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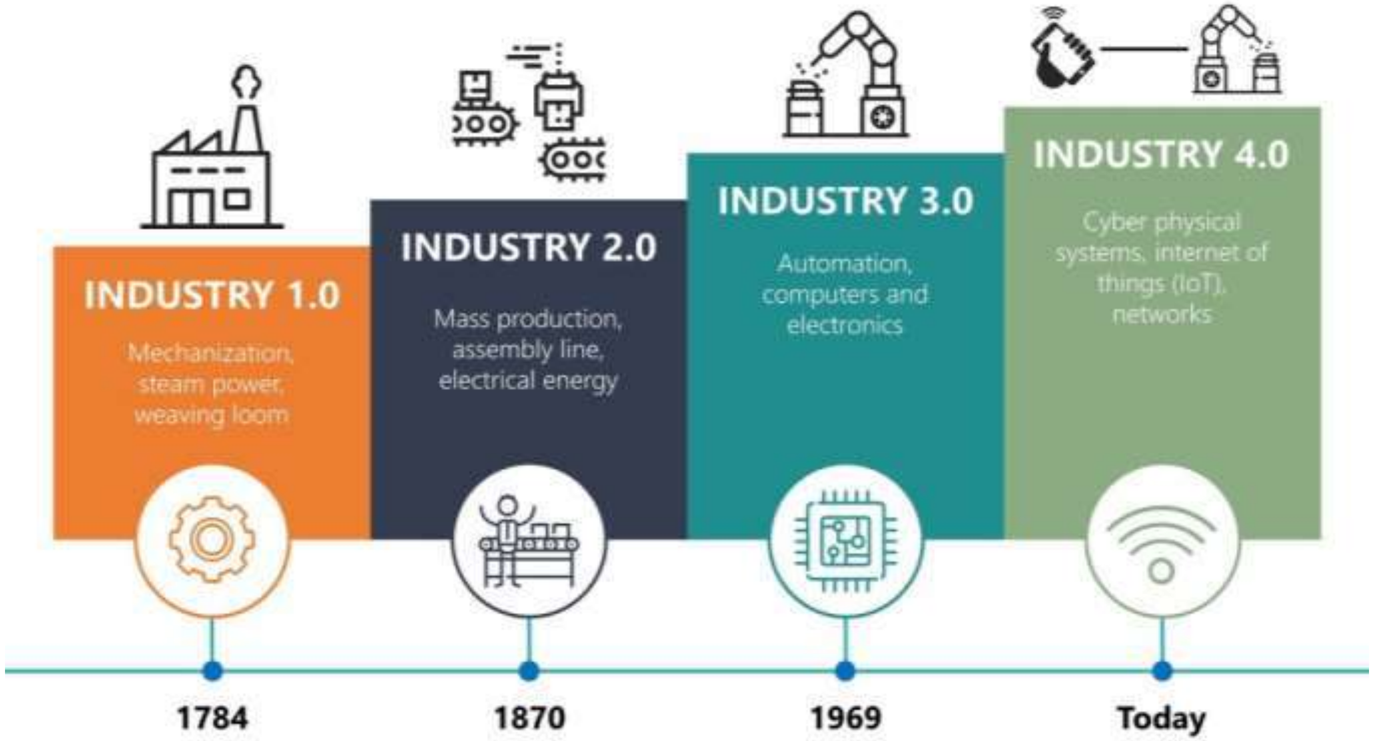
Chromatic Orthogonality: A Sustainable and Eco-Friendly Approach for the Synthesis of Polymeric Materials

Assoc. Prof. Mustafa Ciftci

Industry 4.0



Industry 1.0: The First Industrial Revolution began in the 18th century through the use of **steam power** and mechanisation of production.
"a transition from hand production methods to machines"

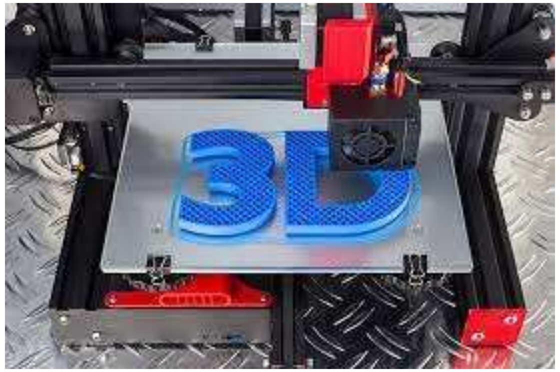
Industry 2.0: The Second Industrial Revolution began in the 19th century through the discovery of **electricity** and assembly line production.
"significantly faster and at lower cost via modern production line"

Industry 3.0: Partial automation using **memory-programmable controls** and **computers**.
"robots that perform programmed sequences without human assistance"

Industry 4.0: Smart factories, in which production systems, components and people communicate via a network and production is nearly autonomous.
*"**Cyber-physical production systems**, robotics and **3D printing (additive manufacturing)**"*

Industry 4.0 / Material 4.0

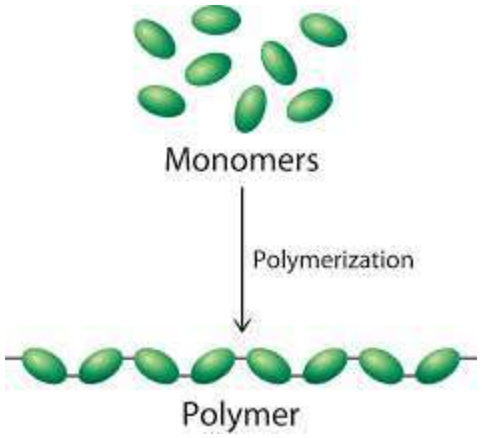
Parallel with the use of smart systems, the desire for the smart materials that can meet the need of such systems has increased. **Polymeric materials** appear to be suitable candidates to fulfill these requirements.



“synthesis, processing, modeling, characterization, and properties of diverse range of materials as a function of micro/nanostructure, physical conditions of pressure and temperature, phase transitions and performance during the fabrication of products and its life cycle, and recycling or handling of product upon its lifetime.”

- Rapid prototyping
- Smart materials
- Functional materials

Material 4.0 / Polymers



Molecular LEGO

A polymer is any of a class of natural or synthetic substances composed of very large molecules, called macromolecules, which are multiples of simpler chemical units called monomers.

"A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass." (IUPAC)

