

Rebinding Molecular Dynamics Simulations of Nitric Oxide to the V68FMyoglobin Mutant

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The study of reactive processes in chemically and biologically relevant systems is a topic of much current interest. Here, an atomistically detailed picture of NO rebinding from myoglobin V68F is presented. Using reactive molecular dynamics [1] the rebinding probability as a function of time after dissociation is calculated. Reactive molecular dynamics considers two intersecting potential energy manifolds which dissociate to different adiabatic states. During the simulations, crossings are detected by monitoring an energy criterion and the surfaces are mixed over a finite number of time steps. The unbound surface (Fe...NO) is a standard force field, whereas the bound surface (Fe-NO) is based on *ab initio* calculations. The rebinding is nonexponential in time, in agreement with experimental studies [2] and can be described using two time constants. Particular emphasis is paid to the asymptotic separation Δ between the two potential energy manifolds. An extension of the original reactive molecular dynamics approach with a conformationally varying Δ is discussed.

[1] D.R. Nutt and M. Meuwly, *Biophys. J.* **90**, 1191 (2006).[2] Y. Wang, J.S. Baskin, T. Xia and A.H. Zewail, *Proc. Nat. Acad. Sci. USA* **101**, 52 (18000) 2004.**Stark Effect in Rydberg States of Neon**O. Zehnder¹, M. Grütter¹, T.P. Softley², F. Merkt^{1*}¹Laboratorium für Physikalische Chemie, ETH Zurich, 8093 Zurich, Switzerland²Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom

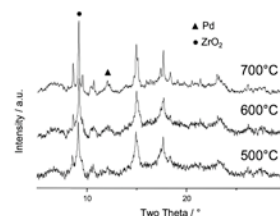
The Stark spectra of Rydberg states of neon with effective principal quantum number $n^*=25$ belonging to the $^2P_{3/2}$ and $^2P_{1/2}$ ionisation thresholds, respectively, have been measured at electric fields between 0 and 180 V/cm following two-photon excitation from the Ne (1S_0) ground state via the $3s[3/2]_1$ and $3s'[1/2]_1$ intermediate states. Spectra of $M_J = 1$ and $M_J = 0$ Stark states are recorded separately using linearly polarised lasers with polarisation vectors either parallel or perpendicular to the static electric field. These spectra are very different in appearance reflecting the very strong dependence of the cross sections to the accessible channels on the polarisation vectors already observed in zero field measurements [1]. The spectra provide information on the quantum defects of the s, p and d Rydberg levels of neon and are analysed using multi-channel quantum defect theory (MQDT).

[1] I.D. Petrov et. al, *J. Phys. B: At. Mol. Opt. Phys.*, **2006**, submitted.**In Situ EXAFS/XRD Study on a Pd/ZrO₂ Catalyst Applied in Methane Combustion**

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Catalytic combustion has received much attention amongst catalysis researchers due to its importance in various technical applications. Potential applications in energy generation, such as in lean-burn natural gas vehicles and gas-turbines, or pollution control have stimulated research in this area, resulting in a plethora of catalysts [1]. Among these, palladium based catalysts have been regarded as the most active for catalytic methane combustion. The nature of the active species in these catalysts is still subject to debate. While PdO seems to be more active than Pd, catalysts containing both metallic and oxidized palladium are reported to outperform even PdO. Relevant data on these systems can almost only be obtained by *in situ* methods [2]. In this contribution an *in situ* EXAFS/XRD investigation of a Pd/ZrO₂ catalyst will be discussed. The effect of temperature and atmosphere (H₂/He, O₂/He, CH₄/O₂/He) on the Pd oxidation state and crystallite size will be shown and correlated to the activity of the catalyst during catalytic methane combustion.

[1] T.V. Choudhary *et al.*, *Appl. Catal. A*, **2002**, 234, 1[2] J-D. Grunwaldt *et al.*, *PCCP*, **2003**, 5, 1481**Bulk Heterojunction Polymer Solar Cells**

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Nanostructured phase-separated blends, or bulk heterojunctions, of conjugated polymers and acceptor materials (e.g. fullerenes, inorganic nanocrystals, or a second polymer) form an attractive approach to large-area, solid-state organic solar cells. The key feature of these cells is that they combine easy processing from solution on a variety of substrates with promising performance. Efficiencies up to 4-5% in solar light have been achieved. Further improvements can be expected when the energy lost in the initial electron transfer step can be reduced. This increases the open circuit voltage and power conversion efficiency. Another important parameter that currently limits the performance of polymer solar cells is the mismatch between the absorption spectrum of the photoactive layer and the solar emission. Typically, the best polymer solar cells absorb light with wavelengths below 650 nm, while the solar photon flux maximizes around 700 nm and extends into the near infrared. Low band gap materials can alleviate this problem. We will present new low band gap polymers that are able to convert solar light up to 1000 nm in bulk heterojunction devices.

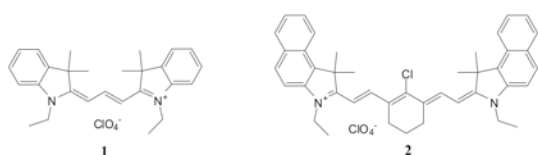
Polymeric Dyes

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Well known since 1856, polymethine dyes are nowadays well established in photonic technologies like laser technology, telecommunication, sensors etc. Due to recent developments in the field of organic photovoltaics and organic light-emitting devices there has been a renewed great interest in the area of tailor-made "functionalized" organic dyes.

Our contribution to the photovoltaic research field is manifold including both synthesis and device fabrication. Previous work proved that cyanine dyes (**1**, **2**) are generally suited as photoactive materials in solid solar cells [1]. In order to improve the photovoltaic performance, new device concepts were developed by using blends of cyanine dyes and MEH-PPV [2] or nano-structured polymer films.



From a molecular point of view we developed polymeric dyes with efficient maximum absorption in the NIR. The present work focuses on synthesis and analytic characterization of the polymeric dyes. First applications are also discussed.

[1] Meng, F., et al., Applied Physics Letters, 2003, 82(21): p. 3788-3790.

[2] Castro F. A., et al., Synthetic Metals, 2006, submitted

Towards Helical Dendronized Polymers

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Dendronized polymers with different dendritic layers and polymer backbones have been developed in recent years.^[1] The rigidity or the stiffness of a dendronized polymer can be controlled to some degree by the choice of dendron and backbone, and also by the fact whether they are linked together by a spacer. Here we describe a new type of dendronized polymethacrylates with dendrons made from chiral oligoproline. They exhibit a high compactness and rigidity and their backbones attain helical conformations which is stable over a wide temperature and solvent range. These polymers were efficiently synthesized on the multigram scale via the macromonomer route and obtained in high molar masses for the first two representatives, PG1 and PG2. This contribution discusses synthetic, structural and conformational aspects based on NMR- and CD spectroscopy, optical rotation, and AFM visualization. It also addresses the considerable future potential of these new dendronized polymers.

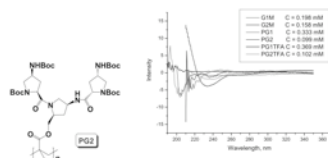


Figure 1. Chemical structure and Circular Dichroism spectra of proline-based dendronized polymers

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Hierarchical and Functional Self-assembly of Polymers driven by Biochemical Interactions

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How is Nature creating functional devices? For example, it is intriguing to realize that only four nucleic acids are needed to code the genetics of human beings. There, functionality is highly inherent to the nucleotide sequence. One single defect in this code leads to serious diseases.

Currently, synthetic polymers represent a highly versatile class of materials due to the relative ease of controlling their composition, structure and properties. However, despite promising bio-mimetic approaches, the synthesis of complex polymers is far from reaching the high level of precision achieved by Nature on the synthesis of bio-macromolecules, which prevents their subsequent hierarchical organization into highly functional structures.

