

# Nanostructured conjugated polymers

## Co-workers

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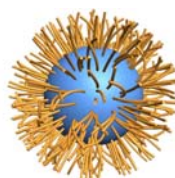
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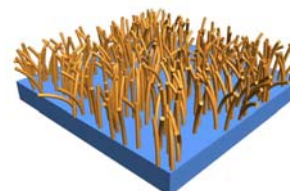
Block copolymers



Molecular brushes



"Hairy" particles



Planar brushes

## Major directions

**Mechanistic studies on the Ni-catalyzed Kumada catalyst-transfer polycondensation**

**Conjugated polymer brushes via surface-initiated Kumada catalyst-transfer polycondensation**

**Hairy particles with conjugated polymer shell via surface-initiated Kumada catalyst-transfer polycondensation**

**Conjugated block copolymers**

**Photovoltaic devices utilized non-conventional architectures of conjugated polymers**

**Conjugated polymer brushes via surface-initiated Suzuki catalyst-transfer polycondensation**

## Projects

1. **"Living" conjugated polymers: a new approach in engineering of complex materials for needs of organic electronics** (DFG, Principal Investigator **Anton Kiriy**, KI-1094/3-1)
2. **Control of the nanoscale morphology of bulk heterojunction solar cells via chemical assembly of conjugated polymers on nanoparticle support** (DFG, SPP 1355: Elementary Process of Organic Photovoltaic, Principal Investigator **Anton Kiriy**, KI-1094/4-1)

(Semi)conductive polymers are highly promising materials for various optoelectronic applications, such as for solar cells, light emitting devices, sensors, etc. State-of-the-art polymer chemistry does not satisfy properly increased demands of organic electronic in conjugated polymers with diverse and precisely controllable architectures (e.g., polymer brushes, block copolymers, "hairy" particles with conjugated polymer shell, stars, etc.) that might self-assemble predictably into well-defined nano-, micro-, and macro-structures.

We develop controlled surface/site-initiated chain-growth Kumada and Suzuki polycondensations to grow conducting polythiophenes and other polymers (e.g., low bandgap polymers) selectively from inorganic and polymer (nano)particles. Polymerization processes

are based on controlled, near “living” polyadditions of monomers to initiating sites instead of usual for polycondensations statistical coupling.

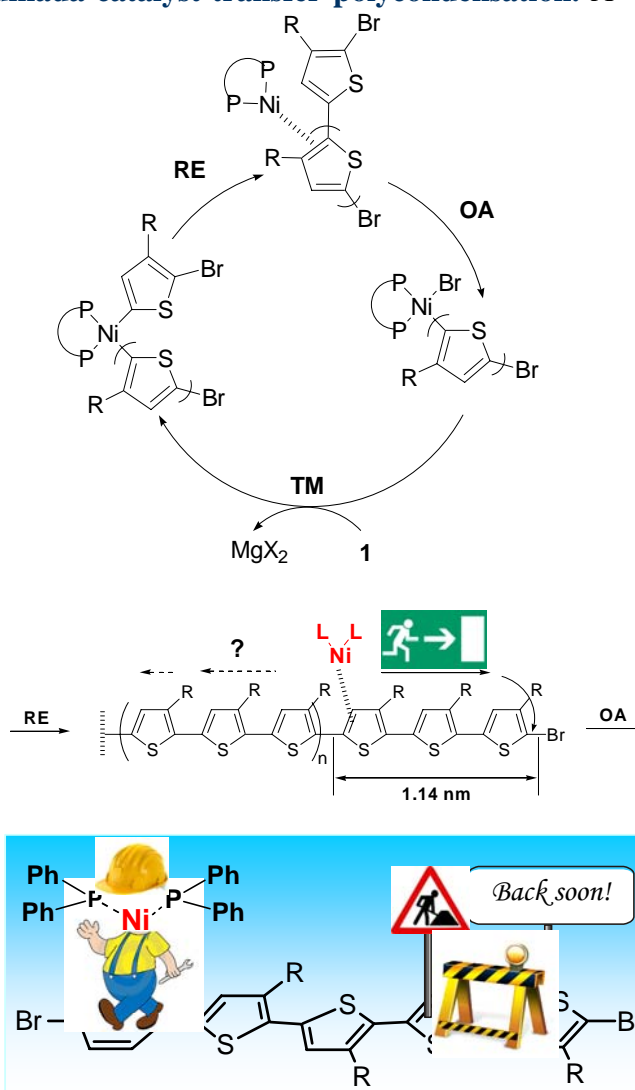
A special attention is paid to detailed understanding of polymerization mechanism of Ni-catalyzed Kumada catalyst-transfer polycondensation.

