

# Molecular dynamics simulation of semicrystalline polymers: from molecular topology to mechanical properties

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Semi-crystalline polymers, such as polyethylene (PE), polylactic acid or polyamide, are used in a wide range of applications such as automotive, pipes, gearing etc. They are characterized by their multiscale complex microstructure, a stacking of crystalline and amorphous lamellae of a few microns length and a few nanometers thickness (see Fig. 1). The mechanical properties of this kind of nanocomposite are mainly governed by the mechanical coupling between crystalline and amorphous phase. In particular the stress transmission is crucial. The anchorage of the amorphous phase in the crystalline phases due to: presence of loops, cilia, tie segment molecules, entanglement [1,2], are key parameters and are generally identified as chain topology. Tie molecules, which link two adjacent crystalline phases are frequently evoked in the literature and are supposed to play an important role in the mechanical properties such as elastic properties, yielding, cavitation, hardening, fracture behavior.

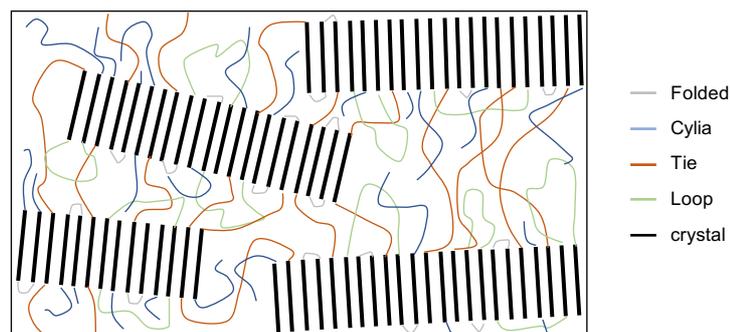


FIG. 1: Complex microstructure of semi-crystalline polymer: chain topology

However, this molecular feature is resistant to direct experimental observations mainly because of the nanometric scale. Their real mechanical action remains essentially unknown, as well as their tension, their average length and their possible interaction with loop or entangled chains. As a consequence, no quantitative description of their contribution on the mechanical properties is available [3]. The concentration of tie molecules as well as the other possible chain topologies are strongly influenced by the conditions of crystallization and by the polydispersity. Indeed, since the 70's huge effort of the chemical industry have been performed to increase the life time of polymer like PE by modifying the distribution of chain length. As an example, bi-modal PE have been developed and the life time of PE used for tubes under pressure has been multiplied by a factor higher than 2. This spectacular result is qualitatively attributed to the optimized density of tie molecules and crystallinity. This research is up to now only empirical and is progressively reaching some limitations. The precise and deep understanding of the mechanical role of crystalline and amorphous phase as well as the chain topology is now mandatory to expect new breakthrough in this field. Thus, all the semi-crystalline polymers dedicated to mechanical use is strongly polydisperse. Many efforts have been made both experimentally and theoretically to explore the crystallization mechanism of polymers, however, very few of which involved polydispersity.

Molecular dynamics simulations, which can benefit from increasing computer power, are excellent tools to overcome the difficulties of experimental measurements and can be used to study the non-equilibrium process of crystallization at the nanoscale and the mechanical properties of nanostructured systems. Molecular dynamics simulations of semi-crystalline polymers can be performed at different length and time scales, with different levels of complexity (see Fig. 2): the explicit atom (EA) models, where all atoms of polymer chains are simulated explicitly, the united atom model (UA), where each unit simulated is a  $CH_2$  or  $CH_3$  group, and the coarse-grained (CG) model, where each unit is a few structural carbons or monomers. The role of tie molecules on the mechanical properties of prefabricated semi-crystalline has been studied with EA model [4], but this type of simulations is time consuming since they treat explicitly C-H bond vibrations: equilibration time very large for system sizes of interest and not suited for studying large deformations. An increase of simulation time is possible with UA model, as we simulate fewer units. In this way, order-oriented phase structure was observed with UA models mimicking n-alkane or polyethylene polymer in vacuum [5,6]. UA Langevin dynamics simulations have been performed to understand early-stage polymer crystallization [7,8] and the diffusion of chains to the crystal growth front [9]. Nucleation processes and crystal growth from an isotropic melt [10–12], along substrates [13,14] or from an oriented melt [15,16], and cold crystallization after a rapid quenching of a melt [14,17] have also been studied with UA models. However, with the UA model does not enable to create a realistic semi-crystalline composed of several lamellae. It is possible to optimize the CG model to quantitatively study the crystallization process of specific systems. For example, the CG-PVA model, optimized for polyvinyl alcohol [18], shown homogenous nucleation and growth of semi-crystalline from a melt [19], but it exhibits a large fraction and density of small crystallites [20,21]. Unfortunately, for all these molecular dynamics models, the computational time to study crystallization would not be sufficient to simulate the growth of several large lamellae. However, this kind of systems are crucial to explore the key points of these issues which is the complex link between crystallites and chain topology.