To overcome this issue we recently implemented the use of entities produced by Nature itself to drive the hierarchical organization of macromolecules into functional structures in the nanometer size range.

In this contribution, we will present the results of our investigations on the conjugation of chemically incompatible polymers to a sequence of nucleotides. Poly(butadiene) being hydrophobic, the nucleotide-polymer hybrid exhibits amphiphilic properties: in dilute aqueous solution, 50 nm large spherical structures are observed by transmission electron microscopy. Docking of poly(ethylene glycol) conjugated to the complementary nucleotide sequence yield to a hierarchical organization driven by base pairing and enhanced by the segregation between the chemically incompatible polymer segments.

Protein-Polymer Amphiphiles: Novel Approaches and Aggregation studies.

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The synthesis and characterization of novel generations of amphiphilic bio-hybrid molecules -also denoted as *Giant Amphiphiles*- will be discussed. *Giant amphiphiles* are bio-block-copolymers that consist of an enzyme (or a protein) specifically attached to a polymeric tail. In the past we have shown that these giant soap molecules aggregate in ways similar to that of their low molecular weight counterparts [1],[2].

Our recent studies are focusing on the development of new methods for the synthesis of di- and tri- block protein-polymer biohybrids. Using the "click" chemistry approach and the "post-functionalization" approach, we have successfully constructed small libraries of BSA-polystyrene and haemoglobin-polystyrene giant amphiphiles. We studied the effect of the polymer length on the resulting superstructures, as well as the effect of the protein head group to the overall supramolecular morphology. Furthermore, we were able to prove for the first time, that giant amphiphiles also form well defined structures in organic solvents (such as dichloromethane). In such a selective for the polymer medium, the proteins are confined in the interior of the superstructures, while the polymer itself is exposed to the solvent. Studies on the intriguing prospect of using such assemblies as nanoreactors are currently in progress and will also be presented.

[1] Velonia, K., Rowan, A. E., Nolte, R. J. M. *J. Am. Chem. Soc.* **2002**, *124*, 4224-4225.

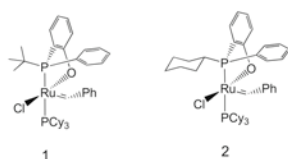
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Sequence Controlled Metathesis Polymerization with Well-defined Catalysts

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The metathesis reaction catalyzed by ruthenium carbene complexes has found wide spread application in current organic synthesis.¹ One important application is the polymerisation of cyclic alkenes known as ring opening metathesis polymerisation (ROMP). Interestingly for ill defined W-based catalysts it has been observed that certain additives like phenoles, allow the copolymerisation of different monomers creating alternating copolymers.² Using mechanism-based³ design we created the well defined catalysts **1** and **2**, which are capable of copolymerising mixtures of strained and unstrained cyclic olefines in a sequence controlled manner generating alternating copolymers without the aid of additives⁴. This novel approach to alternating polymers creates new entries for the synthesis of well-defined functional materials.



1. R. H. Grubbs, R. R. Schrock and Y. Chauvin, Nobel Prize Chemistry, **2005**; A. Fürstner; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012 – 3043; K. C. Nicolaou, Paul G. Bulger, David Sarlah; *Angew. Chem. Int. Ed.* **2005**, *44*, 4490 – 4527.
2. S. Cetinkaya, S. Karabulut, Y. Imamoglu, *European Polymer Journal*, **2005**, *41*, 467 – 474; V. Amir-Ebrahimi, J. J. Rooney, *Journal of Molecular Catalysis A*, **2004**, *108*, 115 – 121.
3. C. Adlhart, P. Chen; *Helv. Chim. Acta*, **2003**, *86*, 941 – 949; C. Adlhart, P. Chen.; *Angew. Chem. Int. Ed.* **2002**, *41*, 4484 – 4487.
4. M. Bornand, P. Chen, *Angew. Chem. Int. Ed.* **2005**, *44*, 7909 – 7911.

Polymer Brushes as Templates for Biomimetic Materials Fabrication of Microstructured Calcite Films

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Surface-initiated atom transfer radical polymerization (SI-ATRP) represents an attractive tool for the fabrication of polymer brushes as crystallization matrices with defined thickness, composition, polydispersity, grafting density and by using lithographic techniques also with well defined micro- and nanopattern. Here we present the use of poly(methacrylic acid) (PMAA) brushes as templates for the fabrication of microstructured calcite films. The strategy that will be presented combines three key elements: (i) the ability of highly dense PMAA brushes to stabilize amorphous calcium carbonate (AAC); (ii) the possibility to convert the metastable ACC phase into a polycrystalline calcite film via a thermal treatment and (iii) the use of photolithographic techniques to prepare microstructured PMAA templates. The unique feature of this strategy is that the resulting inorganic films or objects are an exact 3D replica of the PMAA brush template. The process may be readily extended to other inorganic materials and more complex structures by combining the flexibility of SI-ATRP with regards to the chemical composition and architecture of the polymer brush with the numerous lithographic methods that are available to generate micropatterned surfaces.

- [1] S. Tugulu, M. Harms, M. Fricke, D. Volkmer, H.-A. Klok, *Macromolecules*, submitted.
- [2] S. Tugulu, M. Harms, M. Fricke, D. Volkmer, H.-A. Klok, *Angew. Chem. Int. Ed.*, in preparation.

Spinning around rod-like and entwined molecules

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We are used to look at molecules as geometrically well defined building blocks. One prominent example are poly(*para*-phenyleneethynylene)s (polyPPEs) that are viewed as molecular rods despite of their distinct flexibility. When using molecules as building blocks, knowledge about their intrinsic flexibility is of interest.

Light scattering, the standard approach to determine the stiffness, demands for structurally perfect polymers. However, being realistic, several of the macromolecules of a sample will show structural defects. More reliable data might be available through studies on oligomers because the comparatively small size of oligomers often allows for a step by step synthesis and therefore for a better control of the molecular structure.

Double electron resonance on oligoPPEs with spinlabels, one at each end, gives the end to end distance and thus an indirect information about the stiffness.^[1] Structural variations of the molecules may open an access to the contribution of different structural units within the backbone of the oligomer.

Studies with structurally well defined compounds not only provide information on the specific compounds but also spur on the development of techniques, that will allow for structural elucidation of molecules and molecule aggregates in an amorphous or native state. E.g. the results on oligoPPEs were used to learn about the co-conformation and the dynamics of [2]catenanes with huge and non-interacting rings.

- [1] G. Jeschke, M. Pannier, A. Godt, H. W. Spiess, *Chem. Phys. Lett.* **2000**, *331*, 243-252.
- [2] G. Jeschke, A. Godt, *ChemPhysChem* **2003**, *4*, 1328-1334.

From polymer-metal nanocomposites to polymeric metal wires

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The incorporation of metallic nanoparticles into polymers can result in materials which ally the processibility and toughness of polymers with optical attributes of the particles [1]. A remarkable optical effect – dichroism – is obtained when the nanoparticles form uniaxially oriented linear agglomerates in a polymer matrix [2, 3]. We prepared such materials by drawing of polyethylene containing silver or gold nanoparticles encapsulated in a shell of 1-dodecanethiol. The resulting materials were used for the creation of bi-colored liquid crystal displays.