Efficient engineering of materials with tailored optoelectronic properties requires involvement into chain-growth Kumada catalyst-transfer polycondensation of new types of monomers, including monomers with electron acceptor properties and these studies are underway.

One of the most important application focus is photovoltaics and these works are conducted in a collaboration with Dr. Frederic Krebs group (Risø National Laboratory for Sustainable Energy, TU Denmark: <http://www.risoe.dk/phonebook.aspx?id=3454&type=person>).

### Mechanistic studies on the Ni-catalyzed Kumada catalyst-transfer polycondensation. A

chain-propagation catalytic cycle of Kumada catalyst-transfer polycondensation involves transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) elementary steps. The chain-growth mechanism is provided by the fact that within the chain-propagation cycles the Ni(0) catalytic species eliminated upon the RE step do not dissociate from the chain and do not react with another monomer molecules or other halides, but instead undergo the *intramolecular* OA into a C-Br bond present in the same chain. We found that Ph-Ni(PPh<sub>3</sub>)<sub>2</sub>-Br mediated polycondensations of lengthy AB-type bi- and ter-thiophene oligomers involves predominantly the chain-growth mechanism. This result reflects that in the key polycondensation step the Ni-catalyst undergoes selective *intramolecular* “ring walking” along conjugated systems comprising two or even three thiophene rings. Furthermore, we recently find that catalytic Ni(0) species supported by bidentate phosphorous ligands (e.g., dppe or dppp) are able to “walk” along the polymerizing chain that contains many tens of thienyl rings up to the opposite end and can initiate polymerization there.

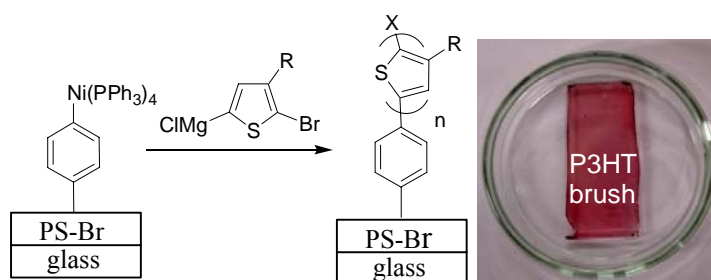


**References.** Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. Kumada Catalyst-Transfer Polycondensation of Thiophene-Based Oligomers: Robustness of a Chain-Growth Mechanism. *Macromolecules* **2008**, *41*, 7817-7823.

Tkachov R.; Senkovskyy, V.; Komber, H.; Sommer J.-U.; Kiriy A. Random Catalyst Walking Along Polymerized Poly(3-hexylthiophene) chains in Kumada Catalyst-Transfer Polycondensation. To be submitted in *J. Am. Chem. Soc.*

## Conjugated polymer brushes via surface-initiated Kumada catalyst-transfer polycondensation.

A method to initiate Kumada catalyst-transfer polycondensation from externally addable and surface-bound Ni initiators was developed. The first generation of externally addable Ni initiators was supported by monodentate phosphorous ligands. Conjugated polymer brushes of regioregular head-to-tail poly(3-alkylthiophenes) (P3AT) were grown via surface initiated polycondensation of 2-bromo-5-chloromagnesio-3-alkylthiophene from photo-cross-linked poly-4-bromostyrene films. Exposure of the initiator layers to the monomer solution leads to selective *chain growth* polycondensation of the monomer from the surface, resulting into P3AT brushes in a very economical way.



