General Topics: New Synthesis and Characterization

Title: Bigger Isn’t Always Better: Precision Synthesis Unveils Nonmonotonic Influence of Persistence Length and Conformational Freedom on Polymer Mechanochemistry

Abstract: The mechanochemical chain scission rate of polymers is widely believed to scale with backbone elongation and sidechain length. However, with the advent of nonscissile mechanophores, a deeper understanding of how mechanical force is distributed along polymer chains, particularly the competition between mechanophore activation and chain fragmentation, has become essential. Although many studies report a correlation between persistence length and mechanochemical reactivity, the underlying mechanisms remain unclear. This gap arises from the challenge of simultaneously probing force distribution along the polymer backbone while systematically controlling structural parameters such as grafting density, chain length, backbone composition, and conformation. Here, we leverage the precision synthesis of multi-mechanophore polymers with systematically varied sidechains to dissect the effects of graft architecture on both chain scission and nonscissile mechanophore activation. Our findings reveal a nonmonotonic relationship between persistence length and mechanochemical transduction, challenging conventional assumptions. Furthermore, we uncover how conformational freedom modulates macromolecular mechanical coupling, offering new insights into the design of responsive polymer systems.