Understanding the Dynamics of Supramolecular Polymers

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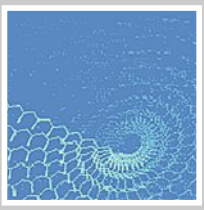

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Understanding the Dynamics of Supramolecular Polymers

Claudio Perego[a] and Giovanni M. Pavan*[ab]

*Correspondence: Prof. G. M. Pavan, E-mail: giovanni.pavan@polito.it,
[a]Department of Innovative Technologies, SUPSI, Manno (CH),
[b]Department of Applied Science and Technology, Politecnico di Torino, Turin (IT)

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Supramolecular polymers (SMPs) are dynamic self-assembled structures formed by non-covalently interacting monomers[1] that continuously exchange in/out the assembly with the external environment according to a well-defined supramolecular equilibrium.[2] Learning how to control such equilibrium would lead to new dynamic structures, for applications ranging from biomedicine to advanced responsive materials. A first key step is to uncover the molecular mechanisms governing the exchange of monomers in SMPs, which remain most often inaccessible, even with state-of-the-art experimental techniques.[3,4]

Recently, we demonstrated that the combination of molecular models[5,6] with enhanced sampling approaches permits to study the mechanism and kinetics of monomer exchange at a level that is inaccessible by experiment.[7] Proven for various types of SMPs (*e.g.* benzene-1,3,5-tricarboxamide (BTA) fibers of Fig. 1)[7–10] and other supramolecular systems,[11] metadynamics simulations allow to explore the process of monomer exchange in/out and within the assembly at a submolecular resolution, providing results in agreement with the experimental evidence and revealing key insights on the dynamics of SMPs. At such a high resolution one can observe the exchange events and unravel the key molecular factors that control the exchange process. s

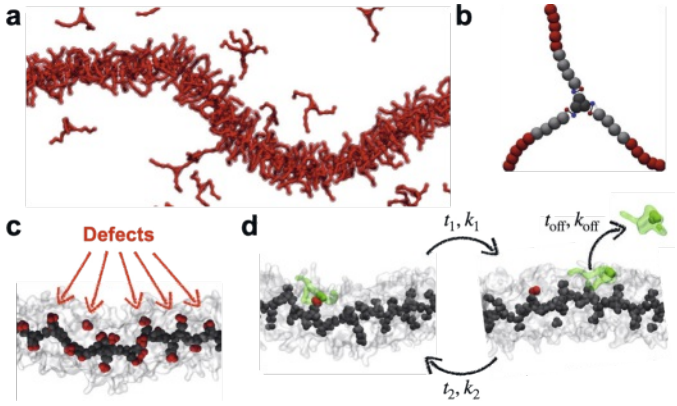

Fig. 1. Modeling monomer exchange in SMPs. (a) Monomer exchange in BTA SMPs. (b) CG model of a BTA monomer. (c) Internal structure (monomer cores in black) and defects (in red) of a water-soluble BTA SMP. (d) Multistep monomer exchange (green) mechanism and kinetics from SMP defects (in red). Adapted with permission from ref. [7].

We revealed that the dynamics of SMPs is controlled by defects that may be present or may form in their structure (Fig. 1c, red). Such defects constitute 'exchange hot-spots' from which monomer exchange ooriginates and proceeds (Fig. 1d: *e.g.* BTA).

While the concept of defects is typically referred to ordered structures (*e.g.* crystals), this is new in soft matter. The identification and study of such defects, which are continuously/dynamically created and repaired in dynamic SMPs, is a non-trivial challenge due to their elusive and statistical nature. Unsupervised machine-learning (ML) and pattern recognition algorithms are particularly useful to this end.[12] These offer the opportunity to gain a complete automatic characterization of defects and their pathways of formation in SMP models (Fig. 2). Such computational approaches are general and applicable to a variety assemblies. The detailed understanding that can be achieved with these methods represents a crucial step toward the rational design of SMPs with controllable and programmable dynamic properties.

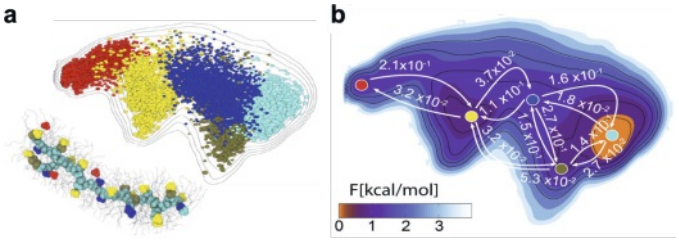

Fig. 2. Defects characterization in SMPs. (a) Clustering analysis of the monomer states in BTA SMPs (monomer cores colored based on their internal order). (b) Map of the internal dynamics of a BTA SMP (transition probabilities between monomer states in white). Adapted with permission from ref. [12] (Copyright 2020 American Chemical Society).

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Prof. Dr. Markus Niederberger, Department of Materials, ETH Zurich
E-mail: markus.niederberger@mat.ethz.ch, Tel.: +41 44 633 63 90