The miniaturization of linear agglomerates of metallic nanoparticles leads to polymeric structures resembling metal wires with atomic diameter that are stabilized by appropriate ligands. Among those, Magnus' green salt [4], [Pt(NH₃)₄][PtCl₄], or poly(dialkylstannane)s might be of interest for their semiconductivity. The use of Magnus' green salt, which is a quasi-one-dimensional inorganic compound containing linear arrays of platinum atoms, is limited since it does not melt prior to decomposition and is largely insoluble in water and organic solvents which makes it difficult to process. We eliminated this deficiency by adequate substitution of the coordinated ligands, including optically active aminoalkanes. Thus, soluble compounds with ultrahigh chiral anisotropy factors, cryochromic behavior, or electric semiconductivity were obtained. A number of the materials were processed to oriented films and fibers. In collaboration with other groups, oriented films were applied as active semiconducting layer in field-effect transistors. Such devices showed remarkable stability towards air and water which was superior to that of unprotected field-effect transistors based on typical organic polymers.

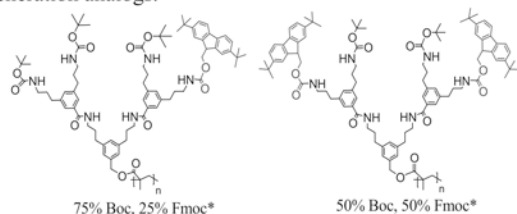
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- [2] H. Ambronn, *Königl. Sächs. Ges. Wiss.* **1896**, *8*, 613.
- [3] S. Apáthy, *Mitt. zool. Stat. Neapel* **1897**, *12*, 495.
- [4] G. Magnus, *Pogg. Ann.* **1828**, *14*, 239.

Synthesis of Orthogonally Protected, First and Second Generation Dendronized Polymers.

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Synthesis of dendronized polymers found a high interest of many researchers in the last years.^[1,2] Up to now, they were synthesized either by the so called attach-to-route or macromonomer route.^[3] The representatives of this class of macromolecules from our laboratory prepared so far carry peripheral amino groups with only one kind of protecting group. This limits a more advanced surface engineering for which it would be interesting to introduce more than one kind of novel functional units. This deficiency led us to build up a new class of first and second generation dendronized polymers with varying proportions of orthogonally protected amine groups. The synthesis uses the macromonomer strategy. The corresponding second generation macromonomers carry Boc and Fmoc* (2,7-Di-tert-butyl-Fmoc) groups in the following ratios: 100:0, 75:25, 50:50, and 25:75, and are polymerized by standard radical procedures. The obtained polymers can either be used directly for modification reactions or as starting materials for higher generation analogs.



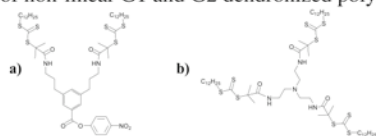
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Introducing a Single and Selective Binding Site to the Backbone of Dendronized Polymers

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The idea of having a single functional group implanted into the backbone of a dendronized polymer opens an access to various interesting aspects which include: (a) Investigation of the chemical behavior of this single unit embedded in the high functional group density of the dendritic layer. (b) Incorporation of a fluorescence tag for localization of it on the backbone. (c) Investigation of the aggregation behavior of oppositely charged dendronized blocks for nanoconstructions. (d) Modification of this group with appropriate biological units for biomimetic and supramolecular applications. Based on the successful usage of RAFT polymerization [1] on dendronized polymers, bifunctional RAFT reagents were prepared and used for polymerization of G1-G2 macromonomers, in which the single site introduction is achieved by functionalizing the RAFT reagent. In addition, latest progress on the synthesis of non-linear G1 and G2 dendronized polymers is reported.



Scheme 1: a) The most recent bifunctional RAFT reagent bearing a *p*-nitrophenyl active ester as the single attachment site, b) trifunctional RAFT reagent for syntheses of 3-armed-star dendronized polymers.

[1] A. Zhang, L. Wei, A. D. Schlüter, *Macromol. Rapid Commun.* **2004**, 25, 799-803

Synthesis and Characterization of Radiation Grafted Membranes for Polymer Electrolyte Fuel Cells

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Radiation induced grafting is a well established method for the preparation of polymer electrolyte membranes for fuel cells. This method allows the use of a wide variety of base films and monomers which may be tailored to the desired end-use and it offers the promise of cost-competitive membranes for the polymer electrolyte fuel cell (PEFC) [1]. Paul Scherrer Institut (PSI) has been committed to developing fuel cell membranes by radiation grafting since 1992. Styrene based membranes using poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP) and poly (ethylene-*alt*-tetrafluoroethylene) (ETFE) films as base material have been prepared by radiation grafting followed by sulfonation. The parameters of grafting were identified to have significant effect on the degree of grafting and were subsequently optimized [1]. The preparation steps and crosslinking affected thermal properties of the films. FTIR /ATR measurements indicated that radiation grafted films were more highly crosslinked in their near surface regions. The fuel cell performance of FEP based membranes was comparable to commercially available Nafion®112 membranes of similar thickness and durability of several thousand hours [2]. ETFE based membranes exhibited encouraging fuel cell performance and there is room for improvement through optimization of that type of membranes [1].

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Phase behaviour, processing and electronic properties of poly(2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-*b*](thiophene) (PBTTT) polymers

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Electronic property of organic semiconductors is often critically depending on their ability of ordering on the molecular level during thin-film formation. In polymer semiconductors, structural features that promote lamellar ordering and extend the π -conjugation generally originates in high field effect mobilities and overall good device performances (1-3). Therefore, it appears that understanding and manipulation of processes controlling the molecular assembly will be the key to the entire field of organic electronics, molecular and thin-film based. Here, we present investigations on the phase behaviour and the influence of nature of solvents and processing conditions on the molecular and structural orientation of a very promising class of organic semiconductors, poly(2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-*b*]thiophene) (PBTTT) (4), - property correlation studies aimed at the understanding and optimisation of solution-processed polymer field-effect transistors.

[1] H. Sirringhaus et al., *Appl. Phys. Lett.* **2000**, 77, 406.

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[3] W.R. Caseri et al., *Adv. Mater.* **2003**, 15, 125.

[4] I. McCulloch. et al., *Nat. Mater.* **2006**, 5, 328.

Influence of crosslinking on irradiated ETFE based grafted membranes

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The radiation grafting method is promising technique for the preparation of proton exchange membranes for fuel cells [1]. Previously, poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) based membranes have been prepared and characterized using styrene as the monomer and the influence of the synthesis parameters were fully investigated [2]. In this study, proton exchange membranes were prepared by pre-irradiation grafting of styrene onto ETFE and subsequent sulfonation in the presence of divinylbenzene (DVB) as the crosslinking agent. The grafted films and membranes with varying DVB concentrations and similar degree of grafting (25%) were characterized by Fourier transform infrared spectroscopy (FTIR-ATR) and differential scanning calorimetry (DSC). In addition, dimensional changes and fuel cell relevant properties were examined. FTIR-ATR measurements revealed that the *p*-isomers are more reactive than *m*-isomers, and the grafted films are more highly crosslinked in their near surface regions than in the entire bulk. It was determined by DSC experiments that crystallinity of the films is not affected by the increase of the DVB content. However, the *ex situ* conductivity, measured at room temperature, decreases considerably with the increase of the DVB content. Further investigation on the chemical and mechanical stability and fuel cell performance will be performed for better understanding of ETFE-based membranes.

[1] L. Gubler, N. Prost, S. Alkan Gürsel, G. G. Scherer, *Solid State Ionics* **2005**, *176*, 2849.