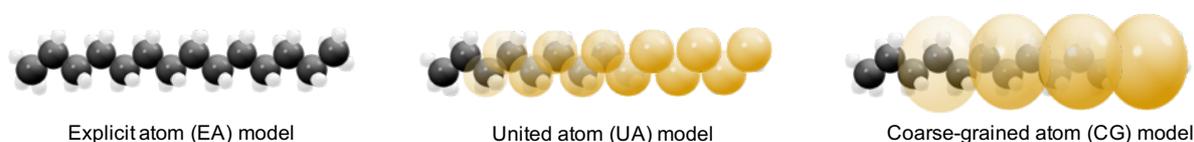
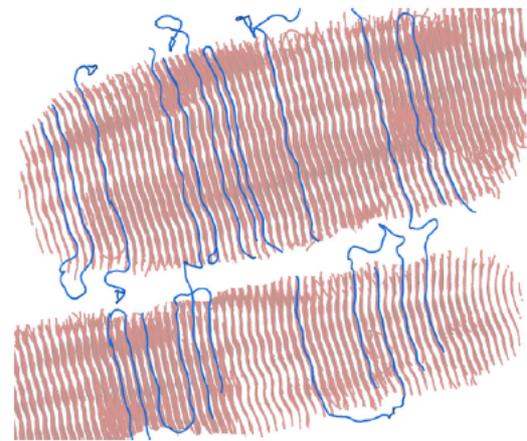


FIG. 2: Molecular dynamics models for semi-crystalline polymer

A solution is the minimal approach of the CG model: the qualitative and not quantitative Kremer-Grest (KG) bead-spring model [22] where bonded chain units are connected by finite-extensible nonlinear elastic bonds that prevents chain crossing and nonbonded chain units by classical Lennard-Jones potential. This CG model has already been used in our group to study the influence of tie and loop chains on the mechanical properties of lamellar block copolymer [23,24]. In CG-KG models, the size of the system as well as the time scale involved are large enough to fully address the problems of the size, thickness, and shape of the lamellae as well as the molecular topology and mechanical properties. Even if the CG-KG approach cannot be directly compared to real polymers in a quantitative way, it is essentially useful to understand the general features of polymer crystallization and examine the realism of alternative ideas and concepts that could be then used for modeling of real polymers. However, up to now, CG-KG model is not usable to study polymer crystallization. Starting from a CG method for polymer chain generation develop in our group [25,26], recently, we have reparametrized the classical CG-KG model in order to create a semi-crystalline polymer from the cooling of a melt [27]. It was verified that the obtained semi-crystalline qualitatively represent all microstructural features exhibited by a real semi-crystalline polymer: (i) chains are parallel in the crystal; (ii) the lattice is never cubic due to the strong difference between the C-C bond length and the weak bond length; (iii) crystallites mainly grow perpendicular to the chain direction, thus forming plate-like lamellae; (iv) chains are partially folded in a single crystallite; (v) formation of several topologies for the amorphous phase: loop, folded, pending and tie chains; (vi) crystallinity degree of linear polymer ranges between

20% and 80% and (vii) a sufficient number of lamellae. An example of complex semi-crystalline obtained microstructure is given in Fig. 3.