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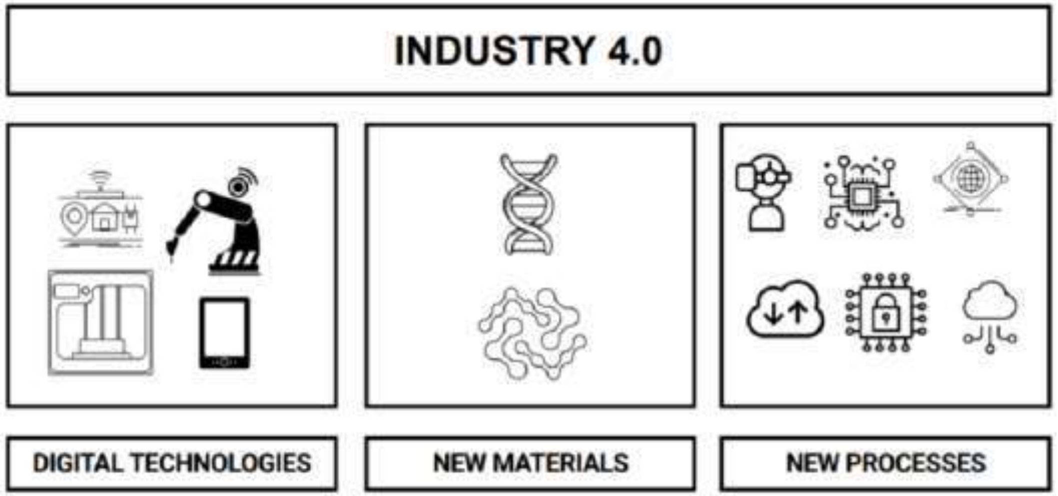
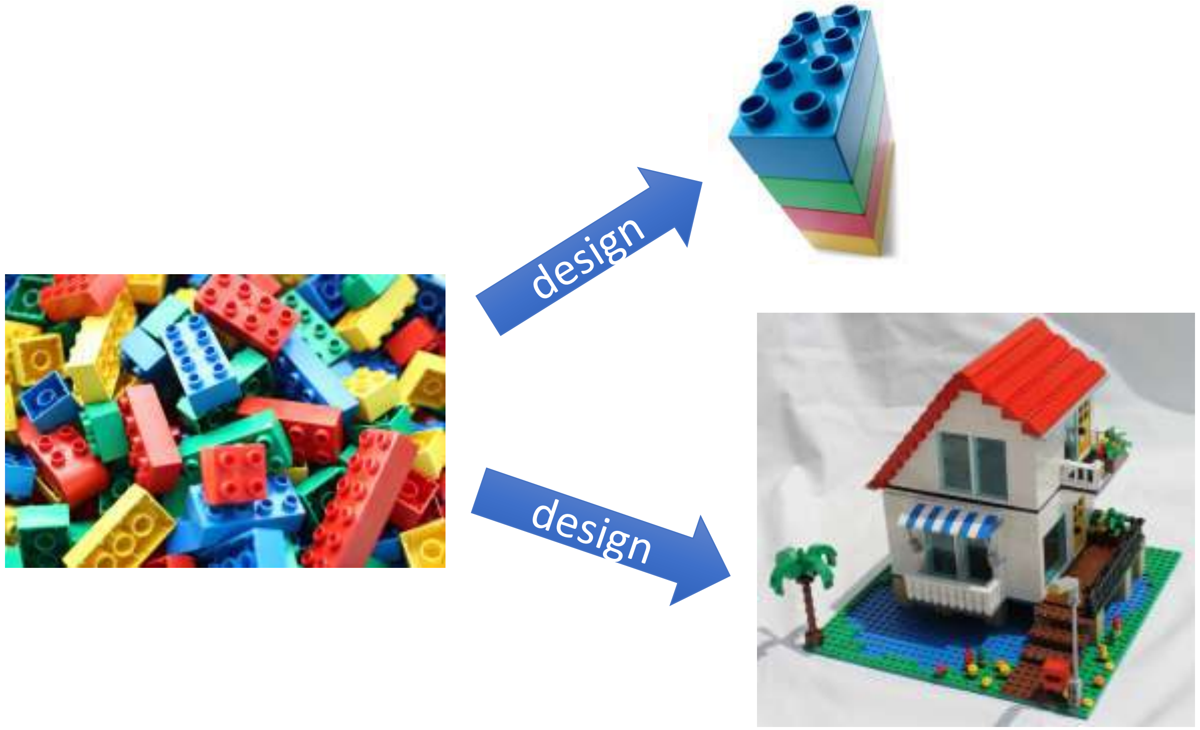
Industry 4.0 / New Processes





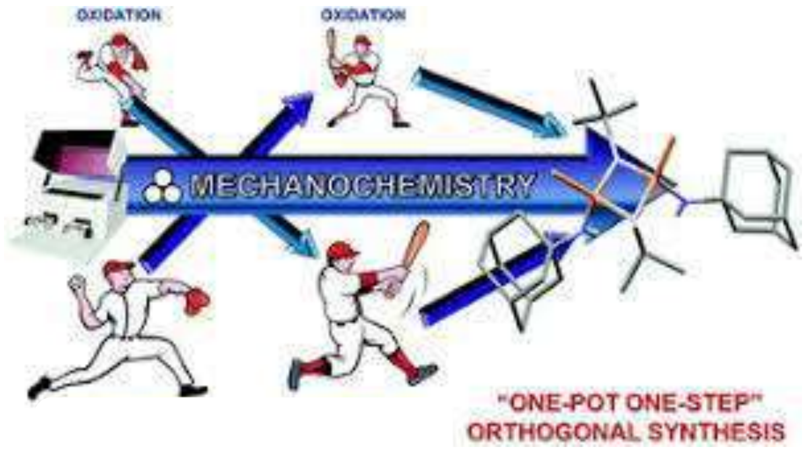
There are many high-tech polymeric materials that represent **superior properties** but which are **not yet used for industrial purposes** and can only be produced on **laboratory scale**. The main reason behind such adaptations cannot be achieved, is the high cost of industrial production of such materials due to the **difficult** and **multi-step synthetic** procedures. In this context, the development of **novel synthetic methods** which allow the obtaining of high-tech polymers by simple and cost-effective methods has become increasingly important in recent years.

New Processes/Orthogonal Reactions

Selective control of chemical reactions independently of one another, i.e. **orthogonal reactions.**

The use of the term “**orthogonal**” in chemistry was first reported by Merrifield in his innovative peptide synthesis approach in 1977.

The Nobel Prize in Chemistry 1984

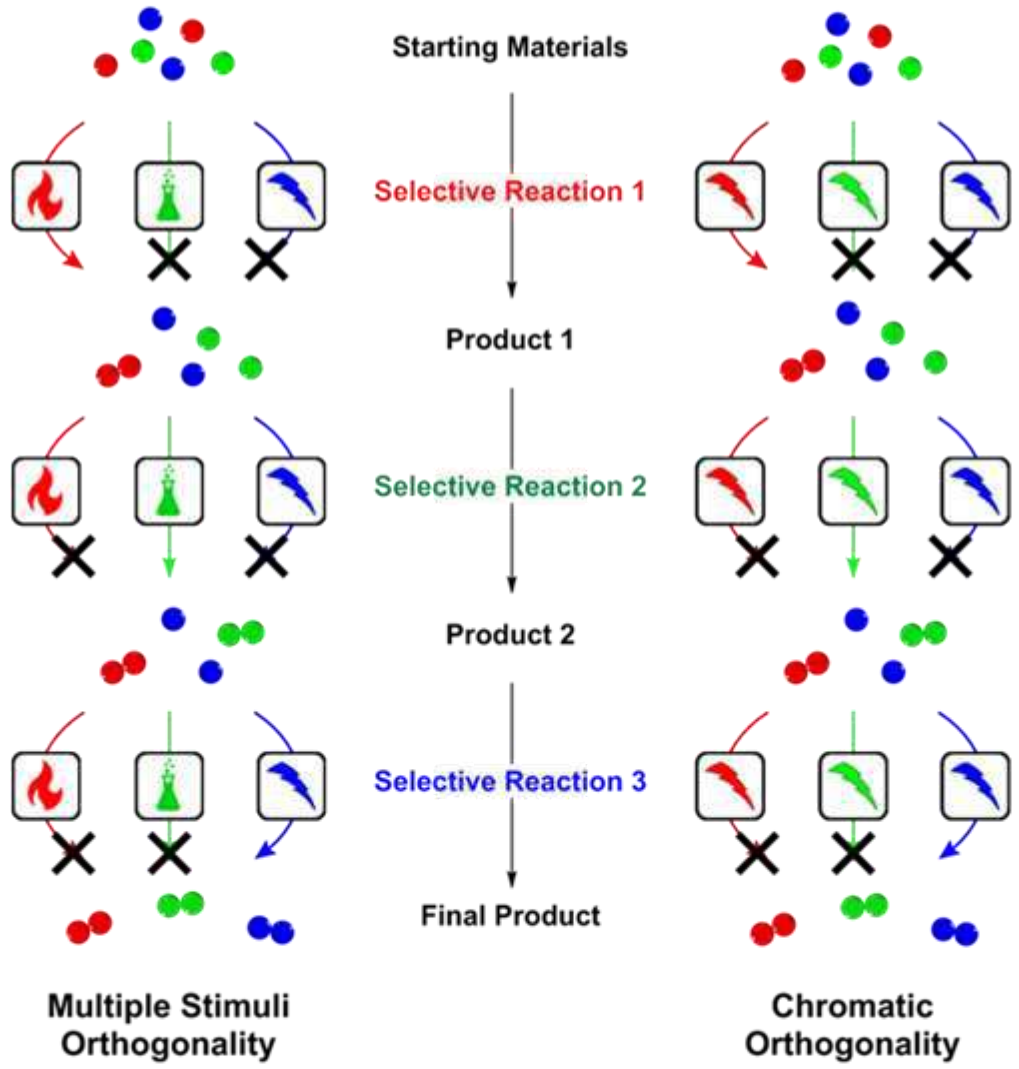


Selective control of chemical reactions is critical for the proper regulation of processes ranging from intricate biological systems to large scale **industrial manufacturing**.