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Ionic Liquid Crystalline Dendronized Polymer-Lipid Complexes

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Supramolecular chemistry based on complexes of polyelectrolytes and oppositely charged ionic surfactants has become an emerging technique to design thermotropic liquid crystalline (LC) phases [1]. Use of non-linear polymers as polyelectrolyte templates, has allowed generating a broad panel of LC phases not accessible with polyelectrolytes with linear backbone [2]. In the present work we have explored the use of water-soluble dendronized cationic polymers with generation 1 to 3 as polyelectrolyte templates [3]. The dendron moieties carried an amount of charges directly proportional to their generation. Anionic sulfonated surfactants with hydrocarbon tails varying between 8 and 18 carbons units were used as mesogenic units to complex with the dendronized polymer in stoichiometric ratio. The resulting complexes, investigated by means of small angle x-rays scattering, differential scanning calorimetry, and cross-polarized optical microscopy, were shown to organize in thermotropic LC phases whose structure, period and order-disorder transition temperature were directly dependent on the dendron generation and the length of the surfactant selected.

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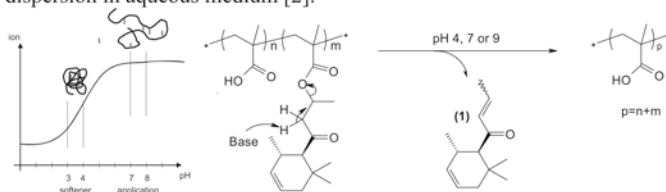
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Controlled Release of Damascones from Random Amphiphilic Polymer-Based Conjugates

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Properfumes, or perfume precursors, have been designed to release fragrance molecules by a chemical process (instead of a physical one) using a trigger, such as pH, temperature or light to deliver the targeted molecules. Our molecular properfumes are derivatives of β -Acyloxy ketones, which have been prepared from enones of the rose ketone family, such as damascones or damascenone via a hydroxyketone [1]. In addition to these molecular systems, the grafting of properfumes onto polymeric materials have been developed and increased the stability of the precursor due to the encapsulating polymer matrix, controlled surface adsorption/deposition, and dispersion in aqueous medium [2].



A series of amphiphilic copolymers has been synthesized for the controlled release of delta-damascone by retro-Michael addition.

[1] C. Fehr, J. Galindo, *Helv. Chim. Acta* **2005**, *88*, 3128.

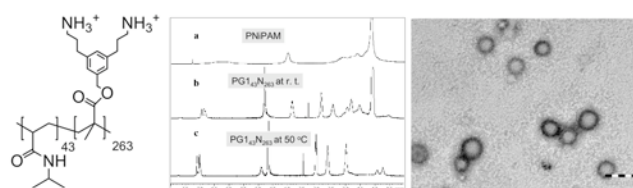
[2] D. Berthier, A. Trachsel, C. Fehr, L. Ouali and A. Herrmann, *Helv. Chim. Acta* **2005**, *88*, 3089.

Thermally reversible vesicles from dendronized block copolymers

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Various self-assembled structures have been found by varying the composition of block copolymers (**bcp**) [1]. In most cases flexible **bcps** were used and vesicles were an oftenly encountered motive. Recently, vesicles made from stimuli responsive **bcps** have attracted more and more attention [2a-2c]. Poly(NiPAM) is the most studied synthetic responsive polymer. There is no report in the literature, however, in which a **bcp** with poly(NiPAM) block led to vesicle formation. We figured that the combination of a rigid block together with this type of stimuli responsive block could eventually lead to vesicle formation. Dendronized polymers are considered more rigid than unsubstituted linear polymer. Here we describe the synthesis of double-hydrophilic diblock copolymers based on charged, dendronized and linear poly(NiPAM) blocks from RAFT polymerization, and their self-assembly behavior in dependence of temperature.



[1] J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc., Faraday Trans. II* **1976**, *72*, 1525.

[2] a) E. G. Bellomo, M. D. Wyrsta, L. Pakstis, D. J. Pochan, T. J. Deming, *Nature Mater.* **2004**, *3*, 244. b) J. Du, S. P. Armes, *J. Am. Chem. Soc.* **2005**, *127*, 12800; *ibid. idem.* 17982. c) J. Rodriguez-Hernandez, S. D. Lecommandoux, *J. Am. Chem. Soc.* **2005**, *127*, 2026.

Poly(dibutylstannane): Synthesis of a Room-Temperature Liquid-Crystalline Semiconductor

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Poly(stannane)s, i.e. polymers of the formula $(\text{SnR}_2)_n$, are a unique class of polymers comprising a backbone of covalently bonded metal atoms. As the polymers which had been synthesized and isolated previously always contained large amounts of impurities (mainly cyclic oligomers) the materials properties of poly(stannane)s are little explored. In fact, they are expected to be electrically conductive or semiconductive because of the sigma-delocalization of the electrons in the metal backbone. Recently, however, we developed a new, facile synthetic route providing pure linear poly(dibutylstannane) of relatively high molecular mass through dehydropolymerization of dibutylstannane with the catalyst $[\text{RhCl}(\text{PPh}_3)_3]$.¹ A reversible phase transition was observed in this material at a temperature of about 1 °C, which was found to be associated with a marked change in crystalline order. The material appeared to be in a liquid-crystalline state at room temperature and could be readily oriented by simple shearing processes, which resulted in highly ordered films. Remarkably, the intrinsically one-dimensional semi-conductivity is in the same range as common pi-conjugated organic polymers.²

(1) Choffat, F.; Smith, P.; Caseri, W. *J. Mater. Chem.* **2005**, *15*, 1789-1792.

(2) de Haas, M. P.; Choffat, F.; Caseri, W.; Smith, P.; Warman, J. M. *Adv. Mater.* **2006**, *18*, 44-47.

Scaling Properties of DNA Knots Studied by Atomic Force Microscopy

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DNA samples consisting of a homo- or heterogeneous mixture of DNA knot types were studied by Atomic Force Microscopy (AFM). DNA knots were irreversibly adsorbed on freshly cleaved mica exposed to 3-aminopropyltriethoxy silane vapors [1]. The DNA contours were analyzed using a customized box counting algorithm, which gives the knot mass as a function of the box size L . The relation between mass and size is given by $\text{Mass} \sim L^{d_f}$, where d_f is the fractal dimension of the knot which is in turn related to the scaling exponent by $\nu = 1/d_f$. This relationship is complicated by the presence of a persistence length of DNA (about 45 nm) which introduces a crossover from a rigid rod behavior to a Self-Avoiding Walk behavior. At present, the data indicate that the fractal dimension is of the order of $d_f = 1.7$, implying a scaling exponent $\nu = 0.58$, very close to the renormalization group prediction for linear self-avoiding polymers in three dimensions. The same kind of study has been done also for DNA knots imaged after deposition onto freshly cleaved mica from a solution containing Mg^{2+} ions. In this case $\nu \approx 2/3$ was found. This value is not equal to the 3D exponent, nor to the two dimensional one ($\nu = 3/4$), indicating incomplete two dimensional relaxation or a different polymer universality class.

[1] F. Valle, M. Favre, P. De Los Rios, A. Rosa, G. Dietler, *Phys. Rev. Lett.* **2005**, *95*, 158105.

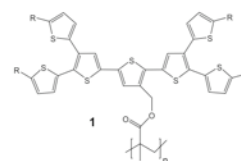
Polythiophene Dendronized Polymers

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Oligo- and polythiophenes are an interesting class of functional π -electron materials and have been well investigated due to their potential application in many fields such as field-effect transistors, photovoltaic cells or photo-switches. In dendronized polymers [1] the dendritic substituents along the backbone can attain a dense parallel arrangement. It was therefore considered attractive to synthesise such polymers with dendrons composed of branched oligothiophenes. If densely enough arranged, the dendritic layer around the polymer backbone could show directed electrical conductivity and/or interesting electro optical properties.



In our work homologous series of dendronized polymers (**1**) with different conjugation were developed by replacing the core unit from benzene [2] to thiophene. The polymers are investigated by their luminescence and photoelectric properties and first optoelectronic applications will be given.

