



# Novel Sulfur Polymers: Yellow is the New Green

Hatice Mutlu

19.02.2024

hatice.mutlu@uha.fr

<https://www.is2m.uha.fr>



Institut de Science  
des Matériaux de Mulhouse



**FST**  
Faculté des Sciences et Techniques  
UNIVERSITÉ HAUTE-ALSACE



- ~ 50 years old
- 5 campuses:  
Mulhouse: Illberg, Collines and Fonderie  
Colmar: Grillenbreit and Biopôle







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Wargaming  
IS-2M - Global wiki. Wargaming.net



Reddit  
IS-2M : r/Warthunder



- CNRS-University mixed research unit located in UHA
- chemists, physical chemists, physicists and biologists
- 8 thematic axes (from Functional Polymer Engineering to Multi-Scale Numerical Simulations)
- <https://www.is2m.uha.fr>

# The Mutlu Group: Who are we?

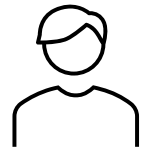


Prof. Dr. Yusuf Yagci (17.03.1952-30.01.2023), an outstanding polymer chemist, expert in photopolymerization.

*"...is one of the luckiest academics because he has always had brilliant colleagues/students in his team..."*



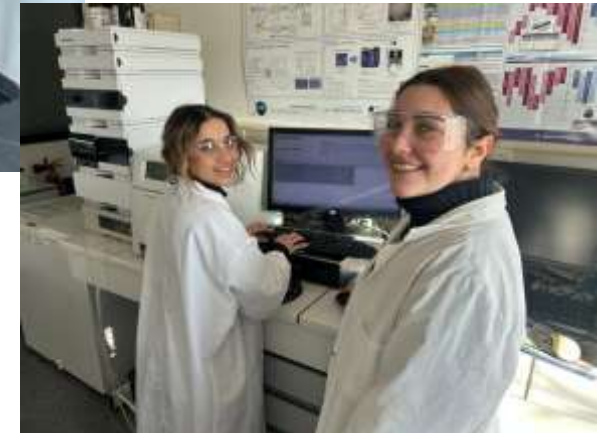
Institut de Science des Matériaux de Mulhouse



Maximilian Hartmann



Linh's talk: 17:25 pm  
Advances in Polymer Synthesis and Characterisation





# Polymers



Since 1940, Polymers are like Oxygen:

...remarkably involved in comfort and facilitation of human life...

...light weight, low cost, and robustness



Sweet

Love is like Oxygen (1977)

Love is Like Oxygen,

You get too much, you get too high,

Not enough and you're gonna die.

Non-renewable raw materials



Türkiye:  
the TRASH BIN of European waste



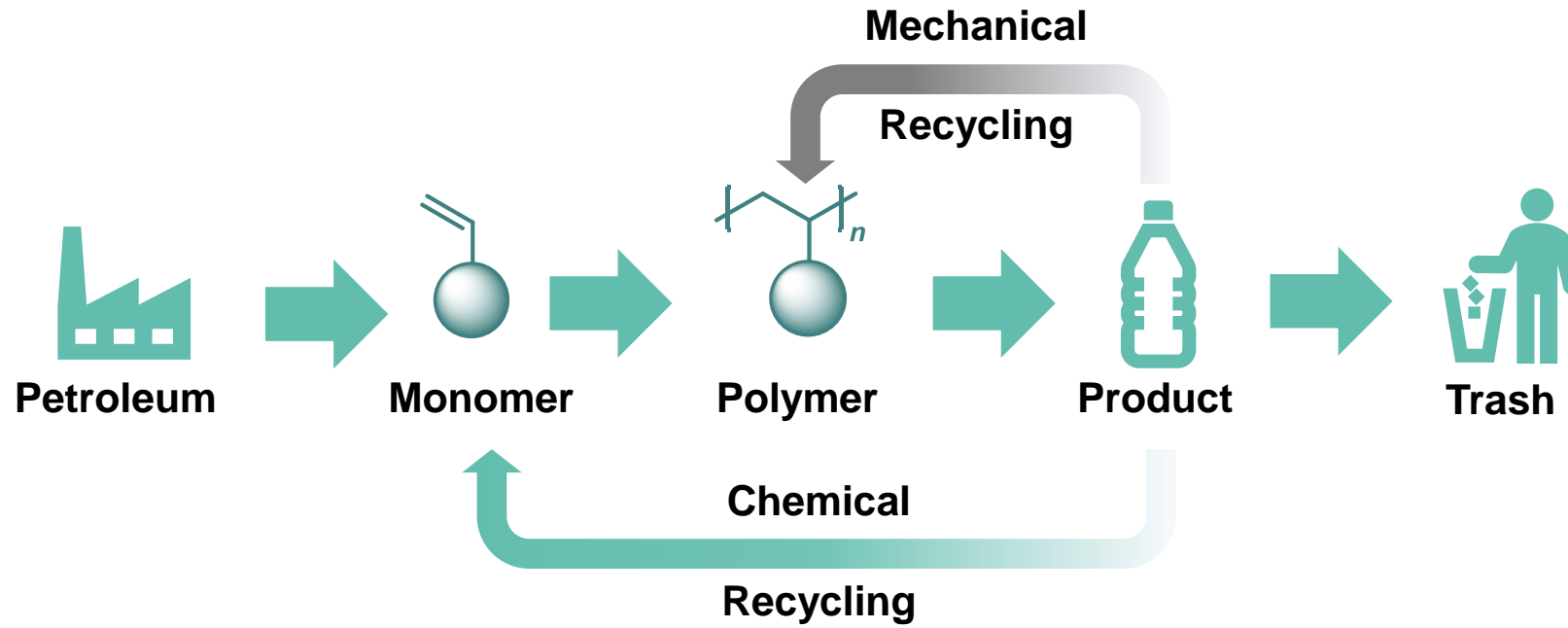
Study Finds Concerning Evidence of Microplastics in Human Breast Milk

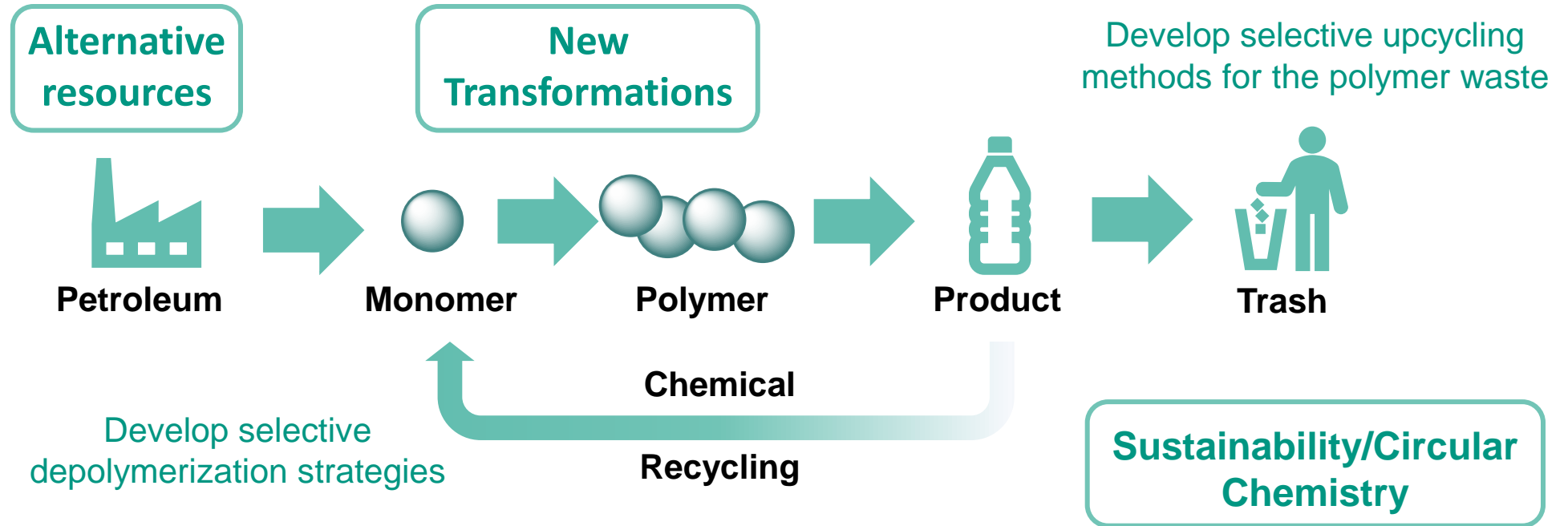


October 18, 2022

3 minute read

Quest for new transformations of alternative feedstocks (either renewable or non-renewable) toward tailor-made/sustainable functional polymeric materials





Getting the Terms Right:  
Sustainable/Green/Circular Chemistry



[M]acro-  
molecular Chemistry and Physics

Perspective | Open Access | CC BY-NC-ND

Getting the Terms Right: Green, Sustainable, or Circular Chemistry?

Hatice Mutlu | Leonie Barner

First published: 03 June 2022 | <https://doi.org/10.1002/macp.202200111>





## Alternative resources

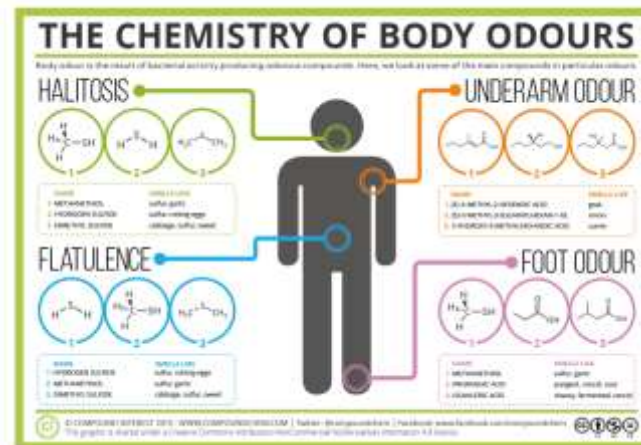
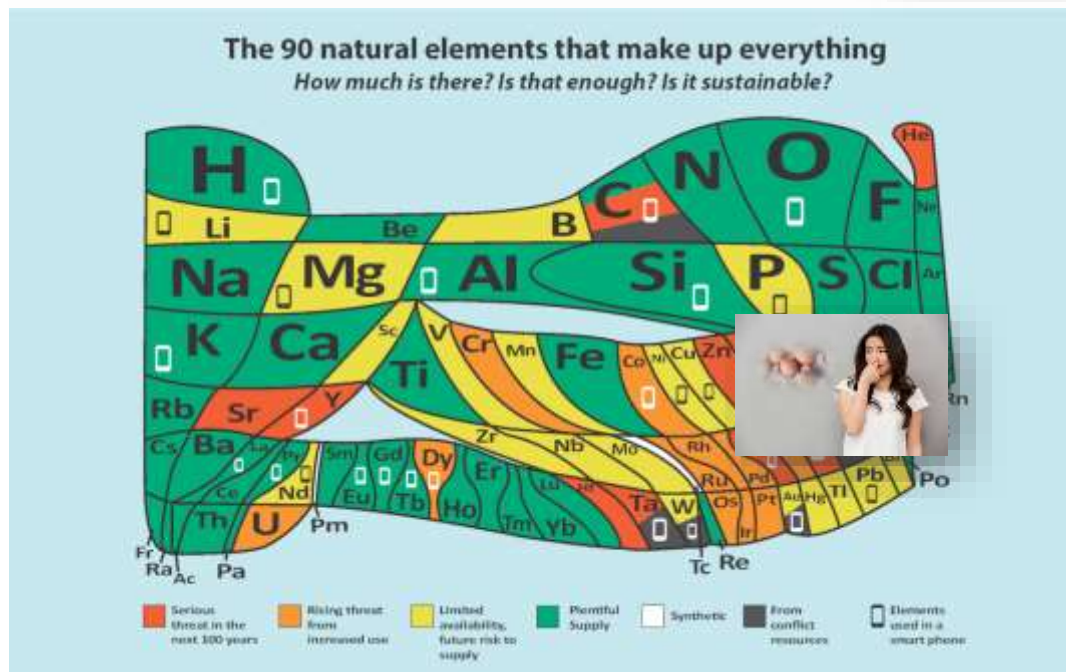


