



Computational Radical Polymerization

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Computational quantum chemistry is rapidly establishing itself as a powerful tool for studying the mechanism and kinetics of radical polymerization processes. Unlike experiment, it allows for the direct calculation of the rate coefficients of individual reactions within a complicated multi-step process, without empirical parameters or (kinetic) model-based assumptions. It also provides useful mechanistic information, such as transition state geometries, charge distributions and radical stabilization energies.

However, to obtain accurate results for these radical reactions, high-level composite procedures are required, and these are currently too computationally intensive to be applied to polymeric systems. We have been working toward adapting computational chemistry for radical polymerization, through the selection of accurate yet economic methods, and the design of suitable model systems capable of mimicking the behaviour of real polymeric systems.

Recently, we reported the first chemically accurate computational predictions of propagation rate coefficients in free-radical polymerization and the first ab initio simulation of an entire polymerization process. We have also utilized our computational approach in the design of a new class of multipurpose RAFT agent, a new type of controlled radical polymerization process and a new method for incorporating phosphorus atoms into the backbones of olefinic polymers. In this talk we outline our computational methodology, discuss its accuracy and outstanding problems, and highlight some of its applications.