[1] A.D. Schlüter, J. P. Rabe, *Angew. Chem. Int. Ed.* **2000**, *39*, 864

[2] P. Sonar, H. Benmansour, Th. Geiger, F. Nüesch, A.D. Schlüter, *in preparation*

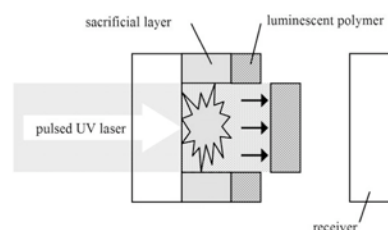
Patterned organic LED fabrication using laser-induced forward transfer

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Conjugated polymers are promising materials for producing optoelectronic devices, such as Organic Light Emitting Diodes (OLED). For display applications it is essential to produce a structured pixel array of organic active materials. A possible method to achieve this is laser-ablation transfer, where a thin layer is ablated by a laser pulse and deposited onto a receiver. However, sensitive organic molecules are degraded under these harsh conditions.



A novel method is proposed, which uses a sacrificial release layer to transfer the luminescent material with little damage upon UV laser irradiation. Living cells have been transferred using this technique [1], showing that this method is suitable for sensitive materials.

[1] A. Doraiswamy et al., *Applied Surface Science* **2006**, *252*, 4743-4747.

Toward Functional, Hierarchically Structured, Optoelectronic Materials Via Self-Assembly

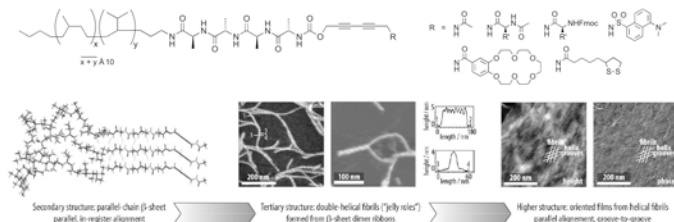
H. Frauenrath,^{a,1} E. Jahnke,¹ A.-S. Millerioux,¹
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Materials aimed at optoelectronic applications at the interface with the bio-sciences must "speak the language" of biomaterials, i.e. provide the chemical functionality and exhibit a similar degree of hierarchical structure formation. We prepared, self-assembled, and polymerized functional diacetylene macromonomers equipped with poly(isoprene)-oligopeptide conjugates and obtained optoelectronically active polymers which match this profile [1, 2]. The macromonomers formed right-handed double helical aggregates. UV induced topochemical polymerization led to poly(diacetylene)s with the same topology. Thin films of the material exhibited a parallel alignment of the helical fibrils with a lateral groove-to-groove register.



[1] E. Jahnke, I. Lieberwirth, N. Severin, J. P. Rabe, H. Frauenrath, *Angew. Chem. Int. Ed.* **2006**, accepted.

[2] E. Jahnke, A.-S. Millerioux, N. Severin, J. P. Rabe, H. Frauenrath, in preparation.

Melt rheology of Polycarbonate/Multiwalled Carbon Nanotubes Composites

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An approach in order to prepare an electrically conductive polymeric material is to disperse carbon nanotubes in a polymer matrix. In such a nanocomposite, the percolation threshold for electrical conductivity is much lower than in composites with conventional conductive fillers like carbon black because of the high aspect ratio of these nanotubes. Therefore these composites can serve as possible antistatic and conductive materials.

Processing of polymeric materials is determined by their flow properties in the molten state. In this study, we explored the rheological properties of an electrically conductive polycarbonate/carbon nanotubes composite in the melt [1]. We performed linear viscoelastic shear oscillations and melt elongation and subsequent recovery experiments. The objective of our study was to elucidate the influence of the carbon nanotubes network on the rheological properties and to investigate the orientation of the nanotubes in elongational flows. Our experimental results revealed that the influence of carbon nanotubes on the flow properties is large if the externally applied stress was small. The orientation and alignment of the nanotubes were studied using transmission electron microscopy. The morphological investigations of the elongated and subsequently quenched polycarbonate/carbon nanotubes composite revealed that isolated carbon nanotubes were oriented by elongational flows.

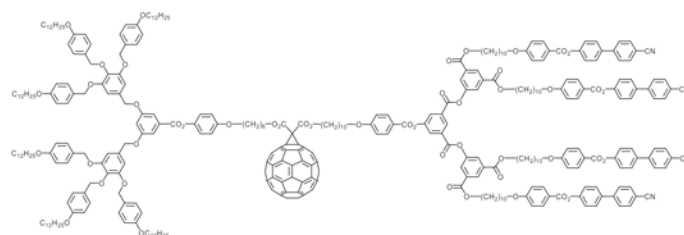
[1] U.A. Handge and P. Pötschke, submitted.

Methanofullerenes Functionalized with two Different Liquid-Crystalline Dendrimers

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Covalent grafting of liquid-crystalline dendrimers onto [60]fullerene (C₆₀) proved to be an effective way to thwart the unfavorable influence of the isotropic C₆₀ unit.¹ We applied the cyclopropanation reaction (Bingel reaction)² to combine C₆₀ with two different dendrons, i.e. a poly(arylester) dendrimer and a poly(benzylether)³ dendrimer, which display smectic and columnar phases, respectively.



Tuning of the mesophases can be controlled and modulated by the size and shape of the dendrimers. Liquid-crystalline properties are indeed depending on the generation, multiplicity of the branches, and connectivity of the dendritic core.

[1] Chuard, T.; Deschenaux, R. *J. Mater. Chem.* **2002**, *12*, 1944.

[2] Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.

[3] Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302.

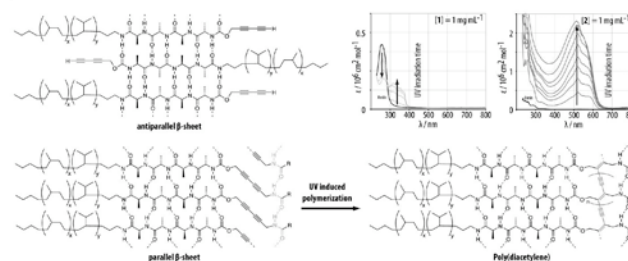
Topochemical Polymerizations in Supramolecular Polymers of Oligopeptide Substituted Diacetylenes

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Beat Meier,² Holger Frauenrath*¹

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Supramolecular self-assembly may provide the order required for topochemical diacetylene polymerizations while the latter are an atom-efficient way of covalent capture which yields optoelectronically active polymers.



We prepared, self-assembled, and polymerized diacetylene macromonomers equipped with β -sheet forming poly(isoprene)-oligopeptide conjugates [1]. Depending on the nature of the end groups, the macromonomers formed parallel-chain or antiparallel-chain β -sheets as evidenced by IR and solid state NMR spectroscopy [2]. In the former case, UV induced topochemical polymerization led to poly(diacetylene)s with complex tertiary structure.

[1] E. Jahnke, I. Lieberwirth, N. Severin, J. P. Rabe, H. Frauenrath, *Angew. Chem. Int. Ed.* **2006**, accepted.

