures with hydrophobic core and hydrophilic exterior (Fig.3b, c).

By changing the size of the counterions from chloride over iodide to perchlorate (Fig. 4) we find a thickening of the cylinder structures which can be explained by stronger condensation of larger ions and thus partial screening of the charge repulsion on the cluster surface.

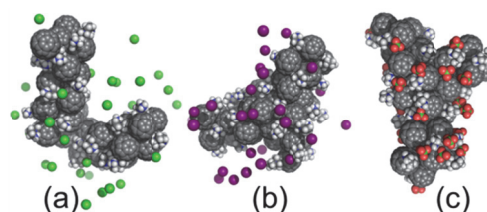


Fig. 4:
Snapshots of fulleropyrrolidine monocation aggregates with different counterions: (a) chloride anions, green CPK spheres, (b) iodide anions, purple CPK spheres and (c) perchlorate anions, green-red tetrahedrons; water molecules are omitted for clarity. Here small, charge-dense Cl^- ions having large and structured hydration shells do not approach the surface of the solute at short distances; they are repelled from the hydrophobic regions of the fulleropyrrolidine molecules, forming a diffuse layer around the cluster. In turn, the significant number of charge-diffuse perchlorate anions is present at the micelle surface forming a Stern layer of adsorbed ions.

The reason for the size dependence of counterion condensation is the formation of a stronger hydration shell in case of small ions which in turn are repelled from the fullerene aggregates. Furthermore, the presence of longer hydrophilic group introduces the more pronounced “linear” stacking (cylindrical micelles, flexible or planar bilayers) which becomes a dominant pathway for fulleropyrrolidine molecules to aggregate (Fig.3c). Such simple tuning of molecular geometry of fullerene molecules and evaluation of critical packing parameters [4] can be used for elementary estimation of their microstructure.

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Keywords
recycling
paper
polymer
surface tension

Thereby, our work opens up the possibility of preparing increasingly complex molecular C_{60} arrangements, whose organization can be controlled.

Further simulations will be focused on the phenomenon of hydrophobic hydration and such factors of self-assembly as the length of the hydrophilic addend, the bis-substitution of the C_{60} -cage, as well as the theoretical investigation of nanoscale amphiphilic polymer/fullerene co-assemblies. The latter case is essential for developing smart nanostructured materials for the technological applications in the field of organic electronics, because the localization of molecular components (polymer donor and fullerene acceptor) having similar polarity in water offers a powerful, non-directional driving force for the self-assembly and folding in amphiphilic systems.

Co-operation:

Center for Information Services and High Performance Computing (ZIH) of the Technische Universität Dresden

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Polymere Druckfarbensammler im Deinkingprozess

Simona Schwarz, Gudrun Petzold, Uwe Geißler

Im Jahr 2010 lag der Einsatz von Altpapier, bezogen auf die Papierproduktion, in Deutschland bei 70 %. Altpapier stellt schon seit langem die wichtigste Rohstoffbasis der deutschen Papierindustrie dar.

Typischerweise muss das Altpapier nach seiner Sammlung und Lagerung zunächst von Verunreinigungen wie Metall, Sand, Glas und Kunststoffen befreit werden, bevor es in den Auflöseaggregaten unter der Wirkung von Wasser und einem kleinen Teil chemischer Hilfsstoffe wie z.B. Tenside zerfasert wird. Um ein helles Papier auf der Basis von Altpapier zu erzeugen, müssen die Rohstoffe von den an ihren Oberflächen haftenden Druckfarbenresten befreit werden. Ziel ist es hierbei, eine möglichst vollständige Ablösung der Farbe von der Faser und deren anschließenden Austrag zu erreichen. Dieser als De-Inking bezeichnete Prozessschritt wird traditionell mit Hilfe der Flotation, also durch das Anlagern der Druckfarbenteilchen an Luftblasen, durchgeführt. Der Prozess ist durch einen hohen Verbrauch an Wasser und Energie gekennzeichnet.

An der Professur für Papiertechnik an der TU Dresden konnte kürzlich nachgewiesen werden, dass sich die von den Fasern abgelösten Druckfarbenteilchen nicht nur – wie bei der Flotation – an Luftblasen, sondern auch an die Oberflächen synthetischer Polymerpartikel wie PA oder PP anlagern und mit diesen aus der Suspension ausgetragen werden können. Diese Anlagerung (Adsorption) kann bei wesentlich höheren Stoffdichten erfolgen als die Druckfarbenentfernung mittels Flotation und somit Wasser und Energie einsparen. Ziel eines gemeinsamen Projektes war es

- die Mechanismen des Adsorptions-deinkings zu untersuchen und damit zur Optimierung der Polymerteilchen bezüglich ihrer Oberflächenchemie beizutragen sowie
- eine Möglichkeit zur Entfernung der Druckfarben und somit zur Regenerierung der Teilchen zu finden.