Orthogonal Reactions/Trigger

For the concurrent and independent control of chemical reactions in one pot, it is crucial to apply **external effects** that can activate the **desired reaction pathway without affecting other system components**.

Among the many external stimuli (redox, heat, pH, light, electric current, etc.) used to enact chemical reactions, **light** has been **employed remarkably well** in recent years due to its favorable properties, including **independence with other external stimuli, temporal and spatial control, and low energy consumption**.



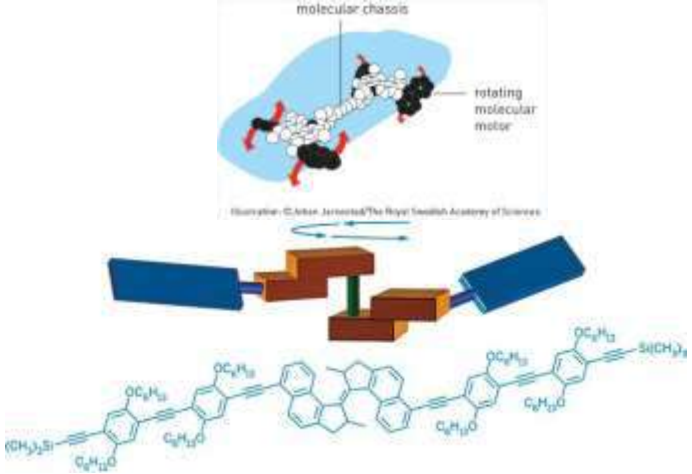
Light

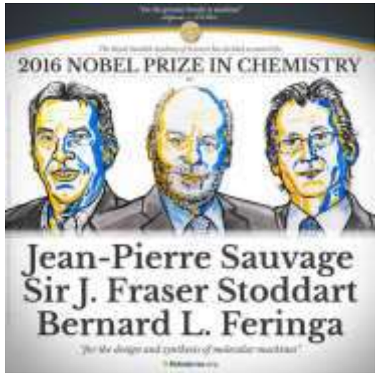
2015 - The International Year of Light and Light-based Technologies

UNESCO
United Nations Educational, Scientific and Cultural Organization
INTERNATIONAL YEAR OF LIGHT 2015

The International Year of Light and Light-Based Technologies (IYL 2015) is a global initiative adopted by the **United Nations** to raise awareness of how optical technologies promote **sustainable development and provide solutions to worldwide challenges in areas such as energy, education, communications, health, and sustainability**.

MOLECULAR MOTOR

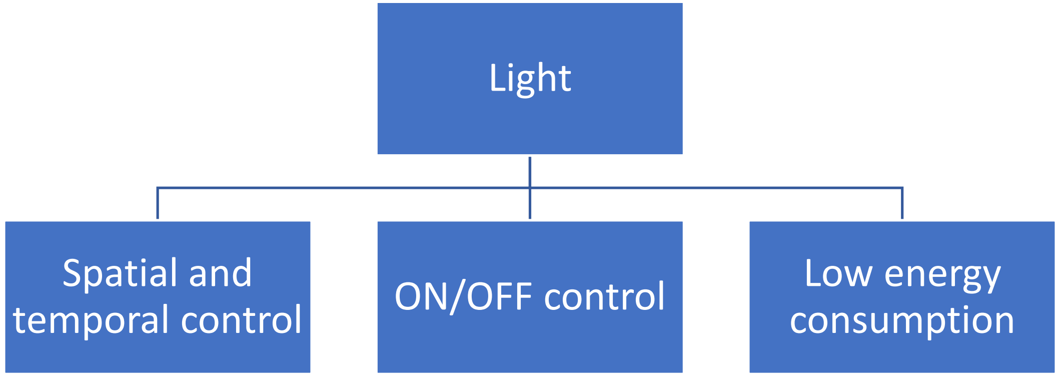


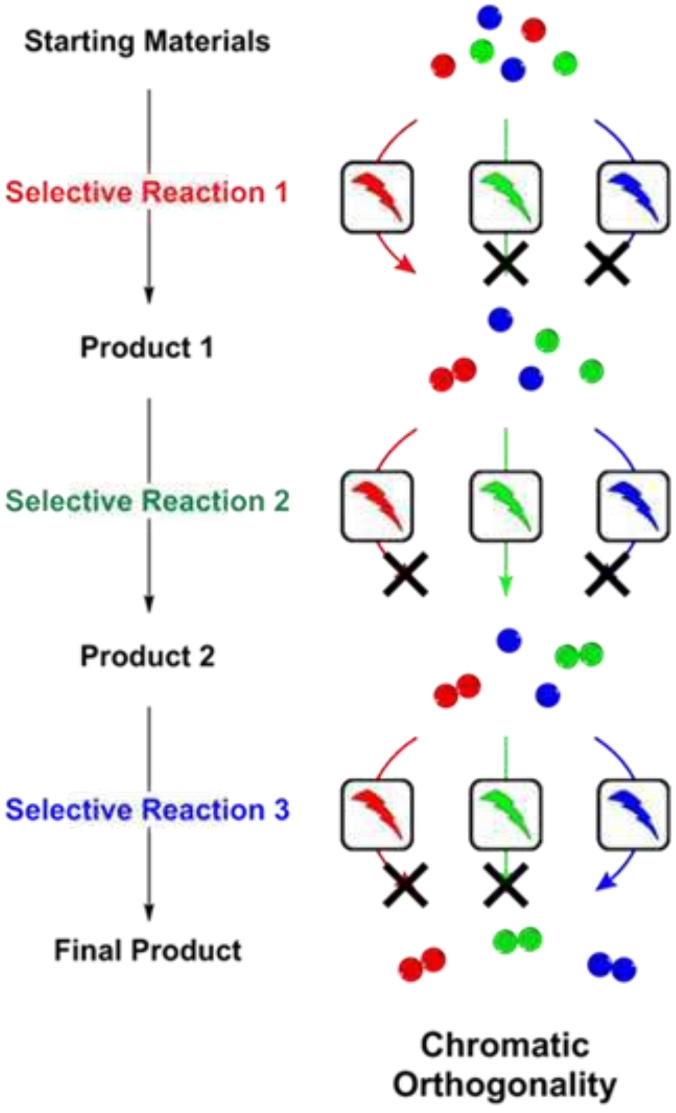


Chromatic Orthogonality

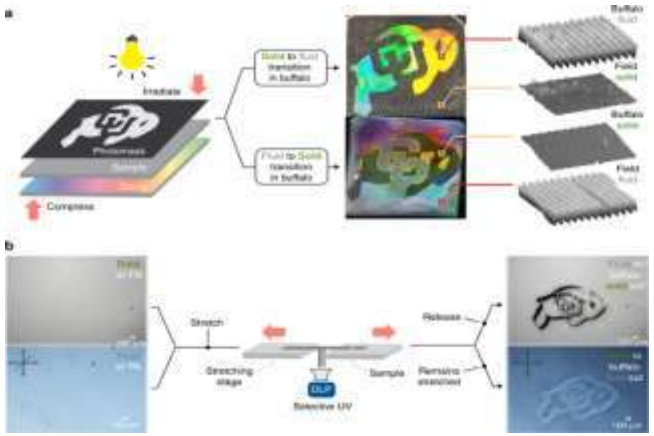
The orthogonal control of multiple reaction pathways is possible by using **different wavelengths of the light**; chemical reaction orthogonality imparted by using **multiple wavelengths of light** is commonly referred to as “**chromatic orthogonality**” or often “**λ-orthogonality**”

Using different irradiation wavelengths to **simultaneously or sequentially** activate distinct reaction pathways allows the possibility to perform **complex synthetic protocols that would be tedious or impossible using conventional chemistry**.