In the continuity of this last work, the objectives of this project are to improve our reparametrized classical CG-KG model in order to : (i) study the evolutions of molecular features as cilia, folded, loop or tie chains, during the crystallization process, in particular by varying the crystallization temperature and compare to in situ Small Angle X-ray Scattering and Wide Angle X-ray Scattering measurements on real materials; (ii) analyze the mechanical properties of the obtained semi-crystalline in function of the conditions of crystallization, e.g. cooling rate, isothermal treatment, and discuss the role of all molecular features on the mechanical response; (iii) study and perform massive molecular dynamics simulations of several systems with various polydispersity and understand the role of the polydispersity on the nucleation and growth of crystallites and on the mechanical properties; and finally, (iv) realize large tensile tests to observe local events such as the initiation of plasticity, cavitation or lamellae bucking will be sought and then compared to local information deduced from experimental data.



*FIG. 3: Lamellae structure obtained with our reparametrized CG model [27]. Here only the amorphous phase of classical molecular features is shown to facilitate reading of the figure.*

- [1] S. Humbert, O. Lame, J.-M. Chenal, C. Rochas, and G. Vigier, *J. Polym. Sci. Part B Polym. Phys.* **48**, 1535 (2010).
- [2] S. Humbert, O. Lame, R. Séguéla, and G. Vigier, *Polymer* **52**, 4899 (2011).
- [3] R. Seguela, *J. Polym. Sci. Part B Polym. Phys.* **43**, 1729 (2005).
- [4] S. Queyroy and B. Monasse, *J. Appl. Polym. Sci.* **125**, 4358 (2012).
- [5] S. Fujiwara and T. Sato, *Phys. Rev. Lett.* **80**, 991 (1998).
- [6] I. Dukovski and M. Muthukumar, *J. Chem. Phys.* **118**, 6648 (2003).
- [7] M. Muthukumar and P. Welch, *Polymer* **41**, 8833 (2000).
- [8] C. Liu and M. Muthukumar, *J. Chem. Phys.* **109**, 2536 (1998).
- [9] P. Welch and M. Muthukumar, *Phys. Rev. Lett.* **87**, 218302 (2001).
- [10] R. H. Gee, N. Lacevic, and L. E. Fried, *Nat. Mater.* **5**, 39 (2006).
- [11] T. Yamamoto, *J. Chem. Phys.* **129**, 184903 (2008).
- [12] P. Yi, C. R. Locker, and G. C. Rutledge, *Macromolecules* **46**, 4723 (2013).
- [13] N. Waheed, M. J. Ko, and G. C. Rutledge, *Polymer* **46**, 8689 (2005).
- [14] T. Yamamoto, *J. Chem. Phys.* **139**, 054903 (2013).
- [15] M. S. Lavine, N. Waheed, and G. C. Rutledge, *Polymer* **44**, 1771 (2003).
- [16] M. J. Ko, N. Waheed, M. S. Lavine, and G. C. Rutledge, *J. Chem. Phys.* **121**, 2823 (2004).
- [17] T. Yamamoto, *J. Chem. Phys.* **133**, 034904 (2010).
- [18] D. Reith, H. Meyer, and F. Müller-Plathe, *Macromolecules* **34**, 2335 (2001).
- [19] C. Luo and J.-U. Sommer, *Macromolecules* **44**, 1523 (2011).
- [20] S. Jabbari-Farouji, J. Rottler, O. Lame, A. Makke, M. Perez, and J.-L. Barrat, *J. Phys. Condens. Matter* **27**, 194131 (2015).
- [21] S. Jabbari-Farouji, J. Rottler, O. Lame, A. Makke, M. Perez, and J.-L. Barrat, *ACS Macro Lett.* **4**, 147 (2015).
- [22] K. Kremer and G. S. Grest, *J. Chem. Phys.* **92**, 5057 (1990).
- [23] A. Makke, M. Perez, O. Lame, and J.-L. Barrat, *Proc. Natl. Acad. Sci.* **109**, 680 (2012).
- [24] A. Makke, O. Lame, M. Perez, and J.-L. Barrat, *Macromolecules* **45**, 8445 (2012).
- [25] M. Perez, O. Lame, F. Leonforte, and J.-L. Barrat, *J. Chem. Phys.* **128**, 234904 (2008).
- [26] M. Mahaud, Z. Zengqiang, M. Perez, O. Lame, C. Fusco, L. Chazeau, A. Makke, G. Marque, and J. Morthomas, *Commun. Comput. Phys.* **24**, 885 (2018).
- [27] J. Morthomas, C. Fusco, Z. Zhai, O. Lame, and M. Perez, *Phys. Rev. E* **96**, (2017).