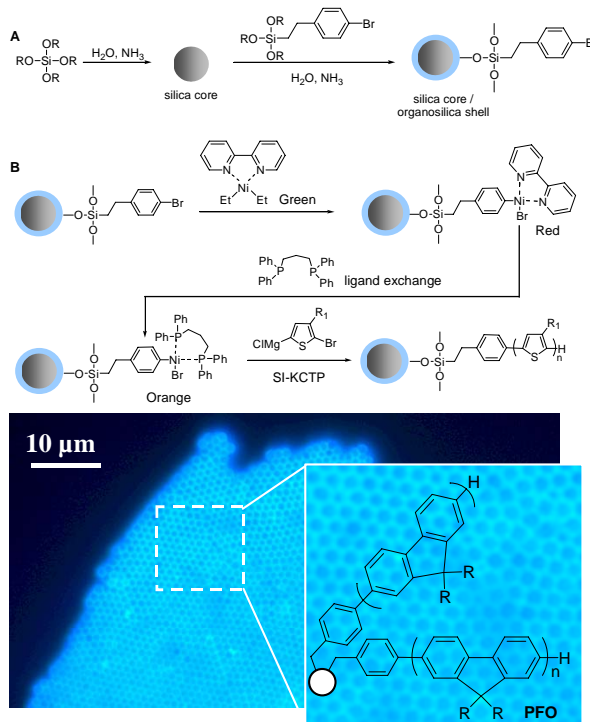
**References.** Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. Conductive Polymer Brushes of Regioregular Head-to-Tail Poly(3-alkylthiophenes) via Catalyst-Transfer Surface-Initiated Polycondensation. *J. Am. Chem. Soc.* **2007**, *129*, 6626-6632.

Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grötzschel, R.; Kiriy, A. Grafting of Poly(3-hexylthiophene) from Poly(4-bromostyrene) Films by Kumada Catalyst-Transfer Polycondensation: Revealing of the Composite Films Structure. *Macromolecules* **2008**, *41*, 7383-7389.

Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. Surface Engineering Using Kumada Catalyst-Transfer Polycondensation (KCTP): Preparation and Structuring of Poly(3-hexylthiophene)-Based Graft Copolymer Brushes. *J. Am. Chem. Soc.* **2009**, *331*, 153-161.

## Hairy particles with conjugated polymer shell via surface-initiated Kumada catalyst-transfer polycondensation

A method to synthesize the second generation of externally addable Ni initiators supported by state-of-the-art bidentate phosphorous ligands (e.g., dppe, dppp) was developed. Poly(3-hexylthiophene), P3HT, a benchmark material for organic electronics, was selectively grown by SI-KCTP from (nano)particles bearing surface-immobilized Ni catalysts that resulted in hairy (nano)particles with end-tethered P3HT chains. Densely grafted P3HT chains exhibited strongly altered optical properties compared to the untethered counterparts (red shift and vibronic fine structure in absorption and fluorescence spectra), as a result of efficient planarization and/or chain-aggregation. The hairy P3HT nanoparticles were successfully applied in bulk heterojunction solar cells. Surface-initiated Kumada catalyst-transfer polycondensation of poly(9,9-dioctylfluorene) (PFO) was also performed from organosilica microparticles that resulted into PFO brushes with densely grafted PFO chains with a significantly enhanced propensity to adopt planar and ordered conformations ( $\beta$ -phase).

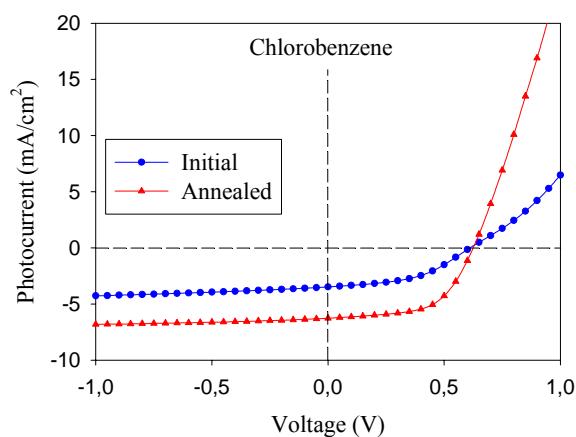


**References.** Tkachov R.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Stamm, M.; Kiriya A. Surface-initiated Kumada catalyst-transfer polycondensation of poly(9,9-dioctylfluorene) from organosilica particles: chain-confinement promoted b-phase formation. *Chem. Commun.* **2010**, 46, 1425-1427.

