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# Toward Sustainable Production of Well-Defined Polymers: (Electro)Redox Catalysis and Dispersed Media

**Francesca Lorandi**

(University of Padova, Department of Industrial Engineering)

*Introduction, prof. Franca Castiglione (Politecnico di Milano, DCMIC)*

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Polymer materials can be designed with pre-determined composition, topology, and functionalities by means of reversible deactivation radical polymerization (RDRP) techniques.<sup>[1]</sup> However, RDRPs typically require costly reactants, such as catalysts or chain-transfer agents, relatively high temperatures and large amounts of organic solvents. Therefore, harnessing external stimuli (e.g. light, electricity) to trigger RDRPs and employing water as reaction medium can improve the sustainability and scalability of these polymerizations.

Electrochemical stimuli are used to modify the oxidation state of Cu-based catalysts for atom transfer radical polymerization (ATRP), tuning the polymerization rate and control, and switching the system on/off.<sup>[2]</sup> At the same time, the electrochemical setup allows for investigating the polymerization mechanism and the interplay between the components of the system. This unique advantage prompted the definition of a redox-mediated cycle to perform reversible addition-fragmentation chain-transfer (RAFT) polymerization at low temperature, by employing suitable mediators to minimize side reactions hampering the RAFT agents.<sup>[3,4]</sup> On the other hand, electrochemical studies in ATRP have revealed the strong interaction between a common, hydrophilic Cu-based catalyst and sulfate-based anionic surfactants. As a consequence, when hydrophobic monomer/polymer droplets are dispersed in water, the vast majority of the Cu complex resides at the water/droplet interface, while a small portion of the complex enters the hydrophobic droplets. The result is a combination of interfacial and ion-pair catalyzed ATRP that enables to prepare well-defined polymers with various architectures in environmentally-friendly emulsion systems.<sup>[5,6]</sup>

### References:

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