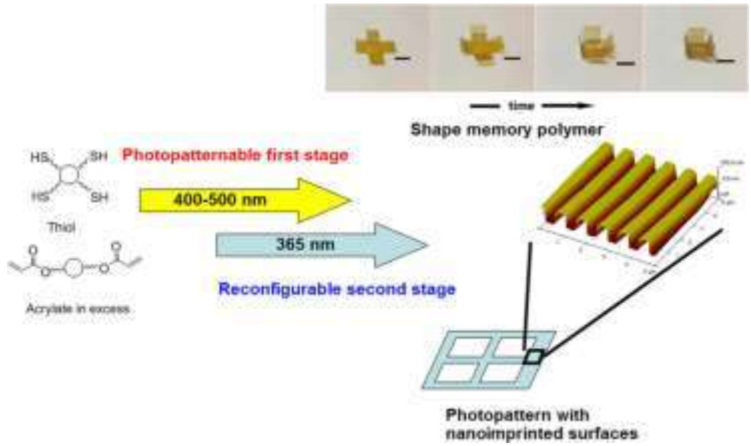




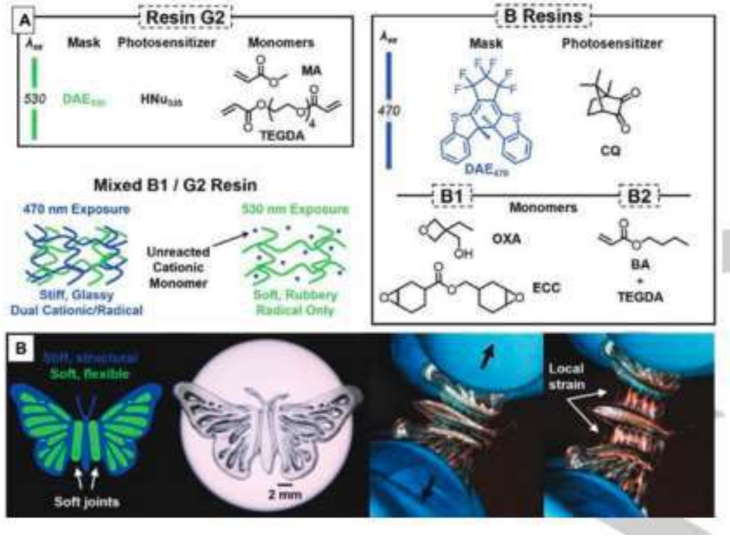
Chromatic Orthogonality/Examples



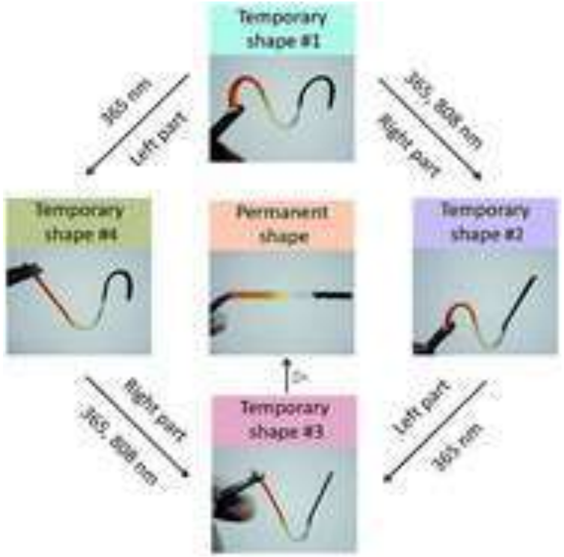
Worrell, B. T.; McBride, M. K.; Lyon, G. B.; Cox, L. M.; Wang, C.; Mavila, S.; Lim, C.-H.; Coley, H. M.; Musgrave, C. B.; Ding, Y.; Bowman, C. N., Nature Communications 2018, 9 (1), 2804.



Zhang, X.; Cox, L.; Wen, Z.; Xi, W.; Ding, Y.; Bowman, C. N., Polymer 2018, 156, 162-168.

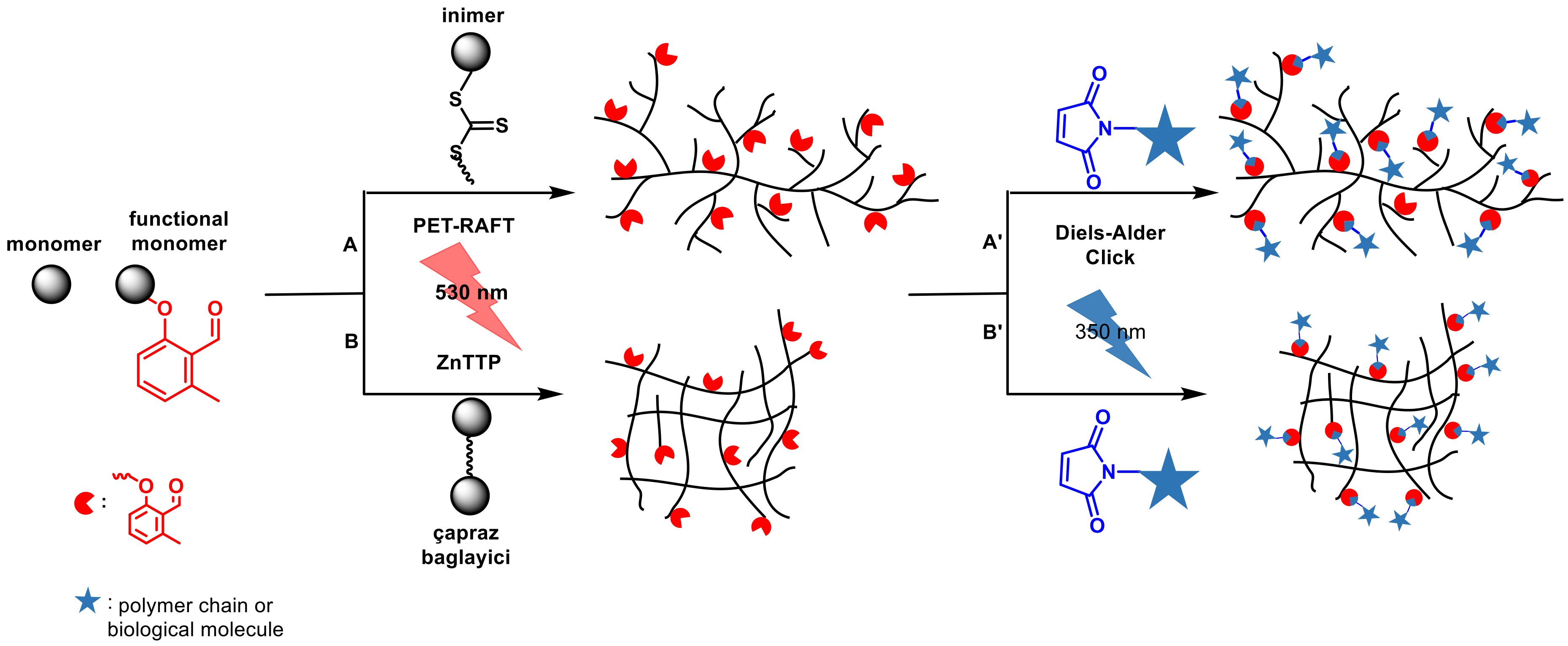


Dolinski, N. D.; Page, Z. A.; Callaway, E. B.; Eisenreich, F.; Garcia, R. V.; Chavez, R.; Bothman, D. P.; Hecht, S.; Zok, F. W.; Hawker, C. J., Advanced Materials 2018, 30 (31), 1800364.