69 million tons/annual

S8 S9

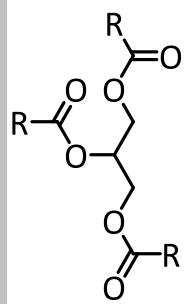
- Stable
- Safe
- Small atomic mass
- Inexpensive
- Easy to handle
- Orderless
- Multiple oxidation states
- Highest S content

\* 1 million tons domestic production, i.e., in Germany  
 \*\* Limited utilization  
 \*\*\* Risks due to careless behavior & Climate Changes: e.g., sulfur pile fire and precipitation of acid rain

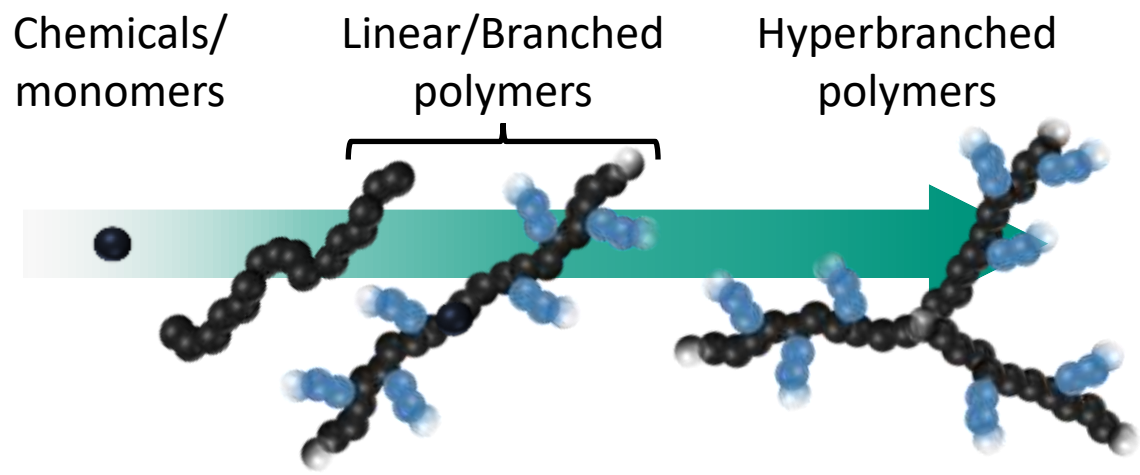
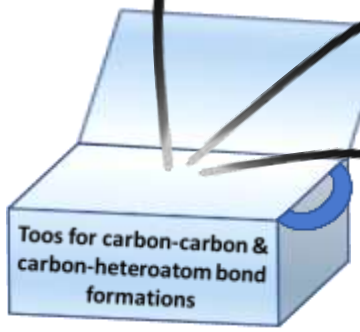
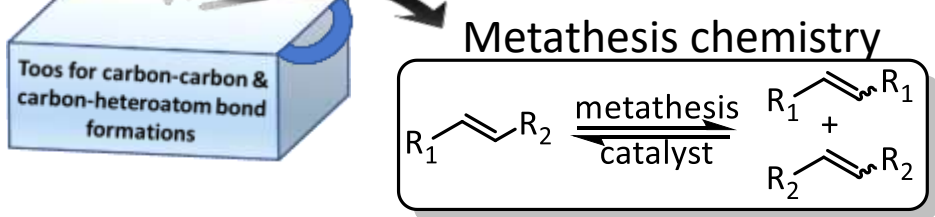
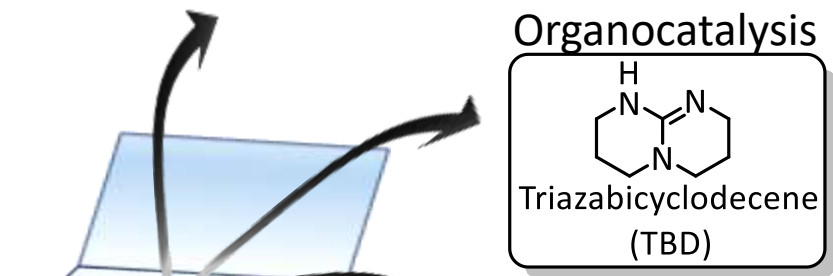
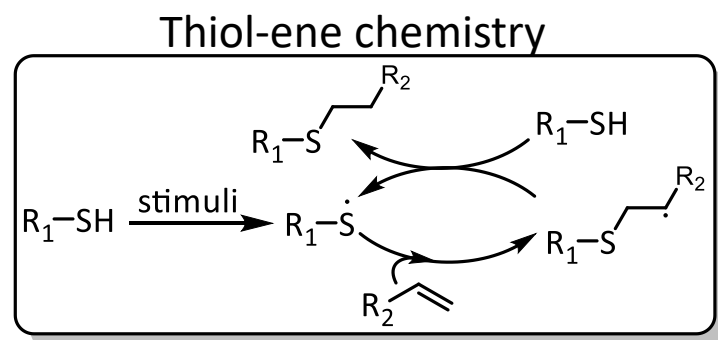




## Alternative resources



R: fatty acid derivatives



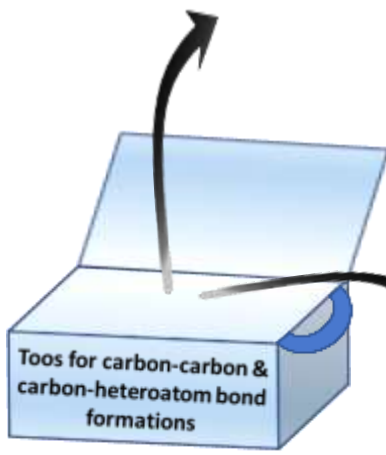
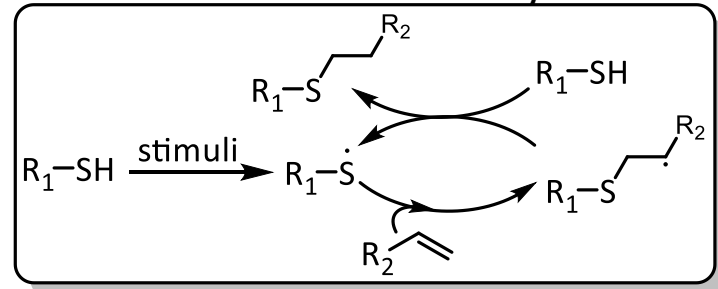
**H. Mutlu** et al., *Macromol. Chem. Phys.* **2009**, 210, 1019; *Eur. J. Lipid Sci. Technol.* **2010**, 112, 10; *Beilstein J. Org. Chem.* **2010**, 6, 1149; *J. Polym. Sci. Part A: Polym. Chem.* **2010**, 48, 5899; *Chem. Soc. Rev.* **2011**, 40, 1404; *Eur. Polym. J.* **2011**, 47, 1467; *Macromol. Chem. Phys.* **2012**, 213, 87; *Green Chem.* **2012**, 14, 1728; *Macromolecules* **2012**, 45, 1866; *Macromol. Chem. Phys.* **2022**, 223, 2100497; *Macromol. Chem. Phys.* **2022**, 223, 2200172; *Macromol. Chem. Phys.* **2022**, 223, 2200111.

## Alternative resources

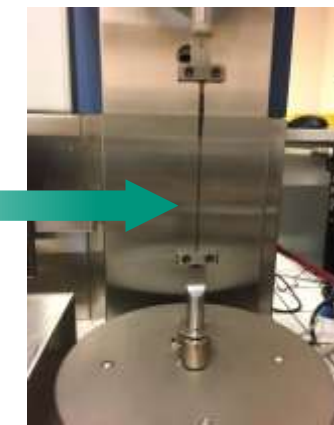
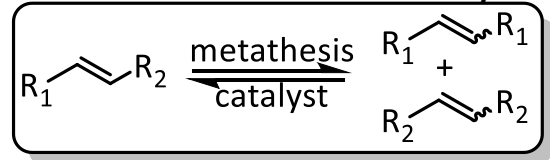
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R: fatty acid derivatives