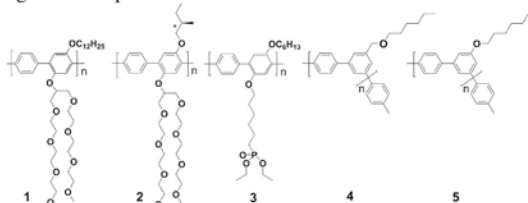
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Novel Synthetic Developments in Suzuki Polycondensation

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Suzuki polycondensation (SPC) is a step-growth polymerization of aromatic monomers to polyarylenes.^[1-2] It involves Suzuki cross coupling (SCC) which is a Pd-mediated carbon-carbon bond forming reaction of aromatic compounds carrying boronic acids (or esters) and usually bromo leaving groups to give biaryls. SPC is a widely used method which has been mostly used for poly(*para*-phenylene)s (PPPs). This poster describes two recent successes in the further development of this reaction, which are its application to amphiphilically substituted monomers and to monomers which lead to poly(*meta*-phenylene)s. Examples comprise the amphiphilic PPPs **1-3** and the poly(*meta*-phenylene)s **4** and **5**. Besides synthetic matters, the achieved molar masses will be discussed as well as the surprising finding that the *meta*-polymers form tough films and have superior fiber forming properties. Finally, the poster will address some mechanistic aspects of SPC such as the identification of end group patterns (by Maldi-TOF) and the degree of Phosphorus and Palladium incorporation (by Laser Ablation ICP-MS) technique using the examples **1** and **4**.



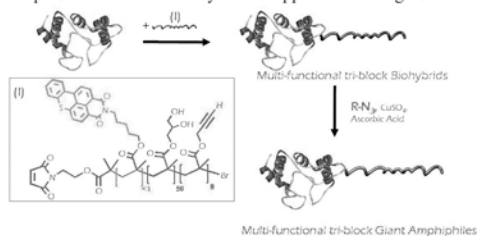
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Formation of giant amphiphiles by post-functionalization of hydrophilic polymers.

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Giant amphiphiles are bio-block-copolymers consisting of an enzyme/or a protein (hydrophilic head group) specifically attached to a hydrophobic polymeric tail. It has been shown in the past that these *bio*-blocks aggregate in ways similar to that of their low molecular weight counterparts.

We present here a novel synthetic approach leading to the first triblock



functionalized with a hydrophilic-polyalkyne-1 polymer (**I**) to form multi-functional tri-block biohybrids. Multiple hydrophobic groups leading to the tri-block giant amphiphiles are introduced on a second step by post-functionalization through the alkyne-1 functionalities and a [3+2]-Huisgen cycloaddition with a variety of azide appended derivatives (Scheme 1).

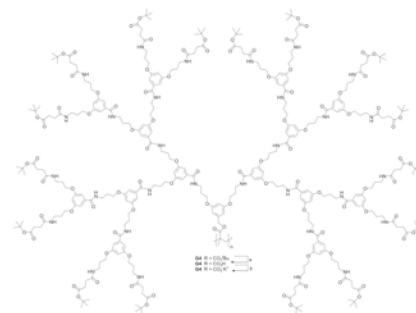
For this approach report on the development of the ATRP synthesis of a series of fluorescent hydrophilic polymethacrylates bearing alkyne-1 side chains on the polymer backbone (**I**), starting from a protected maleimide initiator. The coupling of (**I**) to the proteins has been successfully achieved in aqueous solutions to afford in high yields tri-block hydrophilic biohybrids. These could then easily be post-functionalized by click chemistry with a wide variety of hydrophobic azide derivatives (such as polymers, alkyl compounds or terpyridines) and lead to the first small libraries of giant amphiphiles the properties of which will be discussed. The idea of post-functionalization allowed better reaction yields and multi-functionalization of the proteins.

Synthesis and Superstructure Formation of Anionically Chargeable Dendronized Polymers

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Dendronized polymers (denpols) have received considerable attention due to both their well-defined, nano-sized structures and accessibility to direct visualization by SFM or TEM.^[1] Additionally, they have numerous potential applications ranging from catalyst supports to formation of huge molecular aggregates by self-assembly. Here we describe the synthesis of a series of novel anionically chargeable G1-G4 dendronized polymers and SFM investigations on molecular superstructure formation with G2 charged and non-charged denpols.^[2]

These new denpols, together with their positively charged counterparts, will be used in wrapping experiments^[3] with the ultimate goal to find ways on how to create hierarchically structured, ordered 3D matter by self-assembly.

[1] Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864-883.[2] Kasëmi, E.; Zhuang, W.; Rabe, J. P.; Fischer, K.; Schmidt, M.; Keul, H.; Ding, Y.; Cölfen, H.; Schlüter, A. D., *J. Am. Chem. Soc.* **2006**, *128*, 5091-5099[3] Shu, L.; Schlüter, A. D.; Ecker, C.; Severin, N.; Rabe, J. P. *Angew. Chem. Int. Ed.* **2001**, *40*, 4666

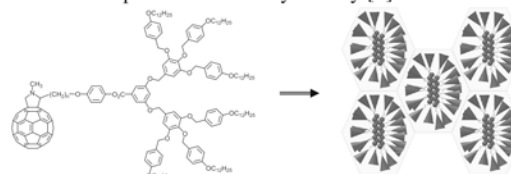
Liquid-Crystalline Fullerodendrimers which Display Columnar Phases

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The exceptional photophysical and electrochemical properties of [60]fullerene (C₆₀) have attracted much attention in various fields, ranging from medical application to creation of new materials. However, the poor solubility of C₆₀ and its tendency to form aggregates are major problems for such practical applications. The organic functionalization of fullerenes has helped to overcome these obstacles.

Fullerene-containing columnar liquid crystals are of interest for electronic and optoelectronic applications (e.g. one dimensional electron transportation). We have demonstrated that covalent attachment of liquid-crystalline dendrimers to C₆₀ is a good way to obtain different anisotropic materials [1]. We decided to use poly(benzyl ether) dendrimers developed by Percec [2] which display columnar and/or cubic phases, to functionalize the fullerene via the 1,3-dipolar cycloaddition. The fullerodendrimers obtained display rectangular columnar phases of *c2mm* symmetry [3].

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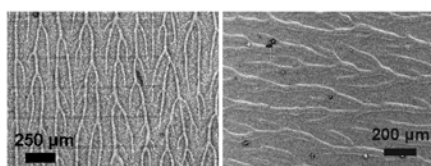
High-speed micro-patterning of polymer films driven by a fluid dynamical instability

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The development and improvement of polymer surfaces with controlled or low adhesion properties have resulted in a vast number of commodity products in the last few decades. Control on the peeling process and resulting forces are crucial for safe production [1]. In the present work we show the rapid, low-cost micro-structuring of HDPE films with poly(dimethylsiloxane) (PDMS) and its advantageous behavior for the use in low adhesion applications [2, 3].

The adhesive properties of the structured coating were compared to unstructured conventional silicone coatings by measuring the release force of pressure sensitive adhesives. For rubber-based tape the release force of patterned PDMS was reduced by a factor of up to eight if compared to smooth reference silicone.



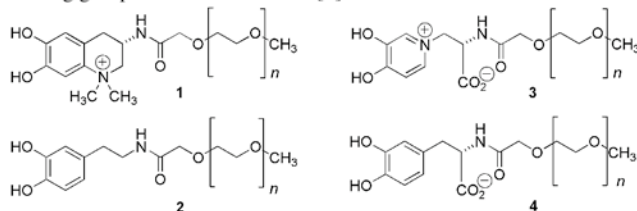
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 [3] S. Loher and W. J. Stark, Method for the application of a structured coating upon a smooth surface, *PCT patent application*, **2005**.

Surface Modification by the Use of Tailor-Made Biomimetic Amphiphiles

Barbora Mališová, David Wäckerlin, Yann Bethuel, Karl Gademann, Stefan Zürcher, Samuele Tosatti, Marcus Textor

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A commonly used method to protect surfaces from non-specific protein adsorption is the immobilization of poly(ethylene glycol) (PEG) via thiol, silane or polyelectrolyte interactions with metals, oxides or polymer substrates [1-3]. We present a novel biomimetic strategy using catechol derivatives, molecules found in mussel adhesive proteins and cyanobacteria, as anchoring groups of PEG to surfaces [4].



