Summer School on Polymeric Networks
for Sustainable Development

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Static and dynamic properties of vitrimers

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Vitrimers are polymer networks cross-linked by dynamic covalent bonds that undergo associative exchange, a process where new bonds form before existing ones break. This mechanism maintains network connectivity while allowing topological rearrangements, resulting in materials that are insoluble yet easily reprocessable at elevated temperatures. Converting conventional polymers into vitrimers enhances their mechanical strength, chemical resistance, and interfacial adhesion with other polymers. Consequently, vitrimers present a promising route toward high-performance and sustainable polymer materials.

This lecture will provide an overview of the fundamental properties of homogeneous vitrimer materials (without macro- or microphase separation).

It is structured into four parts:

1. History of associative cross-link chemistry in polymer networks
   - Dynamic covalent chemistry in polymers prior to the 2000s
   - Seminal contributions by Bowman and Leibler in integrating associative cross-links into polymer networks
   - Representative examples of vitrimer materials
2. Impact of associative cross-link chemistry on static network properties
   - Gel fraction
   - Shear modulus
   - Equilibrium swelling
   - Glass transition temperature
3. Impact of associative cross-link chemistry on dynamic properties, with a special emphasis on understanding the fast and slow relaxation regimes
   - Analysis of the fast relaxation regime through theory, linear rheology, and dielectric spectroscopy
   - Analysis of the slow relaxation regime through theory and linear rheology
4. High priority open questions in the vitrimer field
   - Network topology
   - Glass transition
   - Mechanisms underlying the slow relaxation regime