### Thiol-ene chemistry



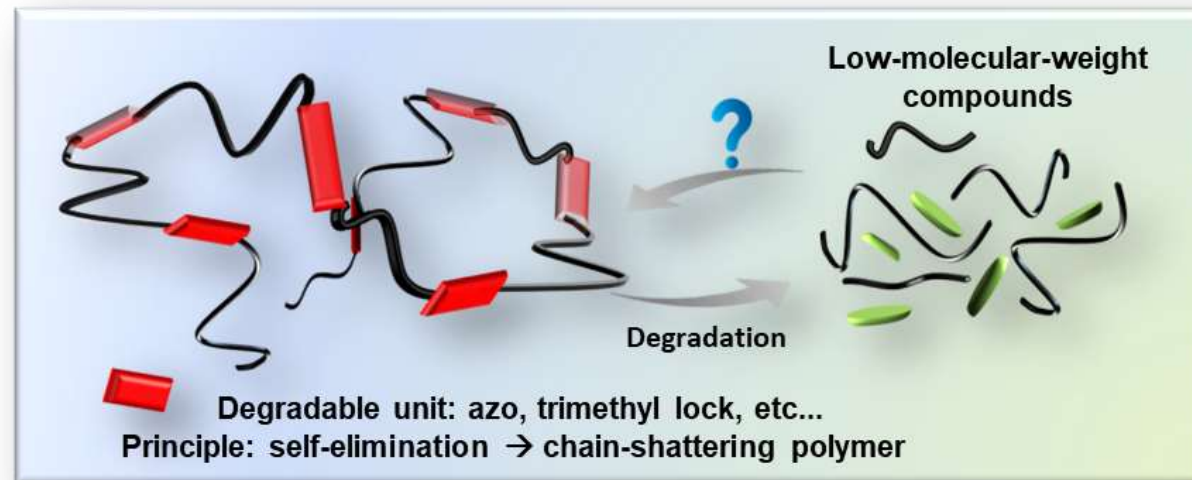
### Metathesis chemistry



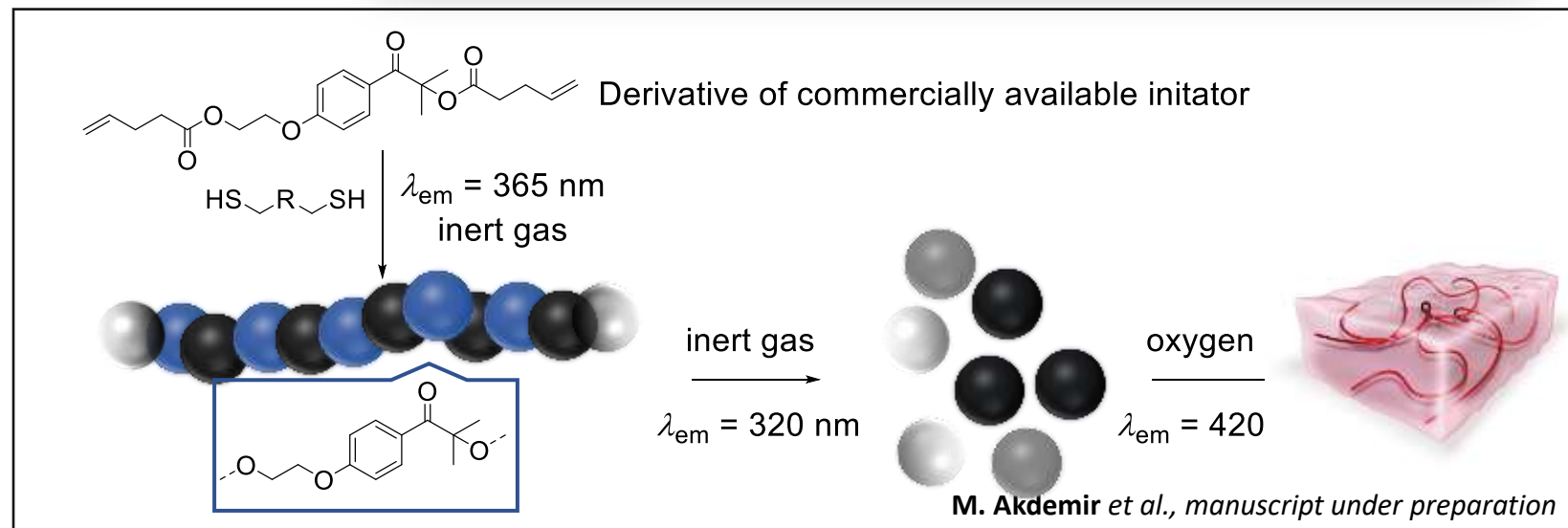
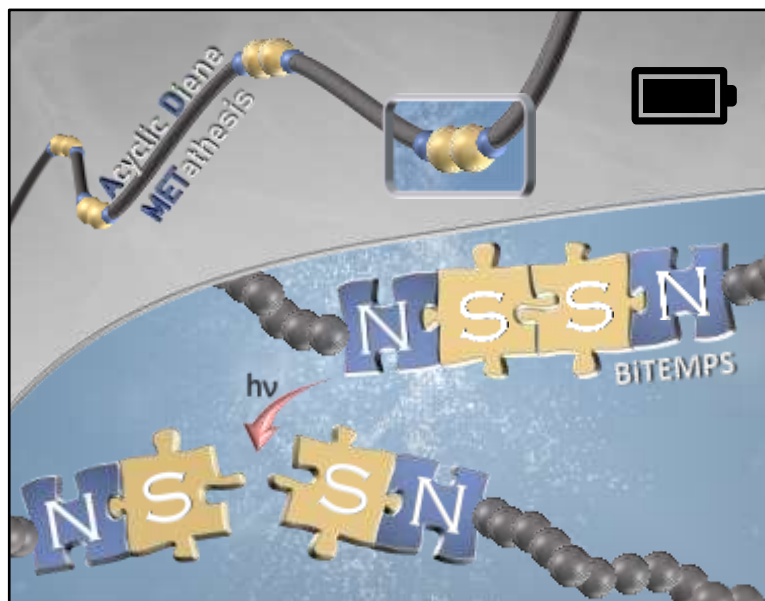
**Collaboration with:**  
**Dr. Johann Kern**  
**(Medical Faculty Mannheim)**  
**Dr. Audrey Llevot**  
**(LCPO, Université de Bordeaux)**

## Alternative resources

### Chemical Up-/Re-cycling/Degradation of Tailor-made Fossil-based Polymers



H. Mutlu *et al.*, *Polym. Chem.* **2016**, *7*, 2272, C. M. Geiselhart *et al.*, *Macromolecules* **2021**, *54*, 1775.



H. Mutlu *et al.*, *Macromol. Rapid Commun.* **2020**, *41*, 2000181; J. Hobich *et al.*, *Macromol. Rapid Commun.* **2021**, *42*, 2100118.



# Solution: Alternative resources



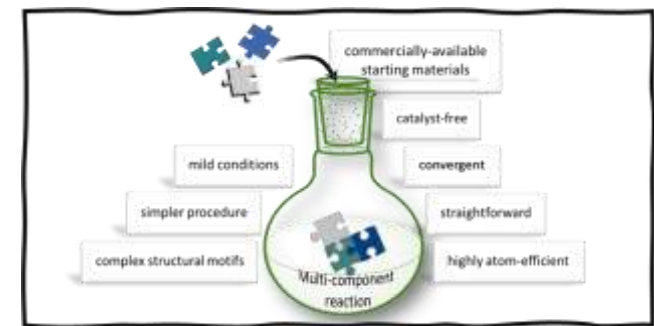
## Alternative resources



69 million tons/annual

$\text{S}_8$   
 Stable  
 Safe  
 Small atomic mass  
 Inexpensive  
 Easy to handle  
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 Multiple oxidation states  
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Macromol. Rapid Commun. 2019, 40, 1800650.  
 Macromol. Rapid Commun. 2020, 41, 2000181.

### 2,4-thiophene decorated (co)polymers

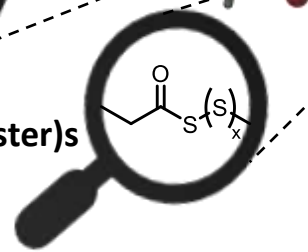
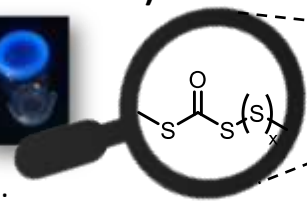
Macromol. Rapid Commun. 2021, 42, 2000695.  
 Small 2024, doi.org/10.1002/smll.202311800.



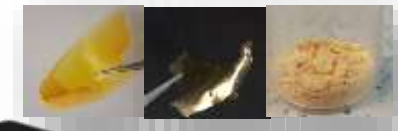
### sulfur-rich poly(dithiocarbonate)s

Polym. Chem. 2022, 13, 5965.

### sulfur-rich poly(thioester)s



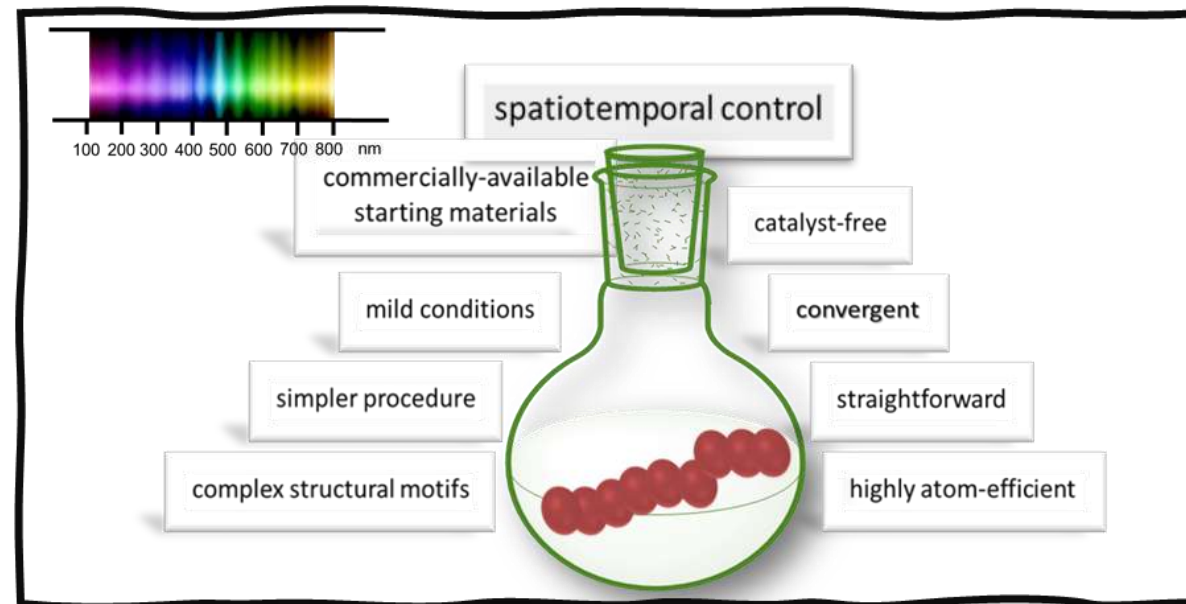
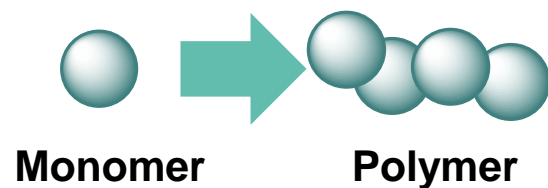
### poly(thiomalonamide)s



### poly(imidazothione)s



## New Transformations

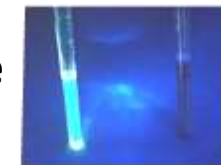


## Self-reporting systems



*Polym. Chem.* **2022**, *13*, 1648; *Macromol. Chem. Phys.* **2021**, *222*, 2100057; *Angew. Chem., Int. Ed.* **2021**, *60*, 17290; *Polym. Chem.* **2021**, *12*, 1732; *Polym. Chem.* **2020**, *11*, 4213; *Sci. Rep.* **2019**, *9*, 14519; *Polym. Chem.* **2017**, *8*, 6199.

## Light (photo)-responsive functional systems

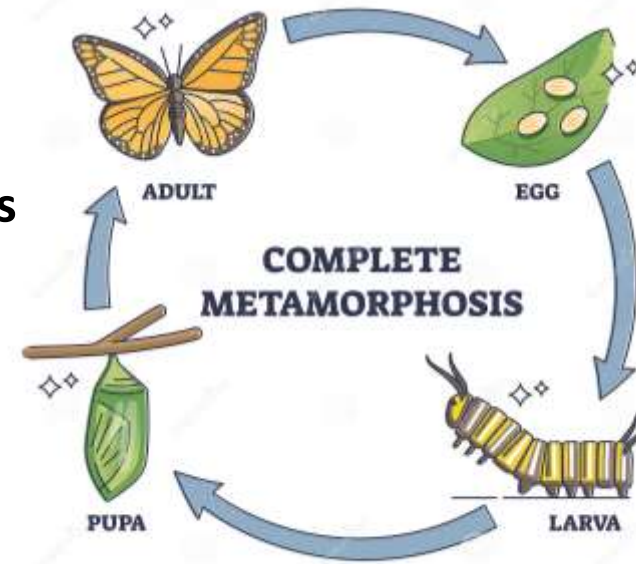
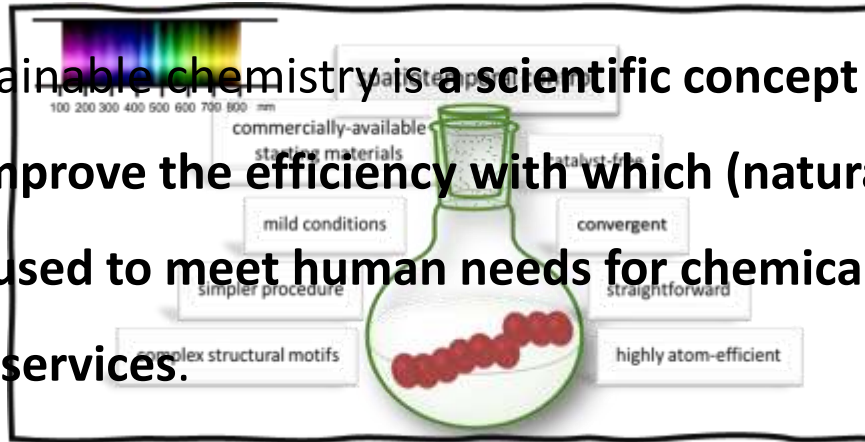


*Angew. Chem.* **2024**, e202315887; *J. Am. Chem. Soc.* **2023**, *145*, 14748; *Polym. Chem.* **2022**, *13*, 5625; *Polym. Chem.* **2021**, *12*, 1732; *Chem. Commun.* **2019**, *55*, 9877; *Polym. Chem.* **2019**, *10*, 4513; *Chem. Eur. J.* **2019**, *25*, 3700; *ChemPhotoChem* **2019**, *3*, 66; *ACS Macro Lett.* **2018**, *7*, 201; *Macromol. Rapid Commun.* **2017**, *38*, 1600598.