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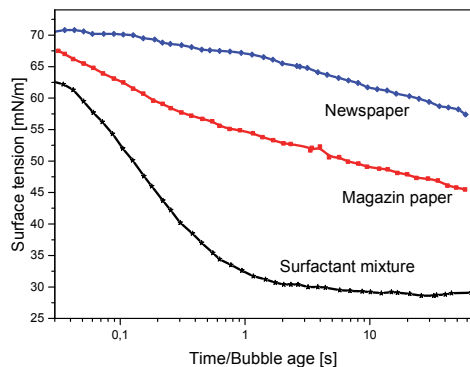


Abb. 1:
Dynamische Oberflächenspannung der Deinking-Lösung im Vergleich zu den Stoff Suspensionen; während die Tensidmischung in Wasser die Oberflächenspannung bereits nach 1 s auf ca. 30mN/m erniedrigt wird das Tensid in Anwesenheit der Papiere adsorbiert, was die Oberflächenspannung erhöht

Im IPF erfolgten vor allem Untersuchungen zur Charakterisierung der Polymere, der Druckfarben und Papiere sowie der Wechselwirkungen in den tensidhaltigen Stoff Suspensionen. Wie in Abb. 1 dargestellt wird sind Oberflächenspannung (und Ladung) sowie Partikelgröße (Abb. 2) geeignete Parameter, um die Stoff Suspensionen zu beschreiben. Diese Parameter verändern sich in Abhängigkeit von Papierart und Druckfarbe. So steigt die Oberflächenspannung der tensidhaltigen Lösung durch Zusatz von Zeitungspapier (Newspaper; NP) stark an, da die Tenside an der Druckfarbe adsorbiert werden. Die Suspension „verarmt“ an Tensid und die Oberflächenspannung nähert sich dem Wasserwert. Jedoch zeigen Magazinpapiere (Light weight coated; LWC) ein völlig anderes Verhalten, das durch den Einfluss der Coating-schicht zu erklären ist, die zersetzt wird und die ebenfalls oberflächenaktive Substanzen freisetzt. Das konnte auch anhand von Partikelgrößenmessungen bestätigt werden (Abb. 2). Während Ruß als Hauptkomponente der Druckfarben eine mittlere Partikelgröße von etwa 10 µm besitzt fällt bei den LWC-Proben ein sehr hoher Feinanteil, der unabhängig von der verwendeten Druckfarbe ist, auf. Es handelt sich um anorganische Partikel, die aus dem Coating freigesetzt werden. Dagegen haben Zeitungsdruckpapiere (NP) den höchsten Anteil größerer Partikel, die

Druckfarbe enthalten. Somit wird die Partikelgröße in Suspension und damit die Effektivität des Deinkingprozesses weitgehend von der Art des Papiers, und weniger von der Druckfarbe bestimmt.

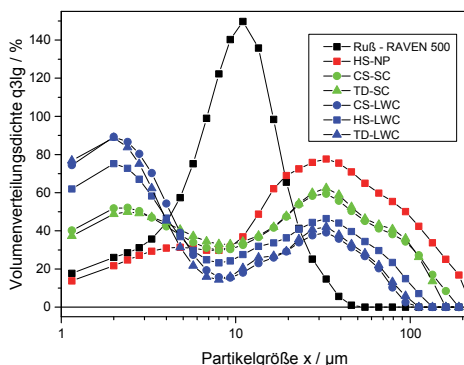


Abb. 2:
Partikelgrößenverteilung in der Stoff Suspension; verschiedene Papierarten (NP, SC und LWC) und Druckfarben (Cold-Set, Heat-Set und Tiefdruck) im Vergleich

In weiteren Untersuchungen gelang es durch eine Kombination von Tensidlösung und Ultraschall, die beladenen Polymerteilchen zu regenerieren, so dass sie dem Prozess wieder zugeführt werden können [3]. Von den getesteten Polymeren erwies sich Polypropylen als am besten geeignet. Somit konnten die Voraussetzungen für eine technische Nutzung des Adsorptionsdeinkings einschließlich des Granulatrecyclings geschaffen werden.

Sponsor:

Das IGF-Vorhaben (Nr. 17561) der Forschungsvereinigung DECHEMA wurde über die AiF im Rahmen des Programms der industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.

Kooperation:

Prof. H. Grossmann, Professur für Papiertechnik, TU Dresden

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