All compounds **1-4** were investigated in terms of adsorption behavior and subsequent resistance against serum adsorption, using variable angle spectroscopic ellipsometry (VASE), and X-ray photoelectron spectroscopy (XPS).

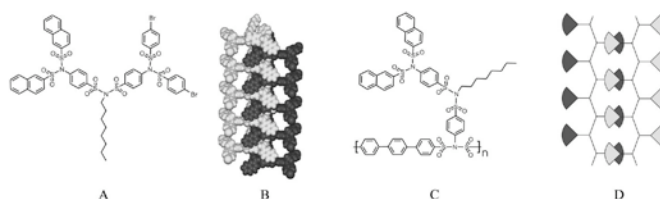
- [1] J. Rundqvist, J. H. Hoh, D. B. Havilland, *Langmuir* **2005**, 21, 2981.
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 [3] S. Pasche, S. M. De Paul, J. Voeros, N. D. Spencer, M. Textor, *Langmuir* **2003**, 19, 9216.
 [4] S. Zuercher, D. Wäckerlin, Y. Bethuel, B. Malisova, M. Textor, S. Tosatti, K. Gademann, *J. Am. Chem. Soc.* **2006**, 128, 1064.

Branched Polysulfonimides: From Molecular to Supramolecular Architectural Control

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Oligosulfonimide dendrimers can be precisely designed with respect to their structural details and thus their shapes [1]. We have discovered that branched structures bearing 2-naphthylsulfonimide functionalities (e.g., as in **A**) efficiently interact via π -donor- π -acceptor contacts between 2-naphthylsulfonyl and *p*-sulfonimidobenzenesulfonyl units. This interaction manifests itself in (i) reproducible packing of different branched structures equipped with 2-naphthylsulfonimide units in the crystalline state, e.g., **B**, (ii) their concentration-dependent ^1H NMR spectra. Linear oligomers, such as **C**, bearing 2-naphthylsulfonimide groups reveal strong aggregation on account of multiple complementary non-covalent intermolecular contacts, schematically shown in cartoon **D**.



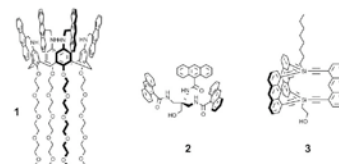
The polymer aggregation was detected by analytical GPC and proved by NMR and AFM studies. The preliminary AFM studies reveal that the polymer aggregates tend to be uniform. Our current goal is to arrive at the complete control over the aggregation behavior of polysulfonimides.

- [1] O. Lukin, V. Gramlich, R. Kandre, I. Zhun, T. Felder, C. Schalley, G. Dolgonos, *J. Am. Chem. Soc.* **2006**, in press.

Towards Monomers for Periodic 2D PolymersCindy Münzenberg,^a Oleg Lukin,^a Katarzyna Kita-Tokarczyk,^b A. Dieter Schlüter^a^a ETH Zürich, Department of Materials, Institute of Polymers, CH-8032 Zürich, HCI J 541, Wolfgang Pauli Strasse 10, Switzerland^b Universität Basel, Institute of Chemistry, CH-4056 Basel, Klingelbergstrasse 80, Switzerland

Two-dimensional, periodic covalent networks reminiscent of sheets of graphite are missing in the landscape of polymer chemistry. All known polymers are either single or double-stranded [1]. An interesting approach was published by Stupp who polymerized two different layers of self-assembled rod-coil-type diacetylenes into 2D objects [2]. Because of random-walk processes, these objects lack periodicity.

This contribution describes a concept which could lead to the targeted 2D macromolecules and the design and synthesis of monomers. The concept involves the ordering capacity of the air-water interface and/or the rigidity of the chosen monomers in order to bring about structurally homogenous sheet-like 2D polymers also in flask-type chemistry. It relies on the anthracene photodimerization as the key growth reaction [3]. Compounds **1** and **2** were already prepared and some aspects of their interfacial behavior will be described. Additionally, the synthetic sequence to the monomer **3** will be presented.



- [1] S. I. Stupp et al. *J. Am. Chem. Soc.* **1995**, 117, 5212.
 [2] A. D. Schlüter, *Adv. Mater.* **1991**, 3, 282.
 [3] H. Bouas-Laurent et al. *Chem. Soc. Rev.* **2000**, 29, 43.

Field-Effect Transistors of Semi-Conducting / Insulating Polymer Blends and Block-co-Polymers

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The established route to semi-conducting block-co-polymers typically combines a crystalline or amorphous conjugated polymer block with an amorphous polymer. We recently reported the synthesis and characterisation of highly regio-regular poly(3-hexylthiophene) and linear polyethylene block-co-polymers that give access to a range of new morphologies. Indeed, we demonstrate that combining the self-organising properties of semi-crystalline P3HT and highly crystalline linear PE allows the exploration of new functional microstructures and expands the processing and structural toolbox of conjugated materials. Here, we present different processing pathways for thin films of crystalline-crystalline block-co-polymers, starting either from solution or melt. The resulting microstructures are compared to those found in the respective blends and homo-polymers by a range of analytical techniques including optical microscopy, differential scanning calorimetry, wide and small angle X-ray scattering and transmission electron microscopy. Electronic behaviour is characterised in field-effect transistor device configuration. The generality of this processing approach has been verified by expanding our investigation from the P3HT / PE model system to other combinations of polymer semi-conductors and insulators.

[1] C. P. Radano, O. A. Scherman, N. Stingelin-Stutzmann, C. Müller, D. W. Breiby, P. Smith, R. A. J. Janssen, E. W. Meijer, J. Amer. Chem. Soc., **127**, 12502 (2005) "Crystalline-Crystalline Block Copolymers of Regioregular Poly(3-hexylthiophene) and Polyethylene by Ring-Opening Metathesis Polymerization"

Poly(4-Methacryloyloxy-TEMPO) via Group Transfer Polymerization and its Evaluation in Organic Radical Battery

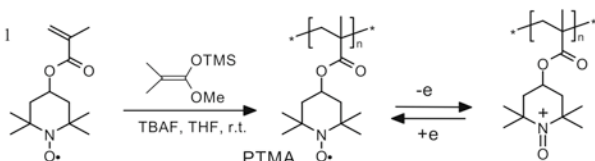
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The reversible oxidation-reduction of nitroxide radicals is the principle of the organic radical battery (ORB)[1]. We report a new GTP polymerization of 4-methacryloyloxy-TEMPO, affording poly(4-methacryloyloxy-TEMPO) (PTMA), containing the theoretical amount of NO^{*} groups (Fig.1). The new PTMA has been tested as an active material in rechargeable ORB. Cyclic voltammetry showed a single, highly reversible redox couple at a potential of ca. 3.6 V (vs. Li/Li⁺). This potential is similar to the potential of the materials (e.g. LiCoO₂) used for the positive electrode in lithium-ion batteries. In galvanostatic cycling experiments between 3.0 and 4.0 V in a half-cell set-up vs. metallic Li as counter and reference electrode, a reversible specific charge capacity of ca. 103 Ah/kg at current rates up to 0.5 C was obtained with the new PTMA. The usable capacity is very stable with cycling, showing only a slight decrease after 200 full charge-discharge cycles at 2 C.

Figure 1



[1] H. Nishide, T. Suga, *The Electrochem. Soc. Interface*, Winter **2005**, 32.