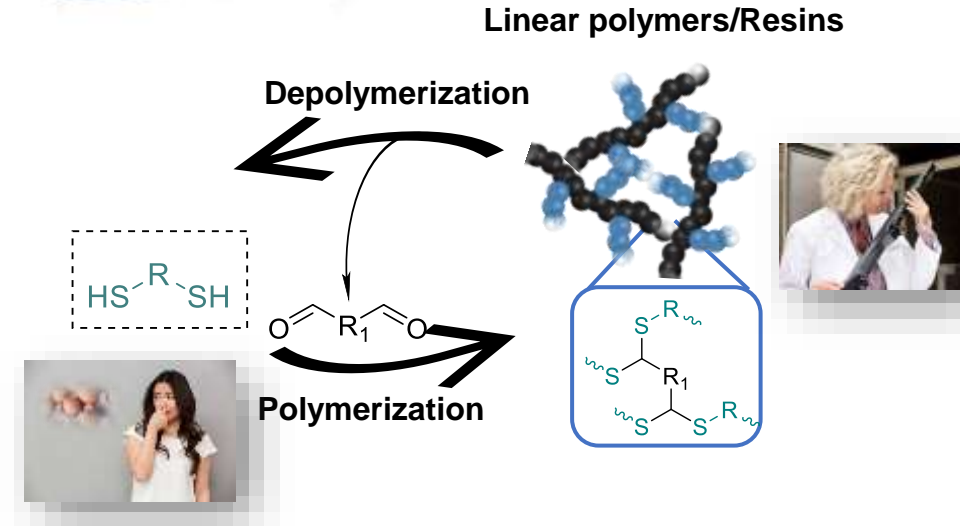
# How we use light towards sustainable sulfur-decorated materials



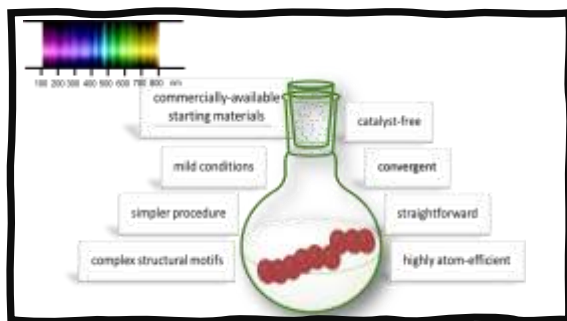
Sustainable chemistry is a scientific concept that seeks to improve the efficiency with which (natural) resources are used to meet human needs for chemical products and services.



1. Avoid chemical derivatives
2. Produce less waste
3. Maximize atom circulation
4. Enhance process efficiency
5. Target optimal design







Research Article [Full Access](#)

## Thiol-Aldehyde Polycondensation for Bio-based Adaptable and Degradable Pheno Polymers

Yu Jin, Chengcheng Hu, Jie Wang, Yongliang Ding, Junjie Shi, Zhongkai Wang, Shichao Xu, Liang Yu

Angewandte Chemie International Edition | Accepted Articles

First published: 19 May 2023

[Abstract](#) ▾

Research Article [Full Access](#)

## Chemically Recyclable Dithioacetal Polymers via Reversible Entropy-Driven Ring-Opening Polymerization

Lasith S. Kariyawasam, Julian Rolsma, Ying Yang

Angewandte Chemie International Edition | Early View

First published: 29 March 2023

[Abstract](#) ▾

Paper

## Synthesis of ROS-responsive poly(thioacetal)s with narrow molecular weight distributions via lactone ring-opening polymerization

Sungwan Kim, Hyein Park, Fabian Fuß and Yan Lee

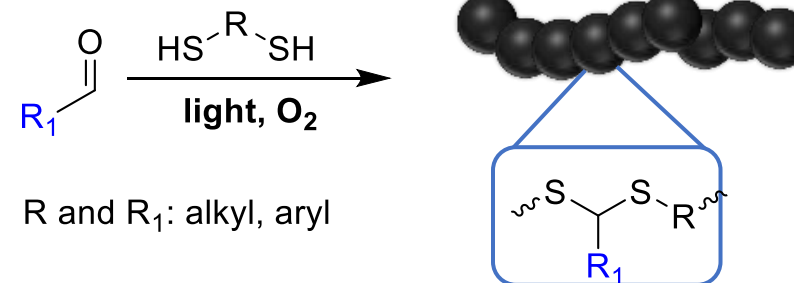
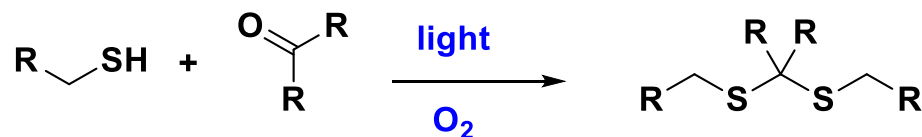
Poly(thioacetal)s with narrow molecular weight distributions were synthesized via lactone ring-opening polymerization. They showed ROS-responsive degradability according to their electronic structures.



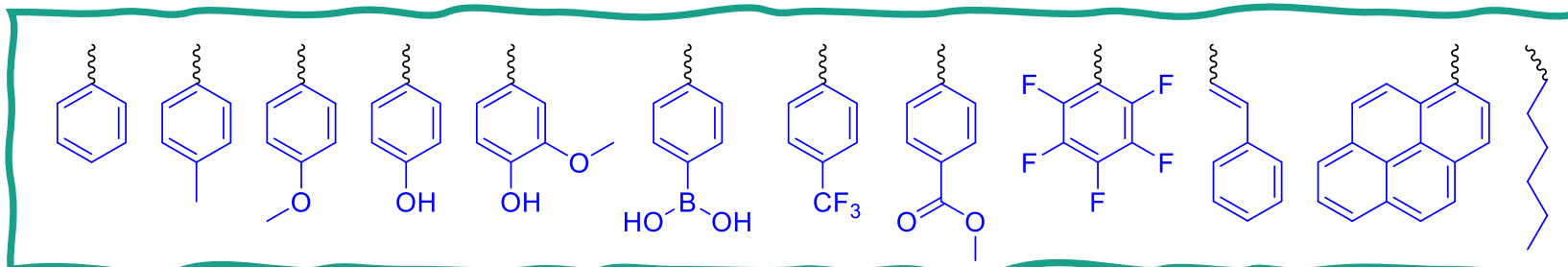
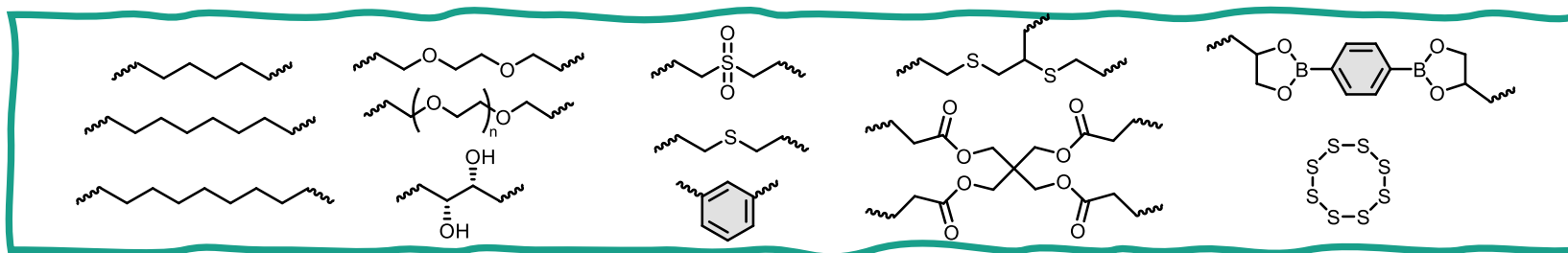
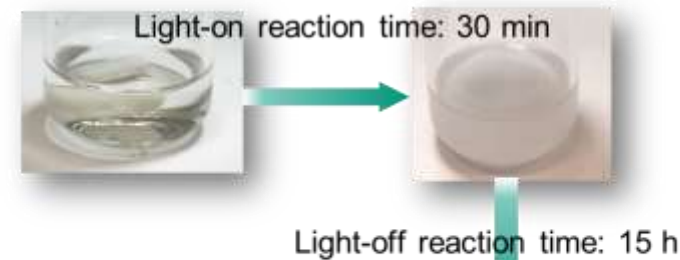
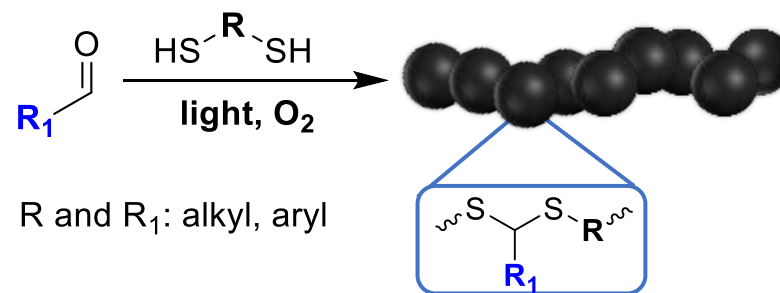
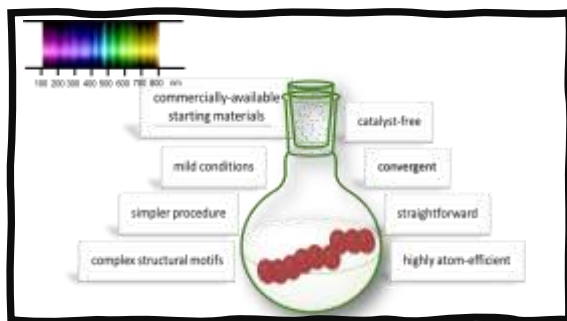
The article was first published on 26 Apr 2023

