



Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

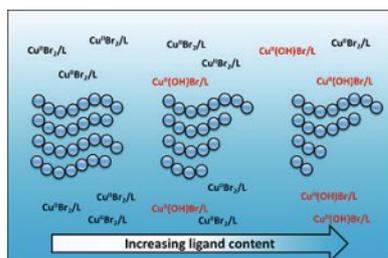
Controlling dispersity in aqueous atom transfer radical polymerization: rapid and quantitative synthesis of one-pot block copolymers

Hyun Suk Wang, Kostas Parkatzidis, Simon Harrisson, Nghia P. Truong*, Athina Anastasaki*, *Chem. Sci.* **2021**, *12*, 14376, <https://doi.org/10.1039/d1sc04241f>
ETH Zurich

A rapid and quantitative method to tailor the dispersity (D) of both homo and block copolymers has been developed for aqueous atom transfer radical polymerization (ATRP). This is the first reported strategy that can control D in aqueous media since all the previous methods operate exclusively in organic solvents, giving slow polymerization rates, moderate conversions, and loss of initiator efficiency. This new method allows for very high monomer conversion (~99%) in a very short time (within 10 min) while maintaining very high end-group fidelity. Moreover, *in situ* diblock copolymers can be synthesized with absolute control over their dispersity, while maintaining monomodal molecular weight distributions.

Authors' comments:

“One of the highlights of this work is its simplicity: By just altering the ligand concentration we can control polymer dispersity in a variety of materials.”



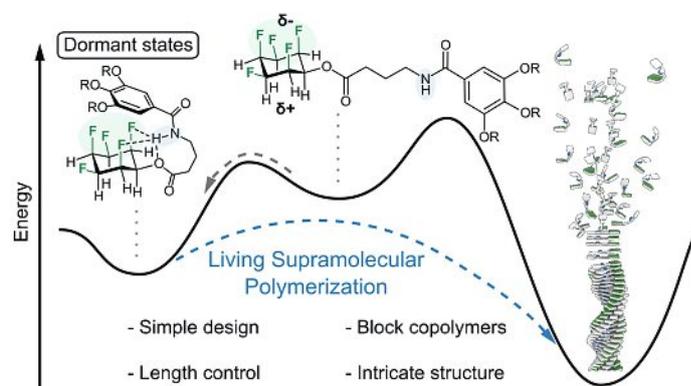
Living supramolecular polymerization of fluorinated cyclohexanes

Oleksandr Shyshov, Shyamkumar Vadakket Haridas, Luca Pesce, Hhayuan Qi, Andrea Gardin, Davide Bochicchio, Ute Kaiser, Giovanni M. Pavan,* Max von Delius*, *Nat. Comm.* **2021**, *12*, 3134, <https://doi.org/10.1038/s41467-021-23370-y>
University of Applied Sciences and Arts of Southern Switzerland, Lugano-Viganello, Switzerland; University of Ulm, Germany; Technical University of Dresden, Germany; Politecnico di Torino, Italy; Università degli studi di Genova, Italy

Living supramolecular polymerization (LSP) is a method of interest for the synthesis of artificial macromolecules. Although the narrow monomer scope and fine-tuning LSP characteristics is a challenge, an innovative minimalistic molecular platform based on all-*cis*-1,2,3,4,5,6-hexafluorocyclohexane was developed. Its large dipole moment was used to thermodynamically drive the self-assembly of supramolecular polymers and to trap metastable monomeric states due to folding. The dormant monomers engage in a kinetically controlled polymerization upon addition of well-defined seeds initiating LSP. Results revealed self-assembled nanofibers of controlled length possessing a peculiar double helical structure. Overall, this study provides a new type of building block for LSP and demonstrates the versatility of the approach by the successful preparation of supramolecular A-B-A block copolymers with variable side chains.

Authors' comments:

“This work got really interesting, when PhD student Oleksandr Shyshov followed up on some really ‘funny’ behaviour of the monomer shown below. A Swiss-German-Italian collaboration was crucial to understand the structure of the nanofibers.”



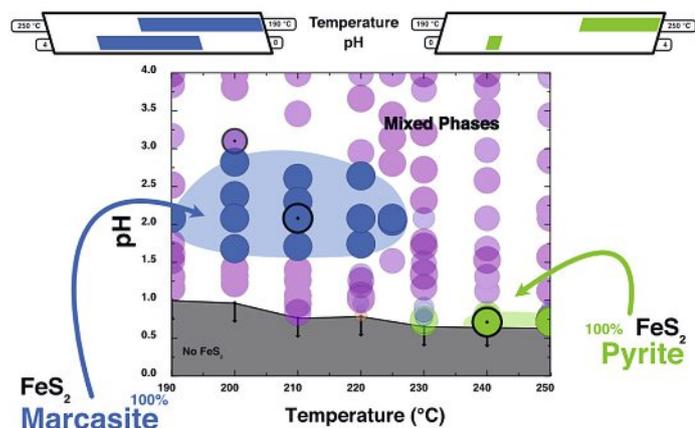
Synthetic control over polymorph formation in the d-band semiconductor system FeS₂

KeYuan Ma, Robin Lefèvre, Qingtian Li, Jorge Lago, Olivier Blacque, Wanli Yang, Fabian O. von Rohr*, *Chem. Sci.* **2021**, *12*, 13870, <https://doi.org/10.1039/d1sc03026d>
University of Zurich

Marcasite is a naturally occurring polymorph of FeS₂ with similar electronic, mechanical, and optical properties as pyrite. Due to the challenging synthesis to obtain pure samples, its application in semiconductor technologies has not been investigated so far. In this work, the authors report a straightforward approach to get high-quality poly- and single crystals of marcasite. The synthesis involves the *in situ* formation of H₂S and sulphur vapor under hydrothermal synthesis conditions at low pH (1.5–2.7) and high temperature (190–225 °C). For the first time physical properties, such as bandgap and transport properties, of pure, laboratory-synthesized marcasite crystals could be analysed. The authors find that marcasite may be a promising alternative to pyrite for applications for solar and photo-electrochemical cells based on earth-abundant elements.

Authors' comments:

“Our results indicate that marcasite is as equally promising as pyrite as a candidate for various semiconductor applications. The here presented synthetic accessibility of marcasite opens up new avenues in this line of research.”



Cassis and Green Tea: Spontaneous Release of Natural Aroma Compounds from β -Alkylthioalkanones

Sarah Bättig, Timothy Egger, Olga Gey, Christian G. Bochet, Felix Flachsmann*, *Helv. Chim. Acta* **2021**, *104*, e2100135, <https://doi.org/10.1002/hlca.202100135>
Givaudan Schweiz AG, Kempththal, University of Fribourg

Molecular precursors designed to enhance the long lastingness of aroma compounds have gained importance in recent years, as they meet some of today's most important sustainability criteria, such as biodegradability and carbon efficiency. In this article, the authors present the release of β -mercaptoketones from readily accessible β -alkylthioalkanones by a novel β -cleavage pathway. Besides β -mercaptoketones, which exhibit potent cassis and tropical fruit scents, this novel precursor class is capable of releasing aldehydes and β -diketones. Thus, different sensory profiles, such as green tea and lily-of-the-valley notes, could be targeted by systematic variation of the precursor structure. A mechanistic model is proposed which suggests that the oxidative degradation occurs through a novel Pummerer-type rearrangement of initially formed persulfoxides.

Authors' comments:

“Based on our findings, we are convinced that β -alkylmercaptoketones are of general interest, e.g. for the slow release of active pharmaceutical ingredients or in agricultural chemistry for the controlled release of crop protection agents.”