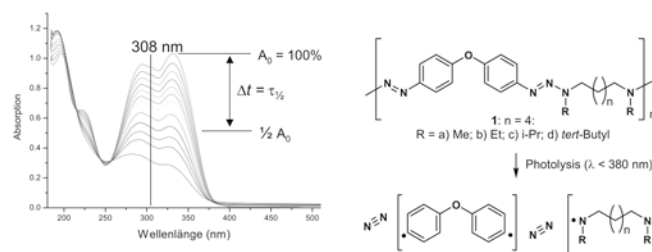
Photodepolymerization of Aryltriazeno Homopolymers

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Polymers with aryltriazeno groups (Ar-N=N-N<) covalently incorporated into the main chain can be easily cleaved by irradiation with uv light and are therefore used for polymer ablation applications with excimer lasers [1]. A homologous series of new aryltriazeno polymers **1 b - d** was synthesized and their photolysis and photodepolymerization behavior was studied at low fluence irradiation (below ablation threshold) in order to derive rational structure-property relations on the effects of the side chains R.



Thin films of photopolymers **1 a - d** (thickness ~ 100 nm) spin-coated on quartz substrates were irradiated with a XeCl* excimer lamp (uv emission band at 308 nm). We found a first order kinetic rate under these quasi-monochromatic irradiation conditions. However, photolysis experiments carried out with polychromatic uv light from a mercury high-pressure lamp showed a more complex photodegradation mechanism.

[1] T. Lippert, *Adv. Polym. Sci.* **2004**, *168*, 51 – 246, and refs. cit. therein.

Polyelectrolyte adsorption on oppositely charged surfaces. A reflectometry study

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The role of pH, ionic strength, pumping speed and polymer concentration on adsorption of poly(diallyldimethylammonium chloride)(PDADMAC) on silica surfaces was studied by reflectometry. It was found that for pH 4.0 and 5.8 an increase in ionic strength leads to an increase in the adsorbed amount of the polymer, while for pH 9.0 there is a maximum at 75 mM salt concentration. When varying the polymer concentration, the plateau value is constant for dilutions up to 10 ppm, and then decreases linearly. Varying the pH, the ionic strength, the polymer concentration or the pumping speed leads to initial adsorption rates of the polymer as expected from the theory.

The thermal analysis of hydrogels obtained from LPEI by crosslinkingCarl Wilhelm Schlaepfer, *Andriy Shkilnyy*

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Water in porous materials is classified into three different types: i) freezing water, with the properties of the bulk water, ii) freezing bound water, with different physical properties and iii) non freezing water, solvating backbone [1]. The distribution of water between these states is important for many applications, such as enzymatic catalysis, permeability, drug solubilization and controlled release. DSC and TG are tools to study the behaviour of water encapsulated in porous materials. Organic hydrogels may also be classified as porous materials, thus the open question is whether the different states of water are observed too [2]. A series of hydrophilic linear poly(ethyleneimine) hydrogels were prepared crosslinking LPEI with heptanedioic and dodecanedioic acids, poly(ethylene glycol)- and 1,4 butandiol-diglycidyl ether. The hydrogels swollen in water were investigated by DSC and TG analysis over wide temperature range in order to determine the phase transitions. Three states of water mentioned above were found to exist in the swollen hydrogels too. A significant difference between melting and freezing enthalpy was observed and explained. The amount of freezable water was determined as a function of the crosslinker, the degree of crosslinking and the heating rate. The model based on experimental results has been proposed.

[1] A. Shreiber, I. Ketelsen and G. H. Findenegg, *Phys. Chem. Chem. Phys.* **2001**, 3, 1185.

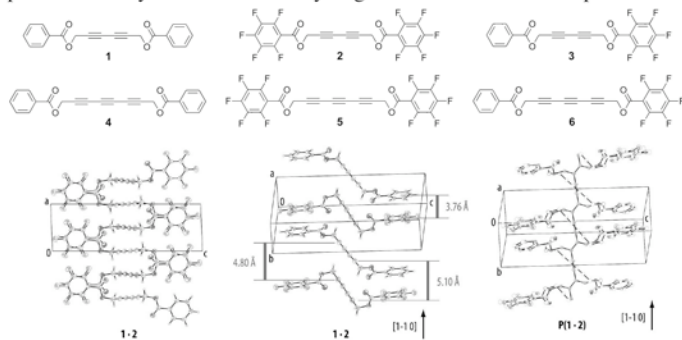
[2] Q. Tian and et al, *J. of Applied Polymer Science.* **2003**, 89, 1258.

Poly(diacetylene)s and Poly(triacetylene)s Utilizing Perfluorophenyl-Phenyl Interactions

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The research in topochemical di- and triacetylene polymerizations has recently been reinvigorated by concepts from supramolecular chemistry. Here, we report the synthesis and polymerization of the crystalline di- and triacetylene monomers **1-6**. All monomers utilize the interaction of perfluorophenyl and phenyl groups which serve as complementary supramolecular synthons similar to hydrogen bond donors and acceptors.



UV irradiation of the 1:1 cocrystal **1 · 2** yielded the alternating diacetylene copolymer **P(1 · 2)** [1]. The perfluorophenyl and phenyl side groups helped to assemble a cocrystal with an alternating placement of the two different diacetylene monomers. The corresponding triacetylenes **6** and **4 · 5** exhibited crystal parameters appropriate for a 1,6-polymerization.

[1] R. Xu, V. Gramlich, H. Frauenrath, *J. Am. Chem. Soc.* **2006**, 128, 5541.

Nucleo-Polymer Hybrids: Use of Biochemical Interactions to Enable the Formation of Functional Nanostructures

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The way Nature creates useful devices is quite astonishing. For instance, only four nucleic acids are necessary to encode the genetics of human beings. Its functionality is highly associated to the nucleotide sequence, and one single defect in this code leads to serious diseases. This specificity and functionality is seen in all biological interactions on the biochemical level, always using limited number of building blocks.

Taking this on account, we intend to use these biochemical interactions between bio-molecules to assemble macromolecules into organized systems. Therefore, the intrinsic precision and control of a sequence of segments (the linking units) enables us to obtain structures on a hierarchy of length-scales with specific order and functions.

Currently, synthetic polymers represent a highly versatile class of materials due to the relative ease to control their composition, structure and properties. However, the synthesis of complex polymers is far from reaching the high level of precision achieved by Nature, not allowing their subsequent hierarchical organization into highly functional structures.

To overcome this issue we are trying to implement the use of entities designed by Nature itself: driven by biochemical recognition, the hierarchical organization of synthetic polymers into nanometer-sized functional structures has been recently demonstrated. The implementation of these structures into biological systems may enable further developments in functional materials, having a high potential to be used in gene therapy or tissue engineering.

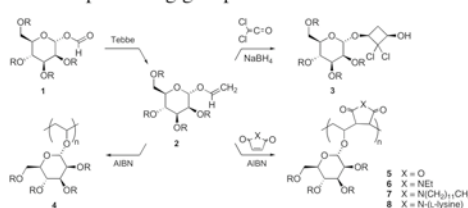
In this scope, using nucleic acids as key-lock linkers for amphiphilic copolymers self-assembly was achieved.

New Glycopolymers via Synthesis and Polymerization of 1-O-Vinyl Glycosides

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A series of anomerically pure 1-O-formyl glycosides **1** was prepared and converted into the corresponding 1-O-vinyl glycosides **2** by Tebbe olefination [1]. The vinyl glycosides were obtained as anomerically pure compounds in good yields. The method was compatible with other functional groups, and the anomeric formate group was regioselectively converted in the presence of ester protecting groups.



The use of various derivatives **2** as the substrates in a [2+2] dichloroketene cycloaddition showed the desired diastereofacial differentiation due to chiral induction by the glycosyl residue. Radical homopolymerizations of **2** in bulk as well as copolymerizations with maleic anhydride and different maleimides yielded glycosylated poly(vinyl alcohol) derivatives as well as their alternating copolymers [2].

[1] J. Yuan, K. Lindner, H. Frauenrath, *J. Org. Chem.* **2006**, accepted.

[2] J. Yuan, K. Lindner, H. Frauenrath, in preparation.