*Polym. Chem.*, 2023, 14, 2610–2616

<https://doi.org/10.1039/D3PY00239J>



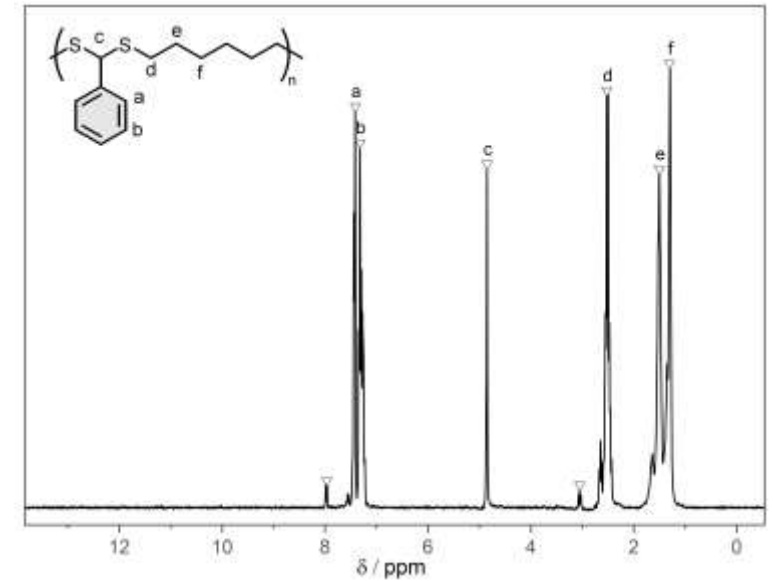
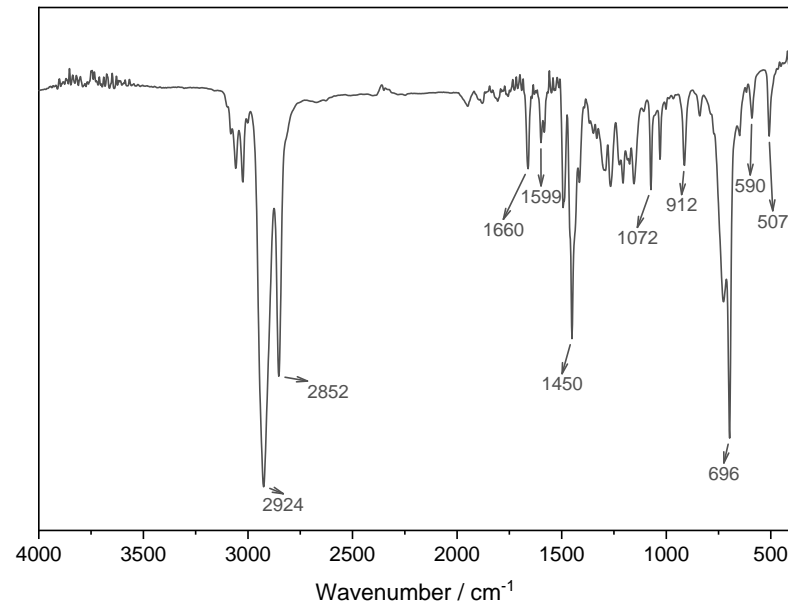
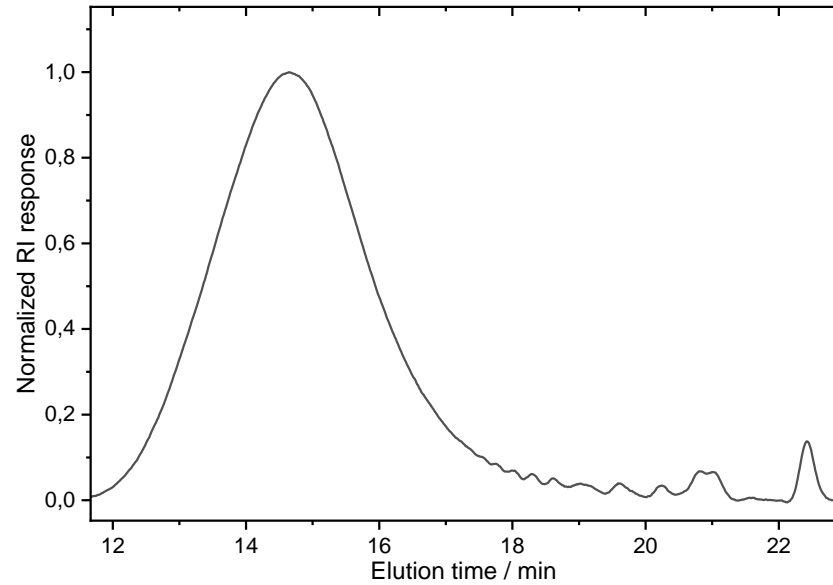
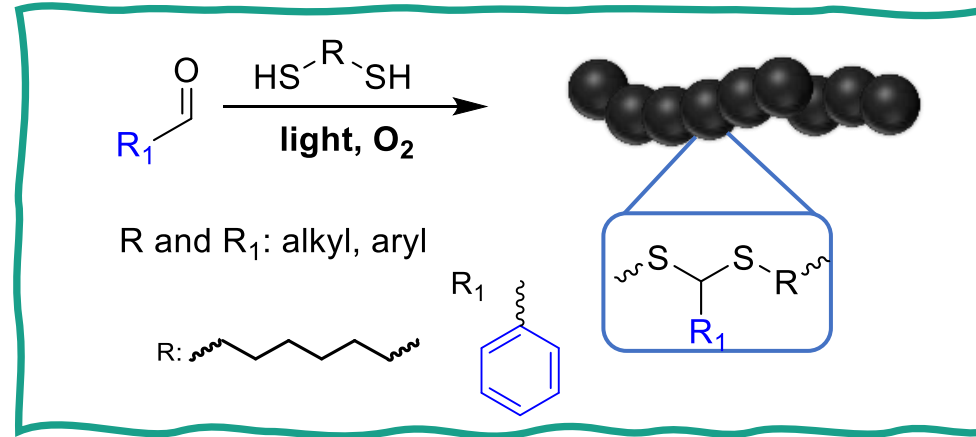
# Marriage of light with sulfur chemistry towards sustainable materials



**Reactions can be performed in bulk and emulsion (Industrially relevant)**

$12\ 600 < M_n < 80\ 000\ \text{g}\cdot\text{mol}^{-1}$   
 $1.7 < D < 2.4$   
 amorphous, semi-crystalline

# Marriage of light with sulfur chemistry towards sustainable materials

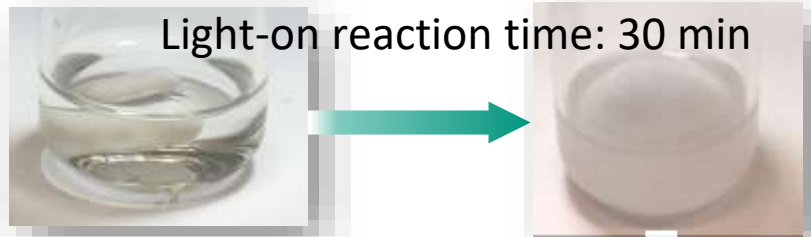






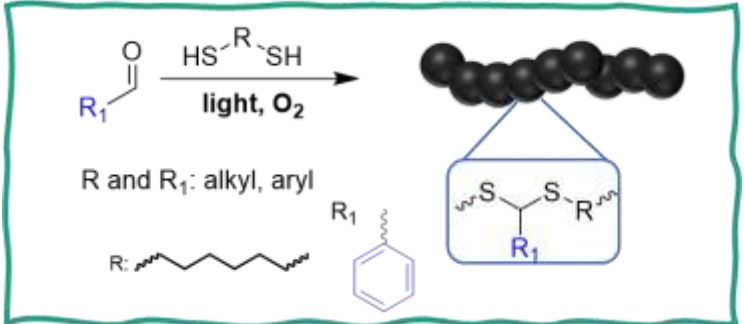
~~Solvent~~

# Sustainability: Re-using the solvent

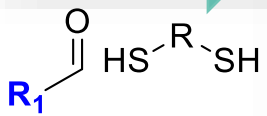
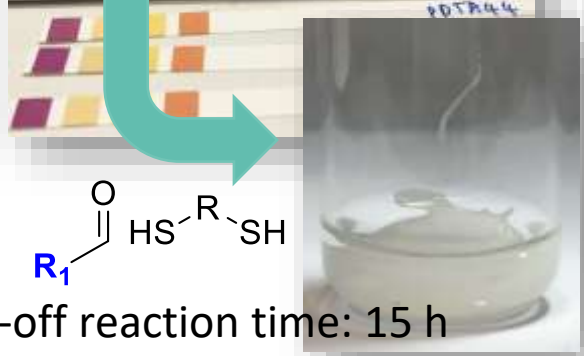


Light-on reaction time: 30 min

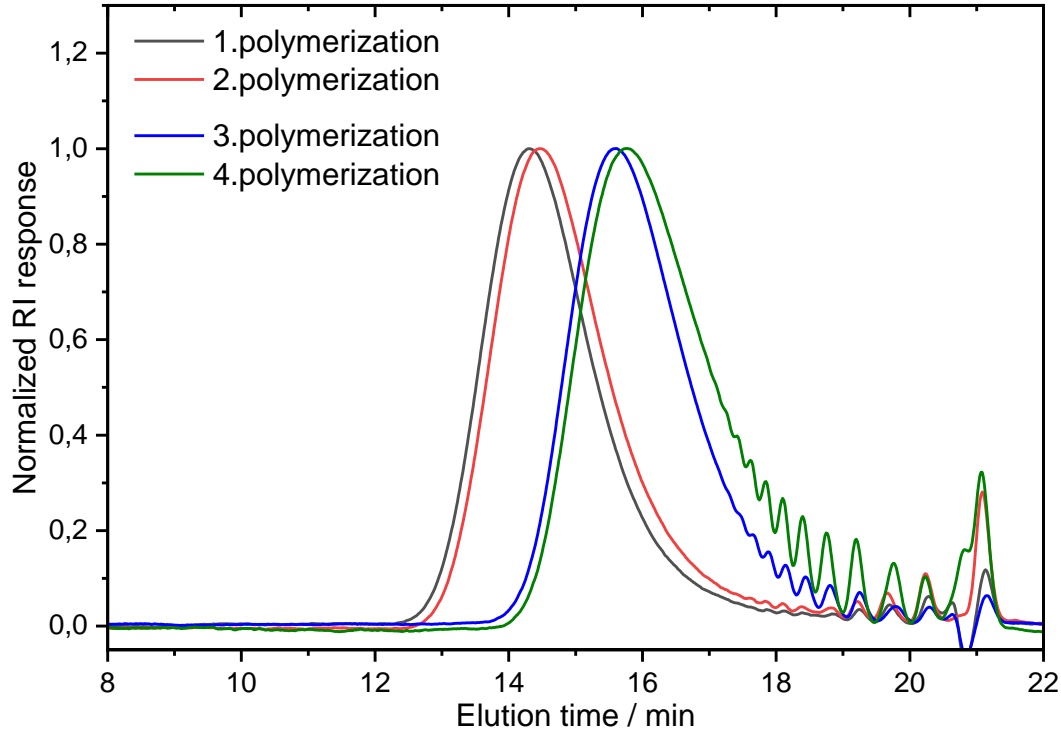
Light-off reaction time: 15 h



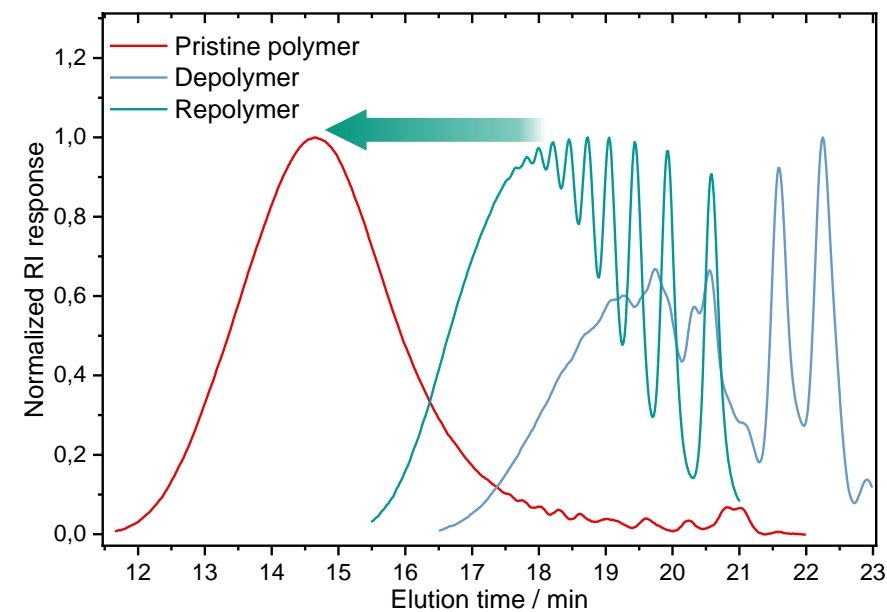
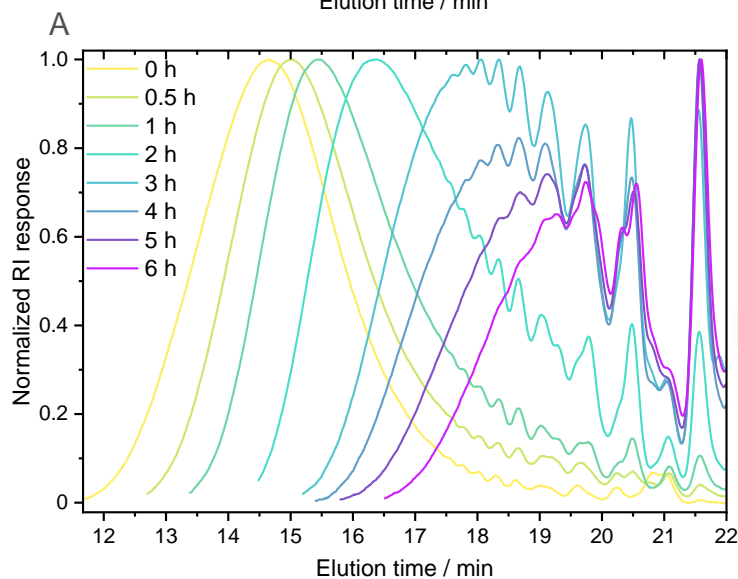
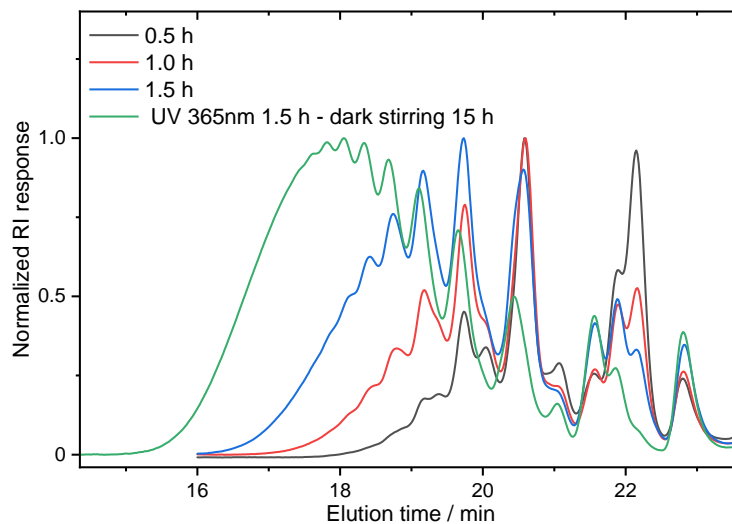
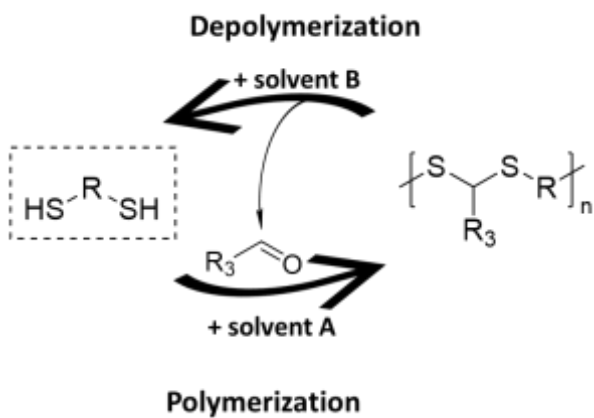
Collect and re-use the waste: solvent



