Coarse-Grained Molecular Dynamics Modeling of Segmented Block Copolymers

Julien Morthomas and Olivier Lame
INSA Lyon, MATEIS, France

Since the 1960s, thermoplastic elastomers (TPE), are widely used in the industry (dashboard elements, wires sheaths, and bitumen modifiers) for their rubbery properties and ease of processing. Their outstanding properties come from the specific chain morphology consisting of an alternation of soft and hard segments along the chain, see the Fig 1. At room temperature soft segments are amorphous and hard segments can associate and form crystal regions leads to a microphase-separated structure of soft and hard domains, see Fig 1. These hard domains behave like physical nodes linking the soft segments. However, the microstructure−properties relationship of thermoplastic elastomers is still unclear. Experiments have pointed out that these materials can exhibit quite different morphologies according to their chemical composition and processing route suggesting that interaction strengths between the blocks, chain rigidity, and thermal history are determining factors.

Where experiences no longer see, simulations, such as molecular dynamics (MD), can provide additional information about the structure and properties of such materials. Recently, we have developed in our laboratory a Coarse-Grained Molecular Dynamics (CGMD) model that has allowed to simulate the phase separation of linear polymers [1]–[3] as well as recently block copolymers [4]. In this project, the PhD student will first extend this CGMD model to study the importance of the chemical composition of the soft segments on the morphologies of the obtained semi-crystal block copolymers. The topology and the crystallinity of systems will study in function of the processing route. The second objective will be to understand the link between microstructures and mechanical properties. Linear mechanical properties will be study thanks to the relaxation of the shear modulus as a function of time using the MD Green-Kubo method. The non-linear mechanical properties are also discussed by studying the stress-strain curves of our different block copolymer systems.

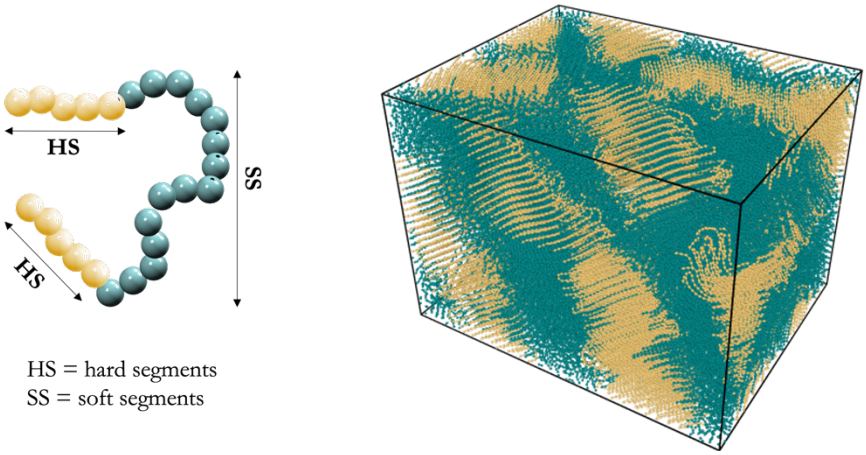

Figure 1 : On the left, a hard-soft segmented chain. On the right, a TPE semi-crystal obtained by CGMD.

This thesis will be carried out at the MATEIS laboratory of INSA Lyon, in the PVMH group. MATEIS is a Materials Science laboratory that encompasses different fields: chemistry, physics and mechanics. The MATEIS laboratory studies three classes of materials (metals, ceramics and polymers), and their composites, incorporating their characteristics by volume and surface and their interfaces.
The PhD student will be supervised by Professor O. Lame and the Assistant Professor J. Morthomas, respectively specialist in semi-crystal polymers and molecular dynamics simulations.
This project is the continuation of the thesis work of Zhaï Zengqiang (china scholarship council 2015-2019), Matthias Nébouy (grant from the French Ministry 2017-2020) and the actual thesis work of Junxiong Wang (china scholarship council 2020-2024).
This project will be enhanced by a collaboration with Dr. Ping Zhu, Assistant Professor in the Institute of Chemistry, Chinese Academy of Sciences, Beijing, China and Dr. Guilhem Baeza, Assistant Professor in MATEIS laboratory, who will respectively synthesize and perform advanced rheological characterization of experimental samples of thermoplastic elastomers based on multi-block copolymers. This will allow a direct comparison between experimental results and simulations of this project.

[1] J. Morthomas, C. Fusco, Z. Zhai, O. Lame, et M. Perez, « Crystallization of finite-extensible nonlinear elastic Lennard-Jones coarse-grained polymers », *Phys. Rev. E*, vol. 96, n° 5, nov. 2017, doi: 10.1103/PhysRevE.96.052502.

[2] Z. Zhai, J. Morthomas, C. Fusco, M. Perez, et O. Lame, « Crystallization and Molecular Topology of Linear Semicrystalline Polymers: Simulation of Uni- and Bimodal Molecular Weight Distribution Systems », *Macromolecules*, vol. 52, n° 11, p. 4196-4208, juin 2019.

[3] Z. Zhai, C. Fusco, J. Morthomas, M. Perez, et O. Lame, « Disentangling and Lamellar Thickening of Linear Polymers during Crystallization: Simulation of Bimodal and Unimodal Molecular Weight Distribution Systems », *ACS Nano*, vol. 13, n° 10, p. 11310-11319, oct. 2019, doi: 10.1021/acsnano.9b04459.

[4] M. Nébouy, J. Morthomas, C. Fusco, G. P. Baeza, et L. Chazeau, « Coarse-Grained Molecular Dynamics Modeling of Segmented Block Copolymers: Impact of the Chain Architecture on Crystallization and Morphology », *Macromolecules*, vol. 53, n° 10, p. 3847-3860, mai 2020, doi: 10.1021/acs.macromol.9b02549.

Contacts: Olivier Lame: olivier.lame@insa-lyon.fr
Julien Morthomas: julien.morthomas@insa-lyon.fr