Senkovskyy, V.; Tkachov R.; Beryozkina, T.; Komber, H.; Oertel, U.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriya A. Surface-Initiated Kumada Catalyst-Transfer Polycondensation (SI-KCTP) of Poly(3-hexylthiophene): a Route to “Hairy” Particles with Tunable Optoelectronic Properties. *J. Am. Chem. Soc.* **2009**, 131, 16445-16453.

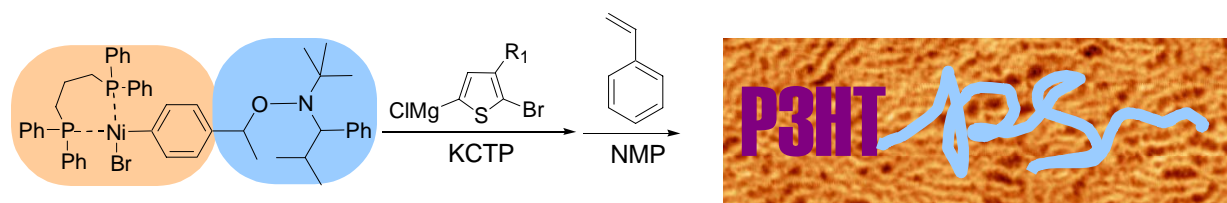
### Photovoltaic devices utilized non-conventional architectures of conjugated polymers.

The challenges associated with obtaining the desired nanomorphology of the active layer in polymer solar cells were addressed through preparation of conjugated polymer chains grown from the surface of seed nanoparticles with a well defined size. P3HT was thus polymerized using a quasi living chain polymerization method initiated by surface modified silica nanoparticles. The nanoparticles with a silica core and a P3HT-corona exhibited excellent solubility and optical properties similar to native P3HT. Upon mixing with PCBM in solution a preorganized ink was obtained that was used to make polymer solar cell modules in a full roll-to-roll coating and printing process operating in ambient air. The polymer solar cells were thus prepared by a mixture of slot-die and flat bed screen printing. Various polymer solar cell modules were prepared ranging from single cells, two, three and eight serially connected cells. The power conversion efficiency for the polymer solar cell modules were in the range of 0.8-1.2 % with an active area of up to 120 cm<sup>2</sup>.



**Reference.** Krebs, F. C.; Senkovskyy, V. C.; Kiriya, A. C. Preorganization of Nanostructured Inks for Roll-to-Roll-Coated Polymer Solar Cells IEEE Journal of Selected Topics in Quantum Electronics **2010**, ASAP.

**Conjugated block copolymers.** A new approach to synthesize rod-coil block copolymers via consecutive Kumada catalyst-transfer polycondensation and nitroxide-mediated free radical polymerization performed from a bifunctional initiator, TIPNO-Ph-Ni(dppp)-Br was developed. The utility of the method was exemplified in a preparation of a model block copolymer, P3HT-*b*-PS with a narrow molecular weight distribution.