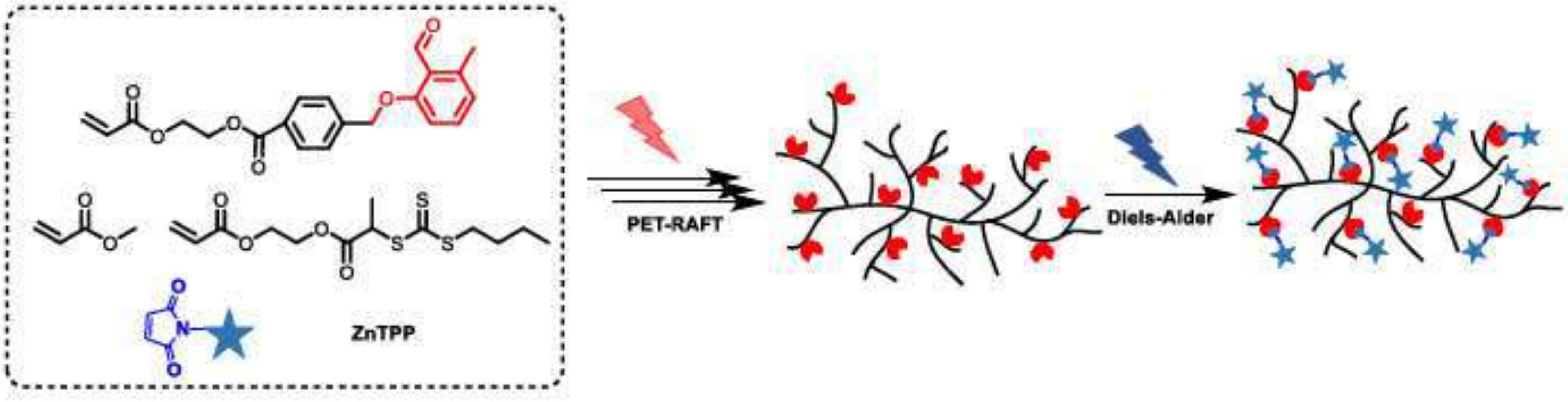
Yu, L.; Wang, Q.; Sun, J.; Li, C.; Zou, C.; He, Z.; Wang, Z.; Zhou, L.; Zhang, L.; Yang, H., Journal of Materials Chemistry A 2015, 3 (26), 13953-13961.

Chromatic Orthogonal Synthesis and Modification of Polymeric Materials with Various Architectures



Synthesis and modification of polymeric materials with two different architectures (hpyperbranched and cross-linked) by a chromatic orthogonal synthetic approach. For this purpose, polymeric structures were synthesized under visible light irradiation, while modification processes was performed at a different wavelength of light (350 nm).

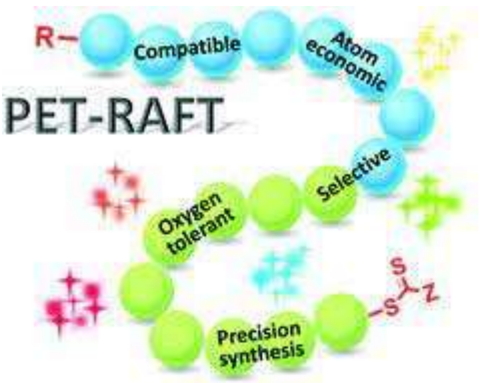
Synthesis and modification of hyperbranched polymers

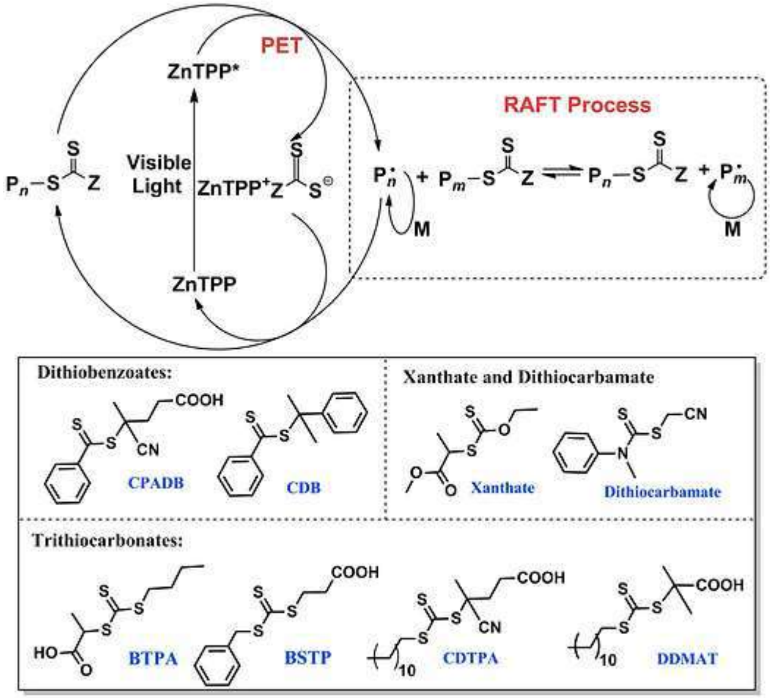


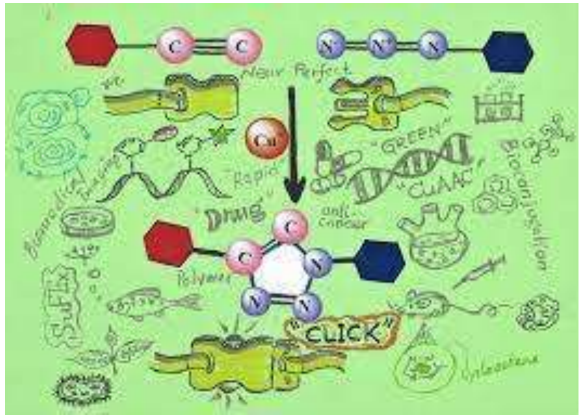
One-pot, chromatic orthogonal polymer synthesis and modification.

