

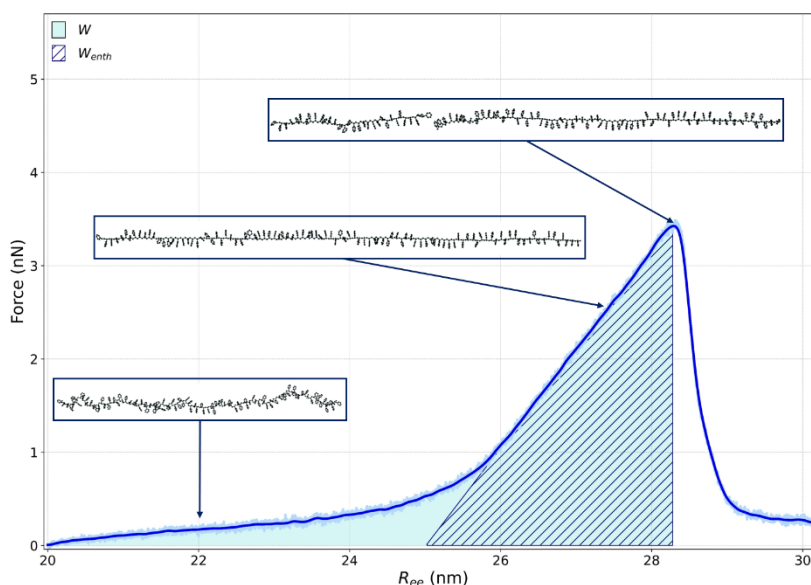
Abstract for MMB25 conference (Mechanics of Bond Breaking: from Single Molecules to Polymer Networks), Brussels, Belgium, March 10-12, 2025

The stereochemistry of chain scission in polyolefins

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The breakup of polymer chains under tension arises in a variety of contexts, and in particular in polymer adhesion.[1] We were brought to this problem by our attempt to discriminate the relative roles of polymer grafting (to the surfaces) and polymer cross-linking in rubbery adhesive layers.[2] Here I will illustrate a comprehensive computational study of single-chain mechanics and scission by atomistic molecular dynamics.[3] These were carried out with a reactive force field for hydrocarbons.[4] The simulations have allowed us to investigate the role of the chains' stereochemistry, by comparing the fracture behaviour of poly(ethylene), poly(propylene), and poly(styrene), including their isotactic, syndiotactic and atactic forms. We have found that the isotactic chains are indeed superior to the others, in terms of fracture toughness. If time allows, I will also discuss the role of the viscous environment (represented by a Langevin thermostat in the simulations) and our recent comparative study of different reactive force fields and ab initio density functional theory.[5]



[1] Raos, G., & Zappone, B. (2021). Polymer Adhesion: Seeking New Solutions for an Old Problem. *Macromolecules*, 54(23), 10617-10644.

[2] Raos, G., & Zappone, B. (2024). Tuning Adhesion and Energy Dissipation in Polymer Films between Solid Surfaces via Grafting and Cross-Linking. *Macromolecules*, 57(14), 6502-6513.

[3] Fakhrayi Mofrad, N., Bahadori, P., & Raos, G. (2024). Ultimate Molecular Mechanical Properties of Polyolefin Chains. *Macromolecules*, 57(9), 3901-3913.

[4] Kański, M., Maciazek, D., Postawa, Z., Ashraf, C. M., Van Duin, A. C., & Garrison, B. J. (2018). Development of a charge-implicit ReaxFF potential for hydrocarbon systems. *The Journal of Physical Chemistry Letters*, 9(2), 359-363.

[5] Liu, L., Raos, G. (2025). A comparative study of reactive force fields for the scission of hydrocarbon chains, *manuscript in preparation*.