Light-off reaction time: 15 h

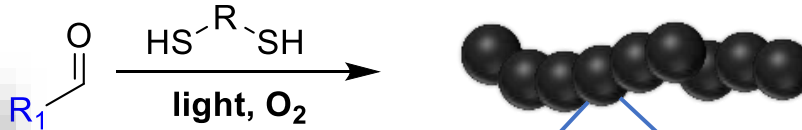


# Sustainability: De- and re-polymerization

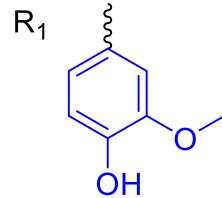
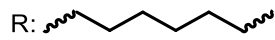




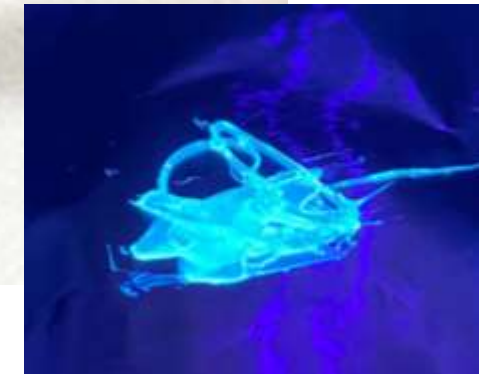
# Potential applications: Adhesives with debonding on demand



R and R<sub>1</sub>: alkyl, aryl

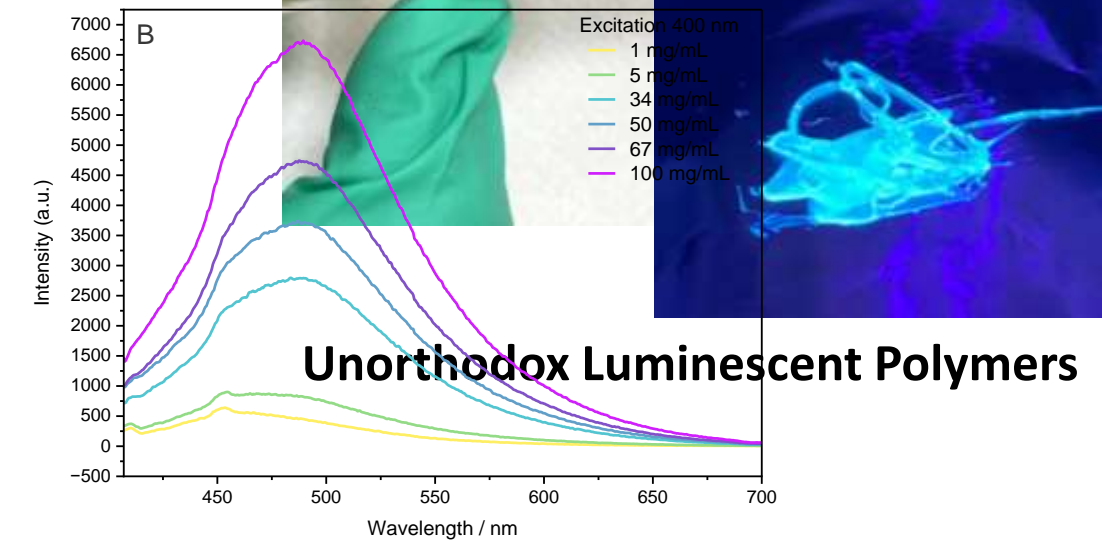
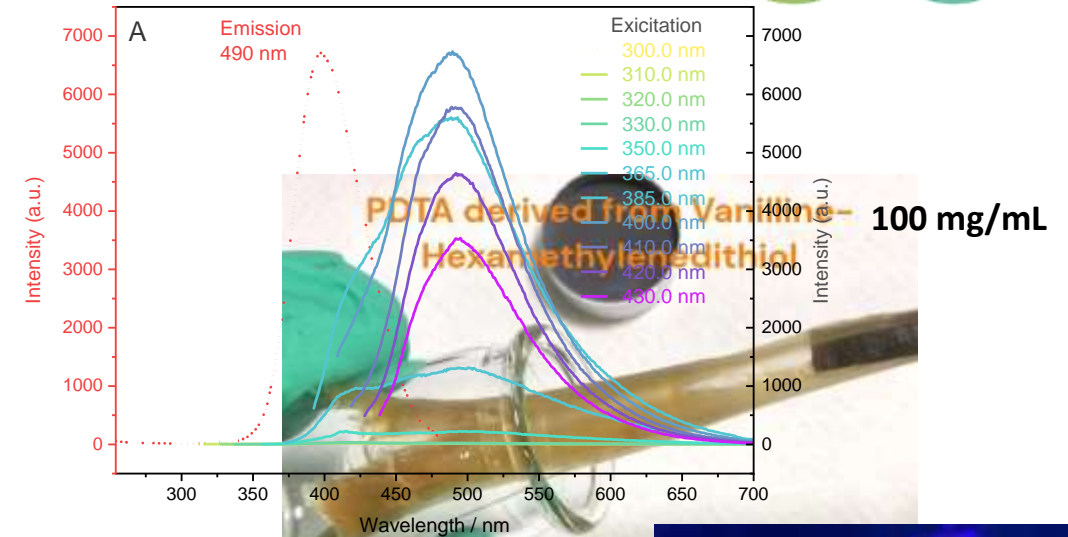


PDTA derived from Vanilline-Hexamethylenedithiol

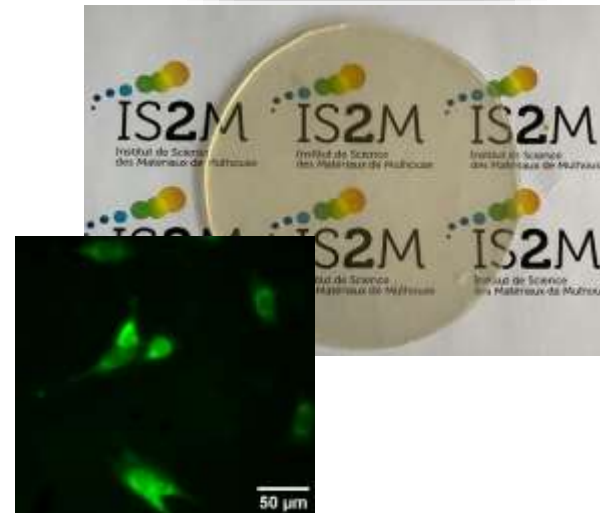
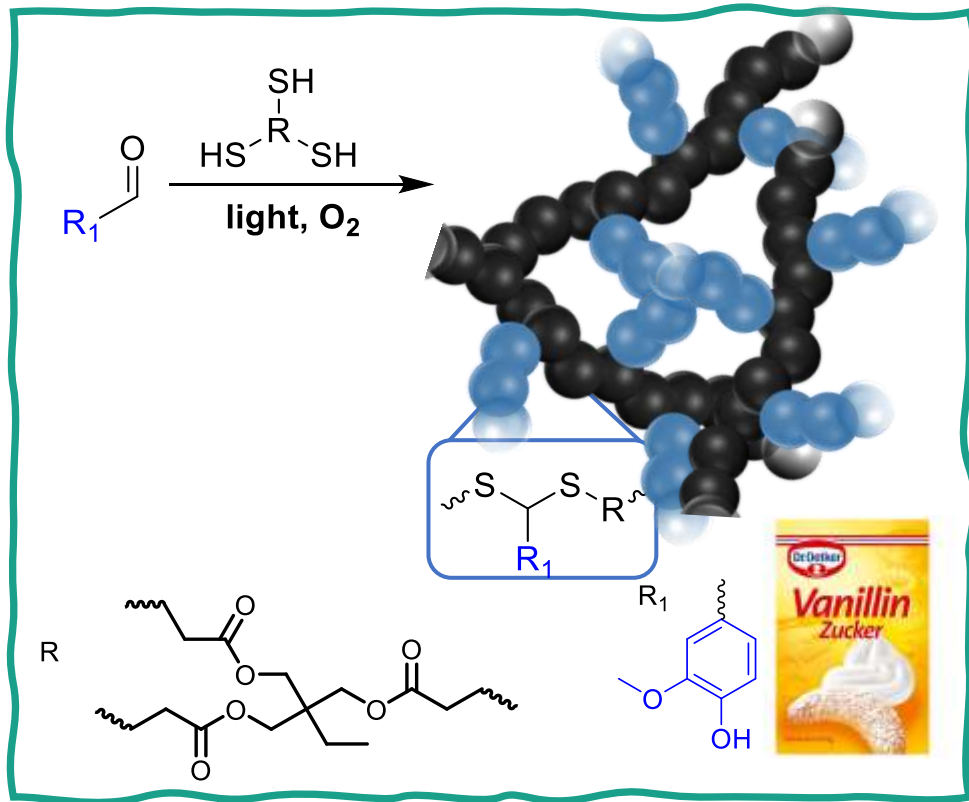