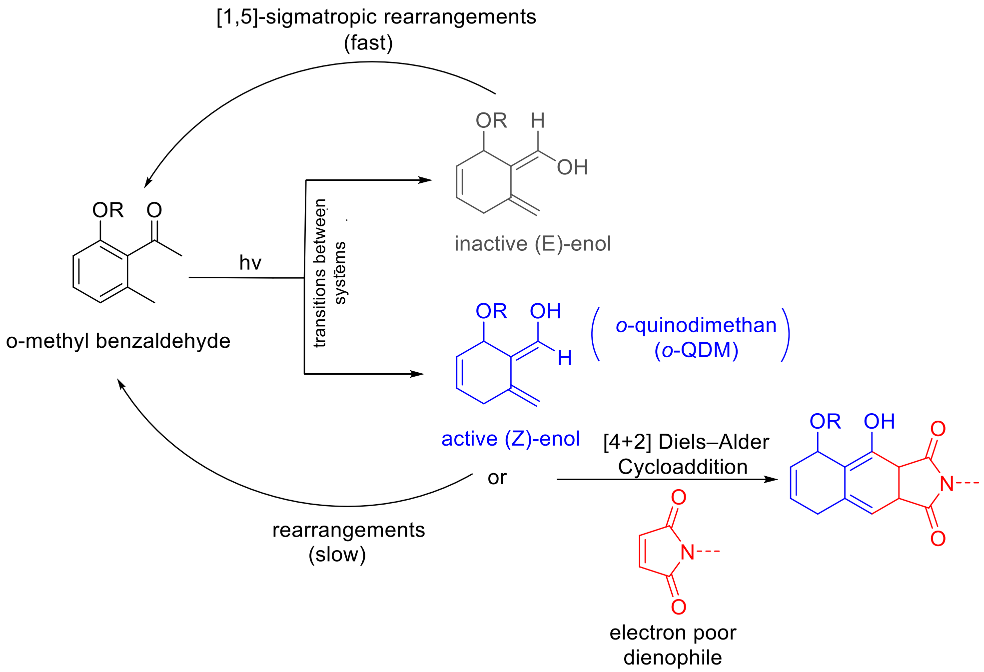
Hyperbranched polymers with o-methyl benzaldehyde functional groups were synthesized in a controlled manner by combination of Self-Condensing Vinyl Polymerization (SCVP) and Photo-Induced Electron/Energy Transfer-Reversible Addition-Fragmentation Chain Transfer (PET-RAFT) methods under visible light irradiation. As the obtained polymers contained o-methyl benzaldehyde functional groups, they were capable to be modified with desired groups through Diels-Alder Click reactions with the effect of light (320 nm). The **modification** processes were illustrated with **four model studies**. First, phenyl-maleimide was used to demonstrate modification with small organic structures then for the production of amphiphilic polymers that have many application areas, a hydrophilic polymer chain (**PEG**) was be attached to the hyperbranched structure. Subsequently, **polycaprolactone** (PCL) was used as modification agent to prove applicability of the system for the hydrophobic structures. Finally, **Bovine Serum Albumin** (**BSA**) protein was conjugated to prove the applicability of the method to biological systems.

