



Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

One-Step Ring Opening Metathesis Block-Like Copolymers and their Compositional Analysis by a Novel Retardation Technique

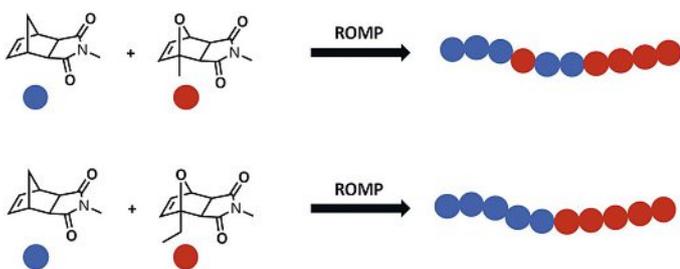
M. Yasir, P. Liu, J. C. Markwart, O. Suraeva, F. R. Wurm, J. Smart, M. Lattuada, and A. F. M. Kilbinger* *Angew. Chem. Int. Ed.* **2020**, DOI: 10.1002/anie.202005366.

University of Fribourg, Max-Planck Institut für Polymerforschung

Block copolymers are highly interesting materials in light of their unique ability to form organized structures *via* self-assembly. Developing one-step syntheses of controlled block copolymers is desirable but challenging, due to the usually low reactivity differences of the used monomers. Ring-opening metathesis polymerization (ROMP) could provide a solution to this problem, in addition to its robustness and chemoselectivity. In this work, the authors investigate the effect of monomer substituents on ROMP rates and block copolymer structures. By mixing monomers with different steric properties, copolymers with the sharpest gradient compositional profile known to date could be obtained. A retardation technique, based on the reversible formation of a Fischer carbene, allowed analysis of the fastest reacting polymers by ¹H NMR spectroscopy. This method could serve as a general tool to study fast ROMP reactions.

Authors' comments:

“Targeting exact block ratios in block copolymers can be a difficult task. Here, all you need to do is mix the two monomers, add a Grubbs initiator and ‘Bob’s your uncle’.”



Sequence-Specific Quantitation of Mutagenic DNA Damage *via* Polymerase Amplification with an Artificial Nucleotide

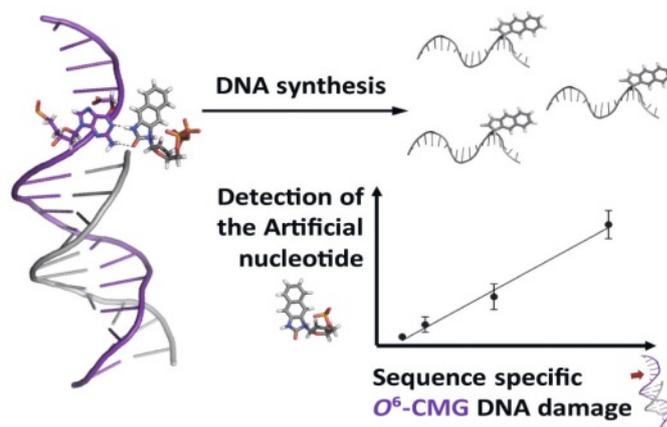
C. M. N. Aloisi, A. Nilforoushan, N. Ziegler, and S. J. Sturla,* *J. Am. Chem. Soc.* **2020**, *142*, 6962–6969.

Eidgenössische Technische Hochschule Zürich

Endogenous and exogenous DNA-reactive chemicals constantly endanger DNA integrity. *O*⁶-Carboxymethyl-guanine (*O*⁶-CMG) is one of the mutagenic DNA adducts often found higher in colonocytes of people who eat meat vs vegetarians, suggesting that colorectal carcinogenesis is induced by its formation. The authors show that the artificial imidic nucleotide triphosphate ExBenziTP selectively pairs with *O*⁶-CMG. This selectivity is attributed to the complementarity of hydrogen bonds and planarity of the *O*⁶-CMG:ExBenziTP pair within the active site of the KlenTaq M747K polymerase. The authors developed a mass spectrometric method showing a linear correlation between the ExBenziTP incorporation during DNA synthesis and the initial *O*⁶-CMG DNA, thus allowing its quantification. This study lays the foundation for the detection of DNA damage for predictive or pre-diagnostic purposes.