Unorthodox Luminescent Polymers

# Potential applications: Adhesives with Debonding on Demand

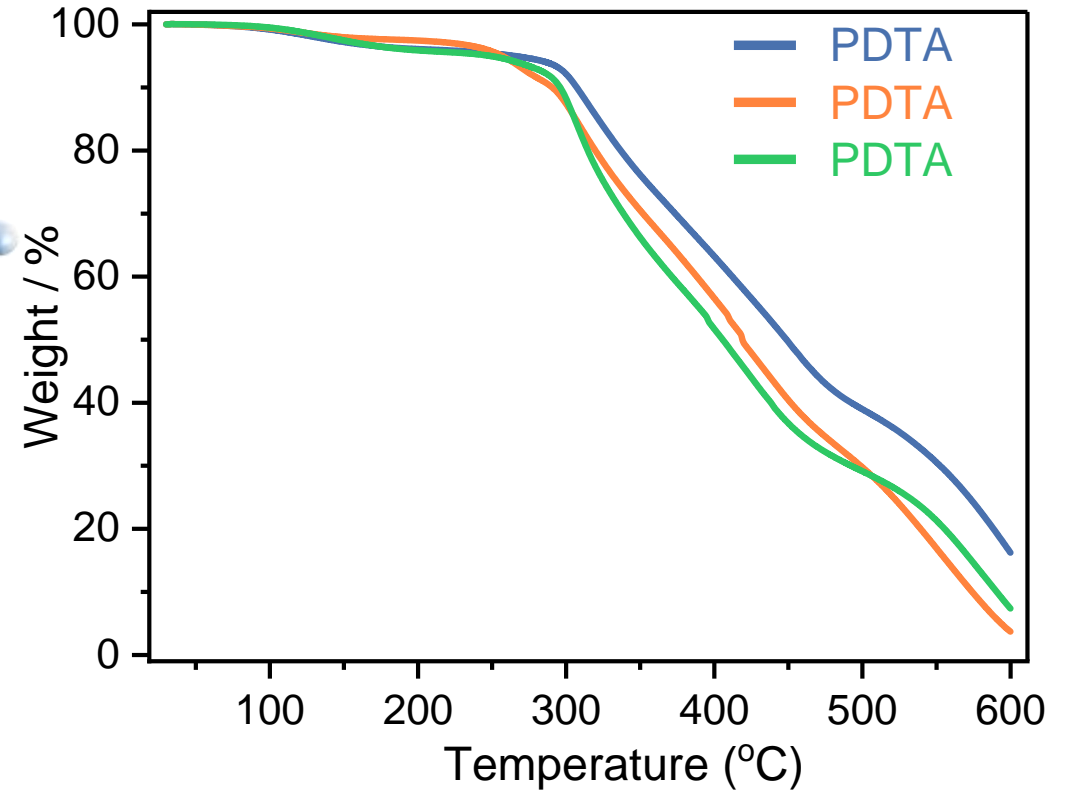
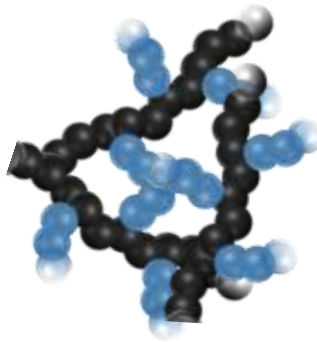
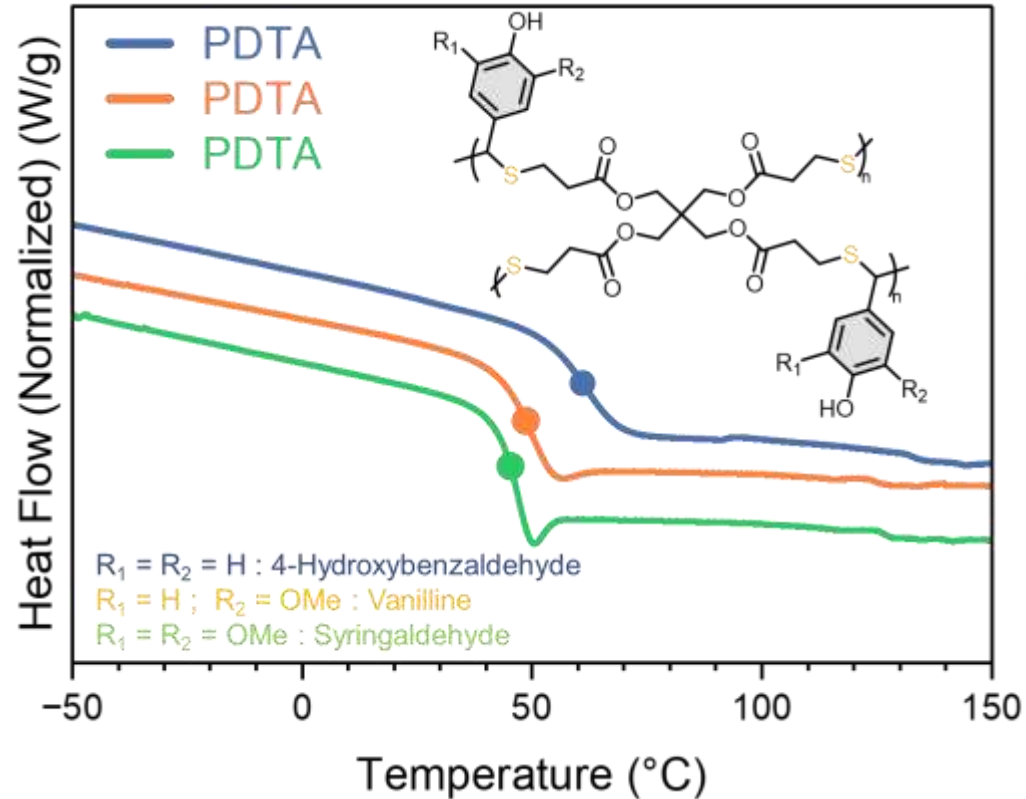


# Potential applications: Plastics with programmable degradation



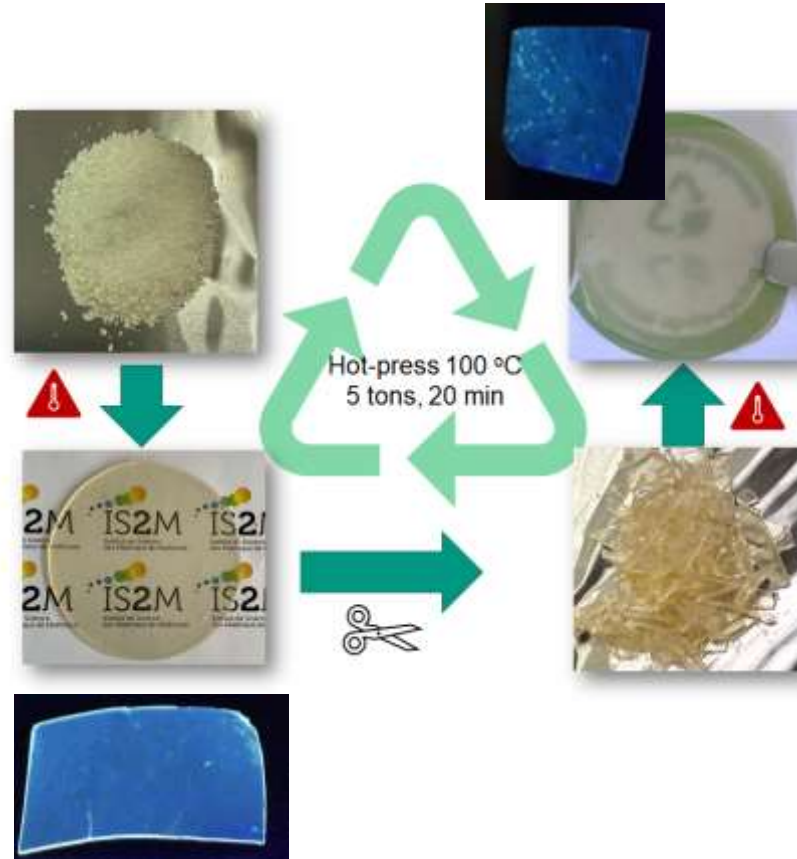
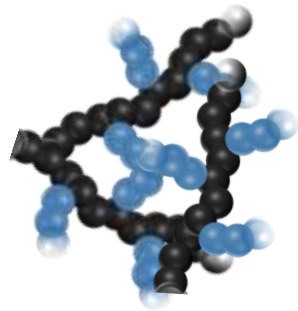


# Potential applications: Plastics with programmable degradation

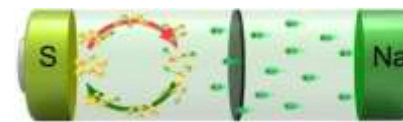
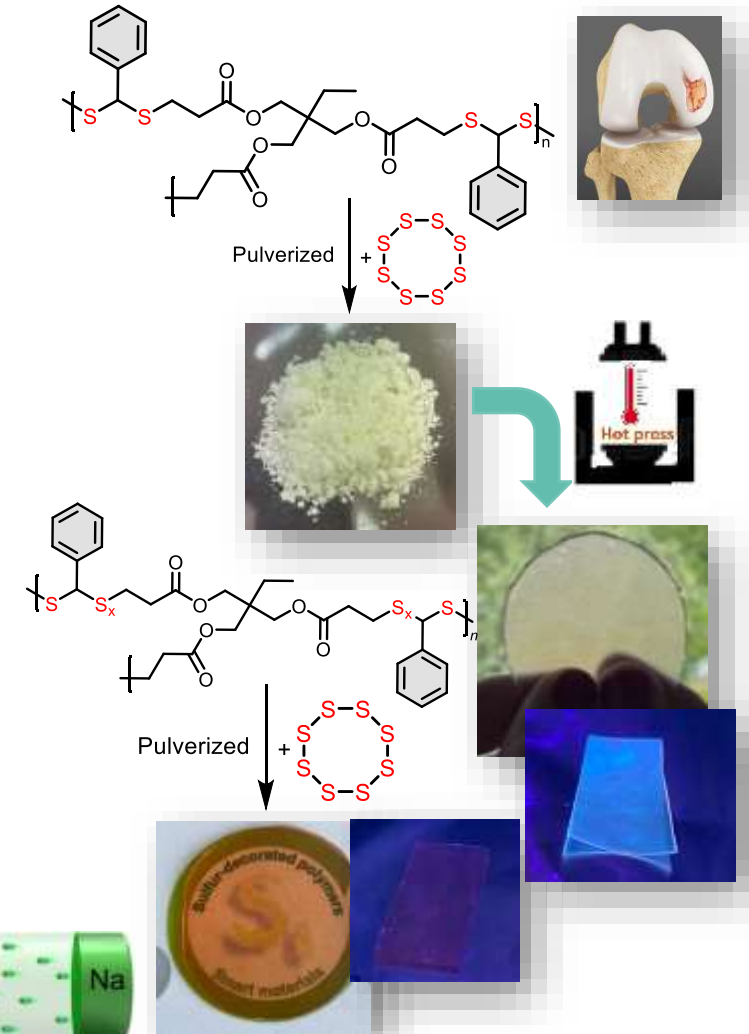


## Sustainability/Circular Chemistry

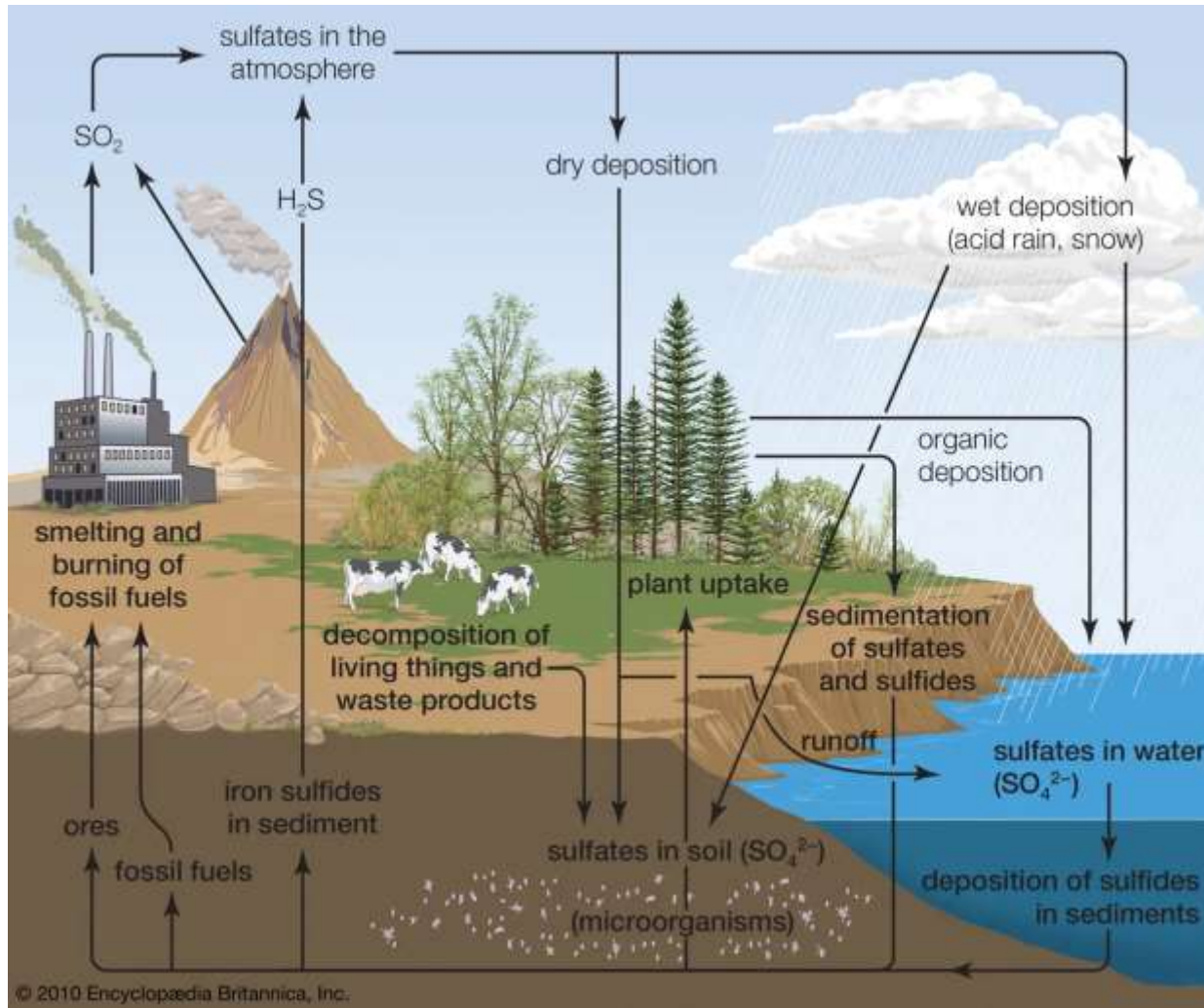
Develop selective upcycling methods for the polymer waste