PET-RAFT and Light-Induced Click Chemistry

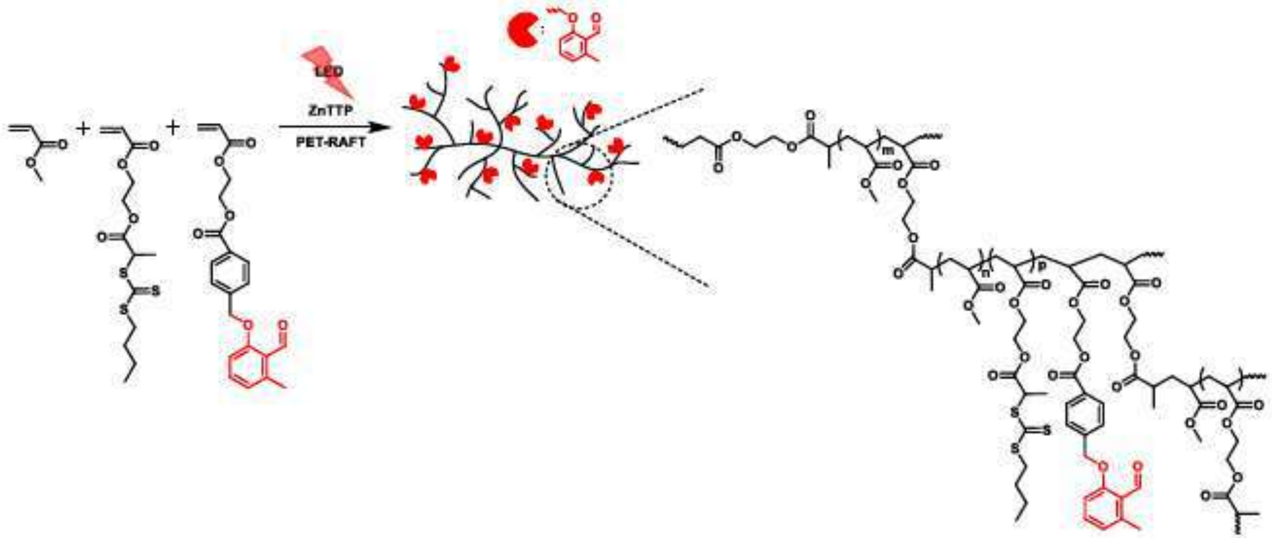




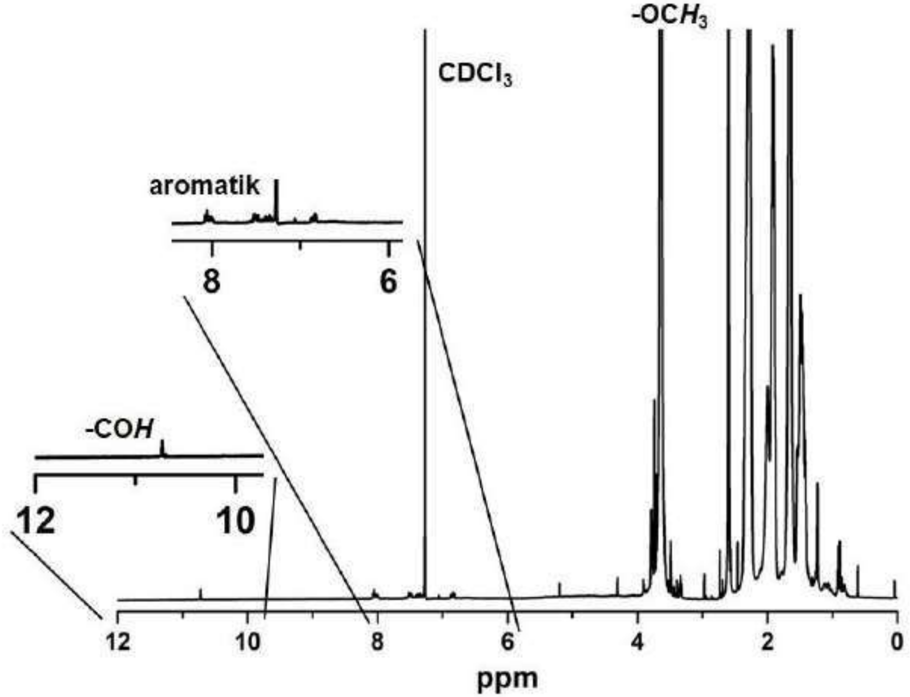




Synthesis of hyperbranched polymers

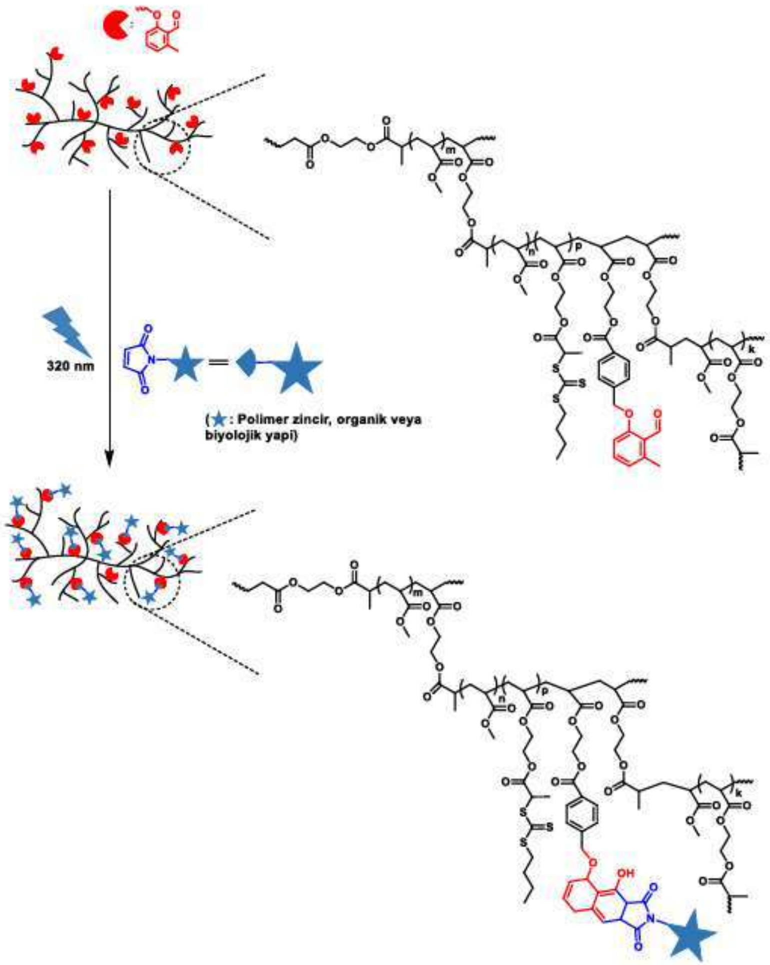


Synthesis of functional hyperbranched polymer by combination of PET-RAFT and SCVP.

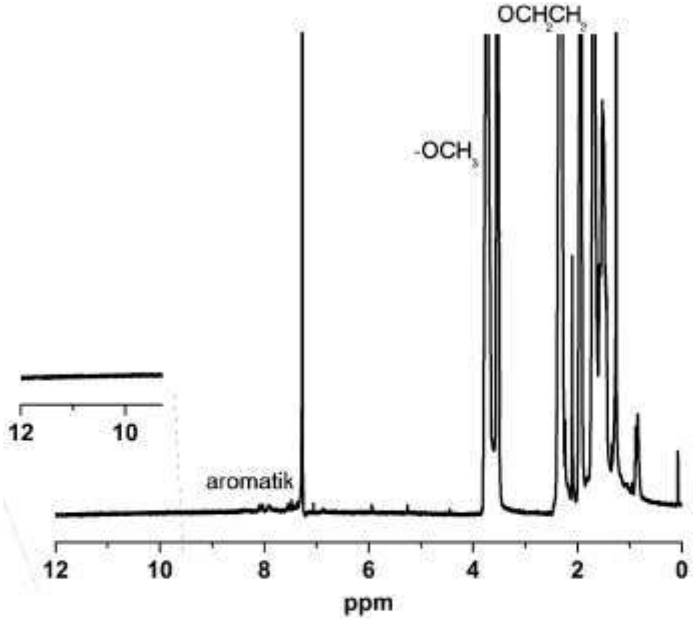


^{1}H NMR spectrum of the functional hyperbranched polymer.

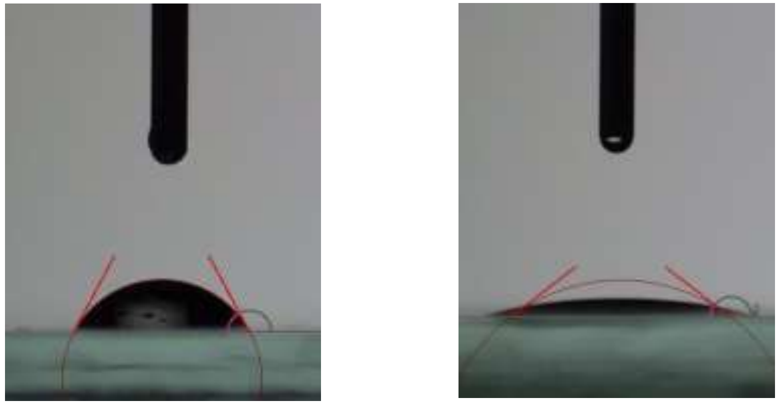
Modification of hyperbranched polymers



Modification of hyperbranched polymers by “click” chemistry

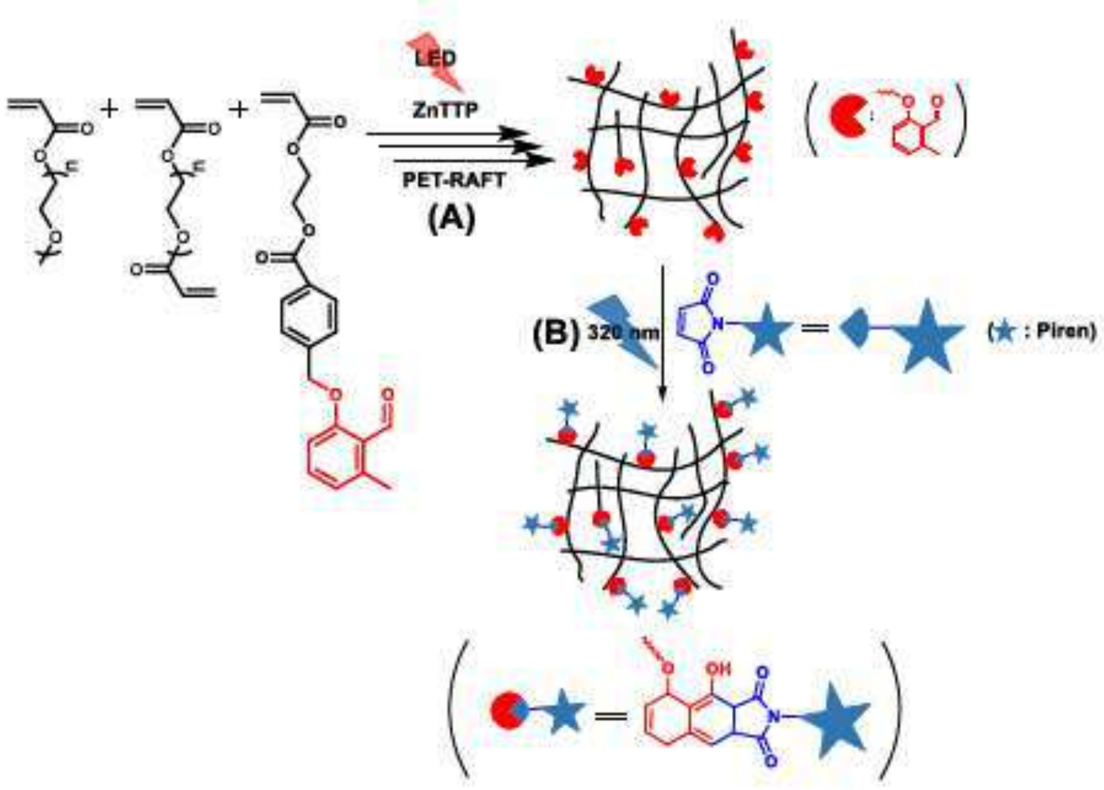


[1]H NMR spectrum of the PEG functionalized hyperbranched polymer.



Shapes of water drops on thin films of hyperbranched polymer (WCA ~82^{o}) and its PEG functionalized analogue (WCA ~40^{o}).