Authors' comments:

“The study provides a chemical basis for addressing relationships between DNA damage and mutations in hotspot regions of the genome, which is a main goal of our research.”



Donor-Flexible Bis(pyridylidene amide) Ligands for Highly Efficient Ruthenium-Catalyzed Olefin Oxidation

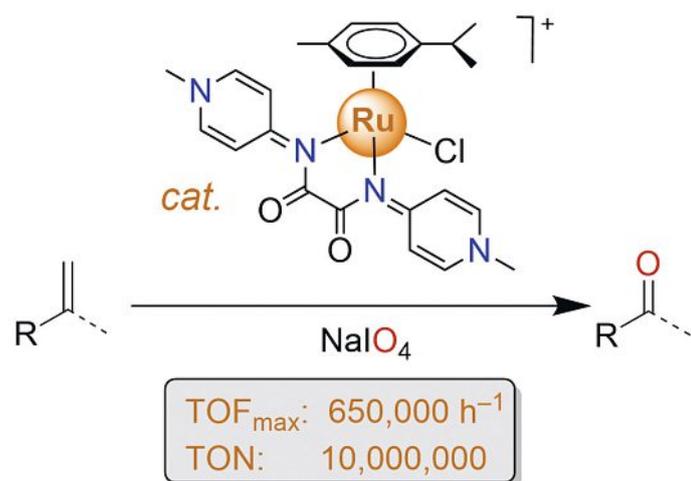
K. Salzmann, C. Segarra, and M. Albrecht,* *Angew. Chem. Int. Ed.* **2020**, *59*, 8932–8936.

University of Bern

The oxidative cleavage of olefins is one of the most common ways to generate carbonyl groups. However, a limited number of catalytic methods exist, and generally require high catalyst loadings or lead to overoxidation products. Herein, the authors report a readily accessible ruthenium complex, supported by the donor-flexible ligand *N,N'*-bis(pyridylidene)oxalamide (bisPYA), which catalyzes the Lemieux-Johnson oxidation of a range of olefins ranging from styrenes to methyl oleate with high turnover numbers and frequencies. Electrochemical and NMR spectroscopic studies indicated that the variable zwitterionic and neutral resonance structures of bisPYA contribute to accelerate the Ru^{II}/Ru^{IV} catalytic cycle. This work advances the catalytic oxidation of olefins and shows a great potential for applications in industry, with the use of ppm levels of readily available catalyst.

Authors' comments:

“Exploring these dynamically bonding PYA ligands continues to be a fascinating journey, especially since they are easy to prepare and have great potential for catalyzing a variety of other oxidative transformations.”



Growing and Shaping Metal–Organic Framework Single Crystals at the Millimeter Scale

A. Sorrenti, L. Jones, S. Sevim, X. Cao, A. J. deMello, C. Martí-Gastaldo,* and J. Puigmartí-Luis,* *J. Am. Chem. Soc.* **2020**, *142*, 9372–9381.

Eidgenössische Technische Hochschule Zürich, Universidad de Valencia

Crystallization is an important process in living organisms but it is poorly understood and controlled by scientists. In particular, the precise control of size and shape of macroscopic single crystals of self-assembled materials remains a great challenge. The authors show that microfluidic environments mimicking microgravity conditions induce the formation of single crystals of CuGHG, a metal-organic framework (MOF) formed by coordination of the tripeptide Gly-L-His-Gly to Cu²⁺, with complex nonequilibrium shapes and sizes up to millimeter scale. Interestingly, they observed that a constant supply of precursors allowed further control of the crystals growth, and that the limited mass transfer in advection-free conditions enabled regrowth to the original shape after laser irradiation damage. These results improve the understanding of fundamental questions in crystallization, and could provide a basis for specific applications of MOFs such as advanced chiral stationary phases for HPLC.

Authors' comments:

“In this contribution, we show for the first time how microfluidic environments mimicking microgravity conditions can be a powerful tool for the on-demand growth of MOF single crystals enabling their design into unprecedented shapes.”