Dr. Johann Kern (UMM)



Prof. Sonia Dsoke (University of Freiburg)



- Reducing global warming caused by the greenhouse gases by absorbing the ultraviolet radiation of the sun
- In ancient times, **dimethyl sulfide (DMS)** acted as the **Earth's thermostat** and prevented overheating

→ regulator for the climate change



## FEATURES

### The secrets of the sulfur cycle

By RACHEL BRAZIL | 28 MARCH 2022

There's still a lot we don't know about the biogeochemical cycling of sulfur, and this could impact our ability to correctly model the climate. Rachel Brazil talks to the researchers trying to fill in the gaps.



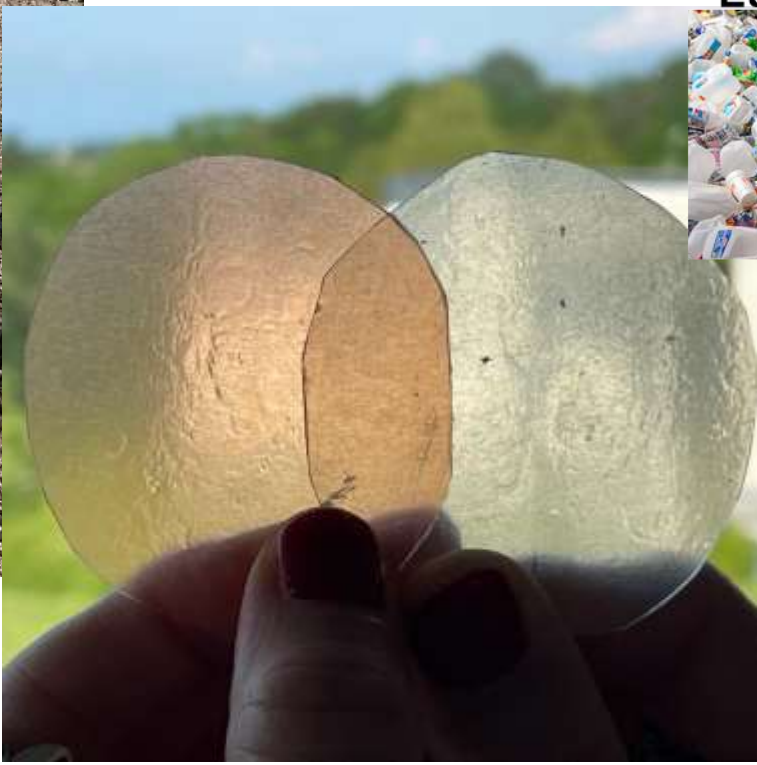
# Sulfur eating bacteria and sulfur-based polymers?



## Sustainability/Circular Chemistry



Türkiye:  
the TRASH BIN of  
European waste

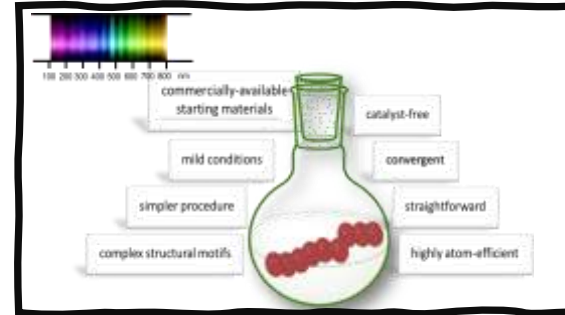
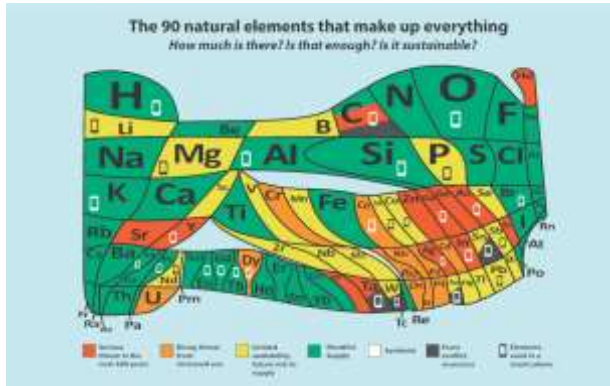


Dr. Mine Güngörmüşler



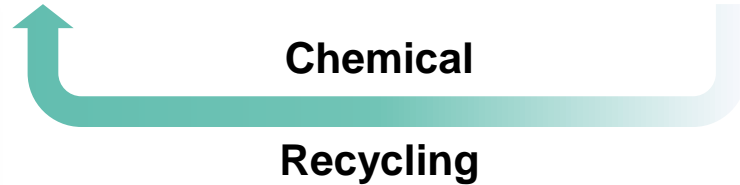
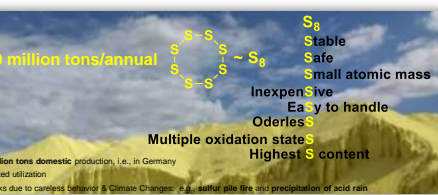
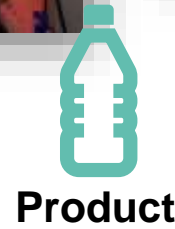
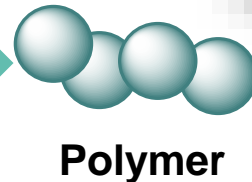
İZMİR UNIVERSITY OF ECONOMICS

# Novel sulfur Polymers: Yellow is the new green

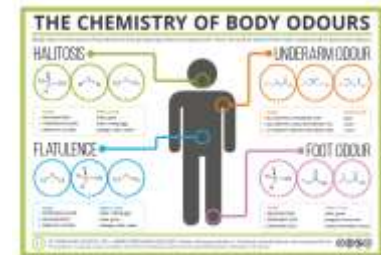


Alternative resources

New Transformations

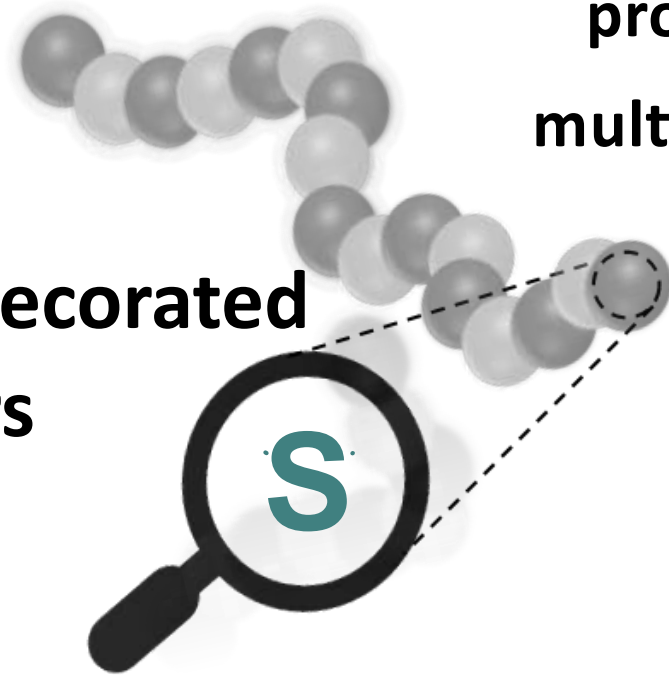


Sustainability/Circular Chemistry





**Sulfur-decorated  
polymers**



**S**tinky  
inexpen**S**ive  
produces less wa**S**te  
multiple oxidation **S**tates

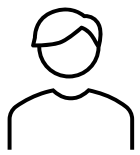
**S**timuli responsive  
**S**maller carbon-footprint

⋮  
**S**ustainable

⋮  
**Green**



# Acknowledgements



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FCI  
FONDS DER  
CHEMISCHEN  
INDUSTRIE

DAAD



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de la recherche  
AU SERVICE DE LA SCIENCE



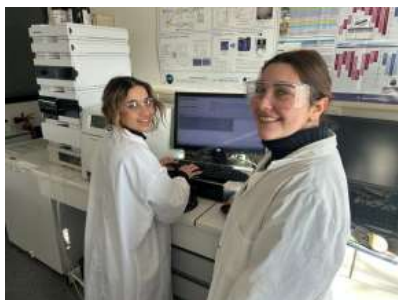
**Prof. Vincent Roucoules (IS2M)**  
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**Dr. Florence Bally-Le Gall (IS2M)**  
**Dr. Arnaud Spangenberg (IS2M)**  
**Dr. Isabelle Brigaud (IS2M)**  
**Dr. Karine Mougín (IS2M)**

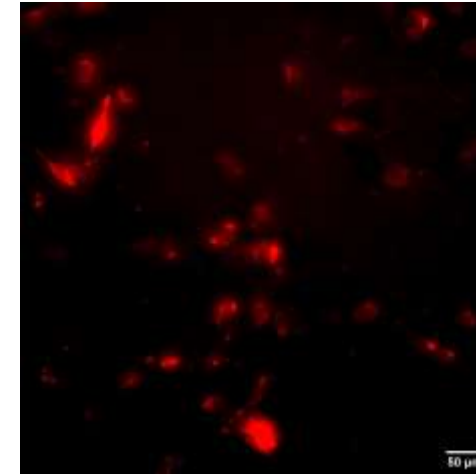
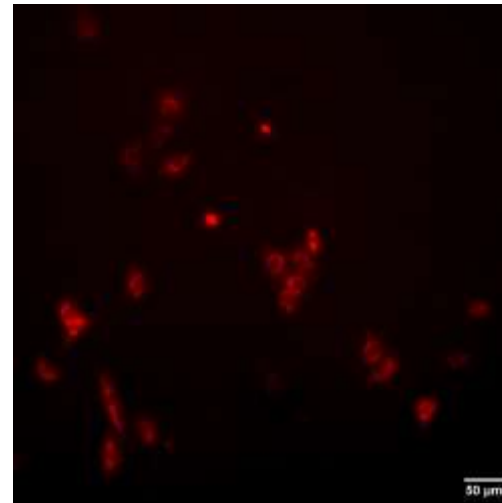


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**Prof. Manfred Wilhelm (KIT)**  
**Prof. Patrick Theato (KIT)**  
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**Prof. Wolfgang Wenzel (KIT)**



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Freiburg)**  
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**Dr. Marina Simian (UNSAM)**  
**Dr. Ljiljana Fruk (University of  
Cambridge)**  
**Dr. Mine Güngörmüşler (IUE)**





~100 gram polymer synthesis without adhesive protein

with adhesive protein (Fibronectin (FN))

Cells seeded on the polymer with or without adhesive protein coatings. After 18h of incubation, cells still attached on the polymer even without adhesive protein (here Fibronectin (FN) has been used). The cells were fixed, stained (red) and imaged with a confocal microscopy.