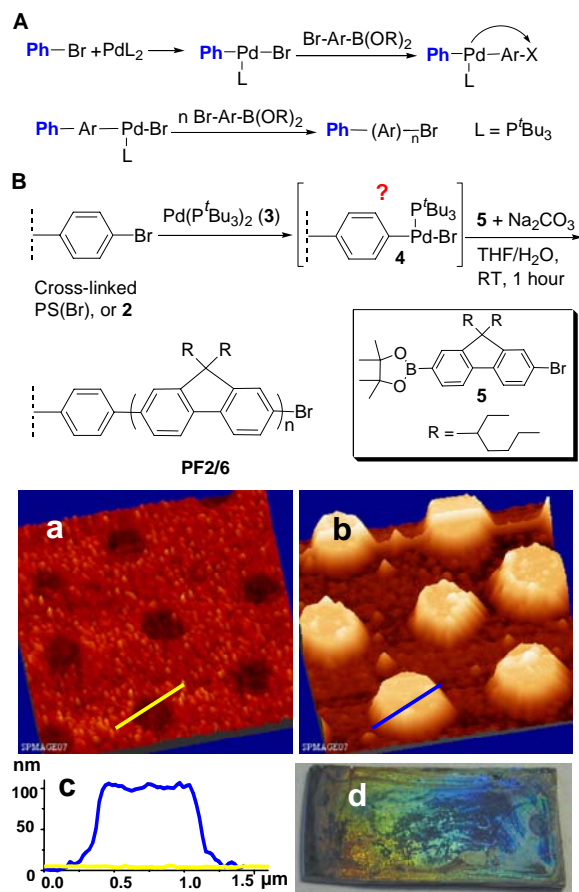


**Reference.** Kaul, E.; Senkovskyy, V.; Tkachov, R.; Bocharova, V.; Komber, H.; Stamm, M.; Kiriya, A. Synthesis of a Bifunctional Initiator for Controlled Kumada Catalyst-Transfer Polycondensation/Nitroxide-Mediated Polymerization and Preparation of Poly(3-hexylthiophene)-Polystyrene Block Copolymer Therefrom. *Macromolecules* **2010**, 43, 77-81.

## Conjugated polymer brushes via surface-initiated Suzuki catalyst-transfer polycondensation.

The first surface-initiated and site specific palladium-catalyzed Suzuki polycondensation to graft and pattern semiconducting and emissive poly[9,9-bis(2-ethylhexyl)fluorene], PF2/6, was developed. Using our method, the grafting of PF2/6 can be successfully performed from surface-immobilized PS(Br) films, as well as from monolayers of small-molecules initiators and (optionally) from patterned initiators. It is important that our grafting process proceeds selectively from the surface and no detectable amounts of the polymer is formed in the solution. Furthermore, the polymerization proceeds fast even at room temperature (RT) and results into grafted PF2/6 films with thicknesses up to 100 nm.

**Reference.** Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Komber, H.; Stamm, M.; Kiriya, A. Surface-Initiated Suzuki Polycondensation of Polyfluorene. *Angewandte Chemie* **2009**, *48*, 2695 – 2698. *Angew. Chem. Int. Ed.* **2009**, *48*, 2695–2698



## Co-operation

1. Dr. **Frederic C. Krebs**, Group-leader of Risø National Laboratory for Sustainable Energy, TU Denmark, Roskilde:

<http://www.risoe.dk/phonebook.aspx?id=3454&type=person>

2. Prof. **Ulrich Scherf**; Bergische Universitaet Wuppertal:

<http://www2.uni-wuppertal.de/FB9/poly>

3. Prof. Prof. Dr. **Thomas Riedl** Lehrstuhl für Elektronische Bauelemente Bergische Universitaet Wuppertal:

<http://www.lfeb.uni-wuppertal.de/index.php?id=2532>

4. Prof. **Wilhelm Huck**: University of Cambridge; Melville Laboratory for Polymer Synthesis

<http://www.ch.cam.ac.uk/staff/wtsh.html>

## Publications

1. Tkachov R.; Senkovskyy, V.; Komber, H.; Sommer J.-U.; Kiriya A. Random Catalyst Walking Along Polymerized Poly(3-hexylthiophene) chains in Kumada Catalyst-Transfer Polycondensation. To be submitted in *J. Am. Chem. Soc.*

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3. Tkachov R.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Stamm, M.; Kiriy A. Surface-initiated Kumada catalyst-transfer polycondensation of poly(9,9-dioctylfluorene) from organosilica particles: chain-confinement promoted b-phase formation. *Chem. Commun.* **2010**, *46*, 1425-1427.
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