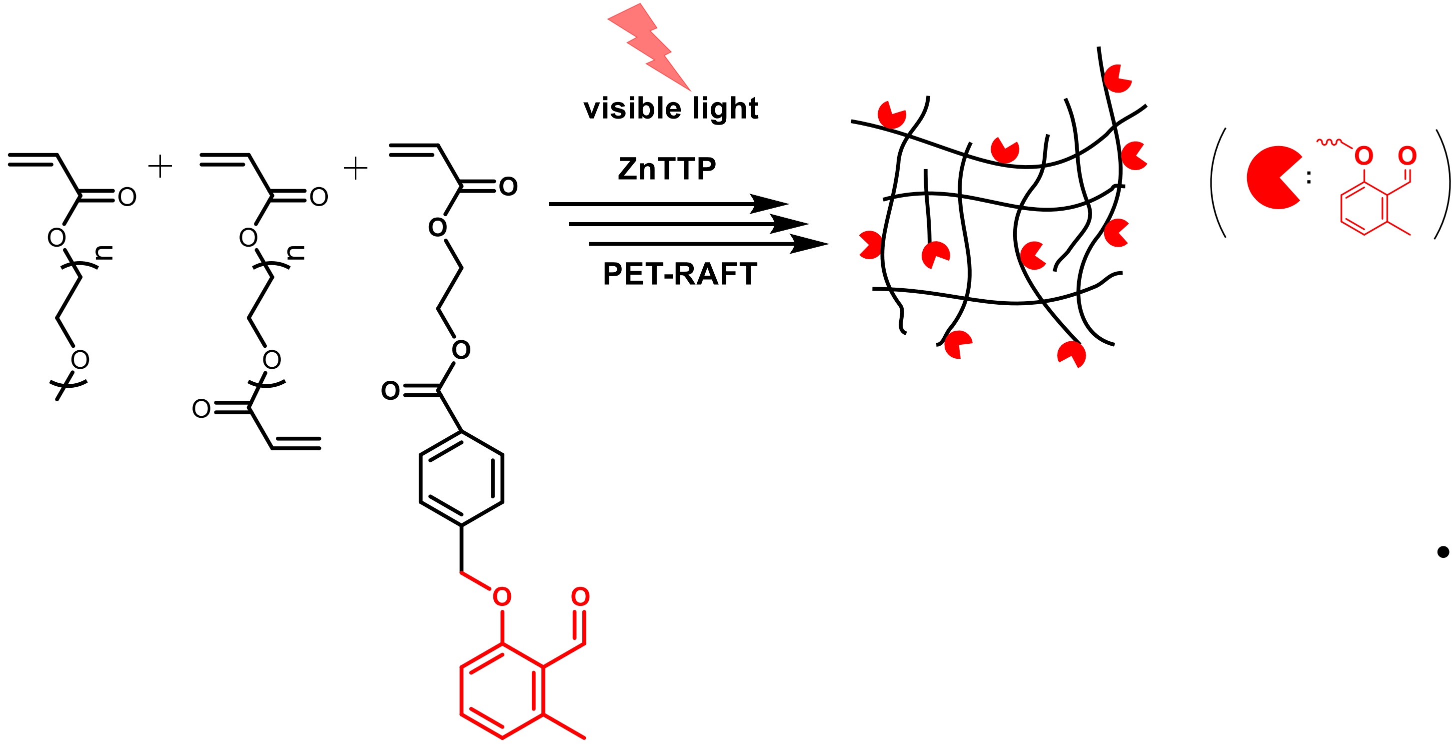
Synthesis and modification of hydrogels



Chromatic orthogonal hydrogel synthesis (A) and modification (B).

Functional hydrogels were obtained by PET-RAFT under visible light. The obtained gels were then modified with under 320 nm light irradiation. Since the related modification process could only be triggered by light, the surface of the hydrogels was modified in a spatially controlled way by using photomasks.

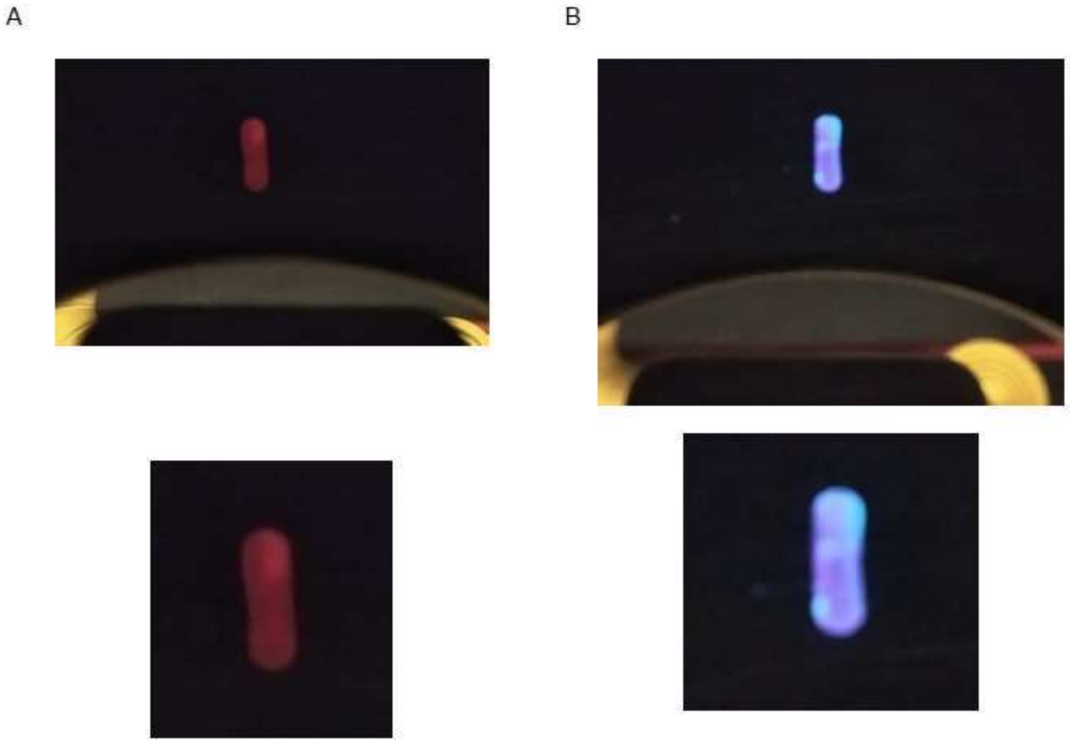
Synthesis of hydrogels



Synthesis of functional hydrogels.

- Adjustable cross-linking densities
- Fully open to air (oxygen tolerance)

Modification of hydrogels



Photographs of before (A) and after (B) functionalization of hydrogels with pyrene under UV light.

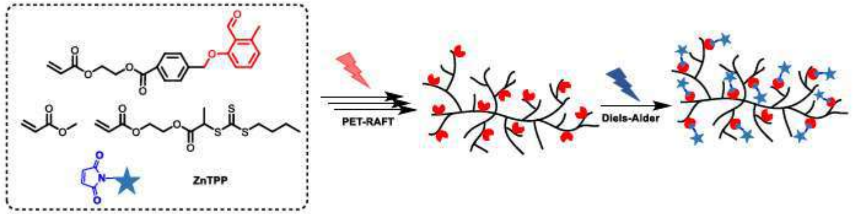
Photograph of functionalized hydrogel using a photomask (photopatterning).

Conclusions

A **novel chromatic orthogonal synthetic protocol** has been developed, in which the synthesis of polymeric materials with different architectures is carried out at one wavelength and the modification is carried out at a **different wavelength**.

Hyperbranched polymers

- Branching densities were manipulated by varying the experimental conditions.
- The applicability of the method has been demonstrated with 4 different model studies.



Hydrogel

- Cross-linking densities were manipulated by varying the experimental conditions.
- Spatial controll by using photomasks.

- Eco-friendly
- Light use only
- Adaptable for various application oriented materials
- 3D/4D printing and lithography
- Additional opportunities for synthesizing advanced and functional polymeric materials compared to traditional synthetic procedures
- Photo-patterning

I Would Like to Thank

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CIFTCI Research group members

I would like to offer special thanks to Prof. Yusuf YAGCI, who, although no longer with us, continues to inspire.

THANK YOU FOR LISTENING